MINERALOGICAL SOCIETY OF POLAND

Vol. 35, 2009

MINERALOGIA Special Papers

Geochemical Mineralogical Petrological Research



formerly Mineralogia Polonica

MINERALOGIA - Special Papers Vol. 35, 2009

PL ISSN 1899-8518

MINERALOGIA, SPECIAL PAPERS Volume 35, 2009

VII Meeting of the Mineralogical Society of Poland organized to celebrate 40th anniversary of the Mineralogical Society of Poland

XVI Meeting of the Petrology Group of the Mineralogical Society of Poland

"Magmatism and metamorphism in the Holy Cross Mts."

Abstracts and field session guide



ŚWIĘTY KRZYŻ, 24-27 SEPTEMBER, 2009

Mineralogia – Special Papers continuation of Mineralogia Polonica – Special Papers

Editor of the series – Marek Michalik Institute of Geological Sciences, Jagiellonian University 30-063 Kraków, Oleandry 2a, Poland marek.michalik@uj.edu.pl

Editors of Volume 35: Łukasz KARWOWSKI, Justyna CIESIELCZUK and Krzysztof SZOPA Faculty of Earth Sciences, University of Silesia

Technical Editors: Justyna CIESIELCZUK Krzysztof SZOPA Łukasz KARWOWSKI Faculty of Earth Sciences, University of Silesia

40th anniversary of the Mineralogical Society of Poland and XVI Meeting of the Petrology Group of the Mineralogical Society of Poland organized together with VII Meeting of the Mineralogical Society of Poland and the issue of the volume 35 of "Mineralogia-Special Papers" were organized with financial support of the Ministry of Science and Higher Education and The Committee on Mineralogical Sciences, Polish Academy of Sciences.

ISSN: 1899-8518

Printed: Zakład Poligraficzny Waldemar Wiliński Chopina 6 44-100 Gliwice VII Meeting of the Mineralogical Society of Poland organized to celebrate 40th anniversary of the Mineralogical Society of Poland

XVI Meeting of the Petrology Group of the Mineralogical Society of Poland

organized by Mineralogical Society of Poland

together with:

University of Silesia, Faculty of Earth Sciences Jan Kochanowski University in Kielce Warsaw University, Faculty of Geology Polish Geological Institute The Committee on Mineralogical Sciences, Polish Academy of Sciences



ŚWIĘTY KRZYŻ, 24-27 SEPTEMBER, 2009

Organizing committee:

Justyna CIESIELCZUK Agnieszka GAŁUSZKA Janusz JANECZEK Łukasz KARWOWSKI Marek MICHALIK Zdzisław MIGASZEWSKI Jerzy NAWROCKI Sylwester SALWA Ewa SŁABY Krzysztof SZOPA Wiesław TRELA Beata ZYCH-HABEL

We would like to special thanks to Prof. Pádhraig Kennan for making language corrections.

CONTENTS

Ryszard KRYZA VII Conference of the Mineralogical Society of Poland and XVI Meeting of the Petrology Group
at Swięty Krzyż, Holy Cross Mountains, 24–27 September 200913
Ryszard KRYZA, Marek MICHALIK, Piotr WYSZOMIRSKI The Mineralogical Society of Poland: 40 th Anniversary14
Barbara KWIECIŃSKA Prof. dr hab. Witold Żabiński (1929–2007) - inicjator i długoletni Prezes Polskiego Towarzystwa Mineralogicznego
INVITED LECTURES
Agnieszka GAŁUSZKA, Zdzisław M. MIGASZEWSKI Valuing geodiversity and its importance for abiotic nature conservation in the Holy Cross Mountains, Poland
Peter HAUGHTON Tracking turbidity currents downslope - new models for the distal run-out of sediment gravity flows
Dušan HOVORKA Mineralogy and petrology in the service of society: challenges for the 21 st century
Pádhraig KENNAN Granite Rb-Sr data, aggregated, define a regional framework: why?43
Zdzisław M. MIGASZEWSKI, Agnieszka GAŁUSZKA The use of geochemistry for assessing environmental quality based on selected case studies in the Holy Cross Mountains (south-central Poland)44
Marek NARKIEWICZ Late burial dolomitization of the Devonian carbonates and a tectono-thermal evolution of the Holy Cross Mts area (Central Poland)
Jerzy NAWROCKI Some features of the Bardo diabase intrusion (Holy Cross Mts.)60

Aleksandra GAWEDA Hydro-fracturing by boron-rich fluid of the granitoid rocks in the Tatra Mountains
Aleksandra GAWĘDA, Magdalena SIKORSKA Alkali feldspar megacrysts from the High Tatra granite – indicators of magma mixing/mingling processes
Aleksandra GAWĘDA, Krzysztof SZOPA Magmatic structures in the High Tatra Granite: a key to the model of the intrusion
Agnieszka GURDZIEL Secondary changes in schreibersite (rhabdite) and cohenite in the Morasko meteorites
Artur JAKUBIAK, Anna PIETRANIK, Ewelina ŁYCZEWSKA Petrography and geochemistry of volcanic rocks from the Niemodlin area (SW Poland)
Aleksandra JAŹWA, Anna PIETRANIK Crystal size distribution of olivine from the Męcinka Basalt (SW Poland)86
Irena JERZYKOWSKA, Jolanta MESJASZ-PRZYBYŁOWICZ, Marek MICHALIK Preliminary study of the mineralogical and chemical composition of soils from Agnes Mine (Mpumalanga Province, South Africa)
Bartłomiej KAJDAS, Marek MICHALIK, Monika KASINA Variety of alterations in gruses from Miłków, Karkonosze Mts
Łukasz KARWOWSKI Marshite – copper iodite from Miedzianka in the Holy Cross Mts
Łukasz KARWOWSKI, Andrzej MUSZYŃSKI, Ryszard KRYZA, Katarzyna HELIOS Phosphates in the Morasko meteorite90
Monika KASINA, Marek MICHALIK, Bartłomiej KAJDAS Mineral and chemical composition of slags – mobilization of elements92
Jakub KIERCZAK, Eliza ŁOZOWSKA, Piotr SZNAJDER Weathering of a slag pile produced by the smelting of Zn ores in the Katowice-Wełnowiec smelter93

Joanna KOSTYLEW, Sylwester SALWA Metamorphic evolution of phyllites from Podmąchocice in the Łysogóry Unit of the Holy Cross Mts. (SE Poland): preliminary data from K-white mica and chlorite investigations
Ryszard KOTLIŃSKI, Justyna CIESIELCZUK, Jerzy ŻABA, Sebastian WOJTYCZKA New data on the internal structure of Pacific nodules (Clarion-Clipperton Zone)
Alicja ŁACIŃSKA, Mike STYLES The Barzaman Formation in the UAE - an example of intensive alteration of ultramafic and mafic rocks in the near surface environment
Jarosław MAJKA, Jerzy CZERNY, David G. GEE Evidence of the c. 650Ma Torellian Orogeny in SW Svalbard inferred from monazite and zircon dating97
Jarosław MAJKA, Anna LADENBERGER, Nikolay KUZNETSOV Crustal growth and crustal recycling in the Neoproterozoic Torellian Orogen, SW Svalbard: U/Pb zircon geochronology and Hf isotopic characteristics
 Krzysztof NEJBERT, Paweł KRÓL, Rafał WIECZOREK Mineralogy and geochemistry of pyrite ores from the Staszic mine at Rudki, the Holy Cross Mountains, Poland
Monika NOWAK, Andrzej MUSZYŃSKI New data on the Cenozoic basanite from Wołek Hill, Kaczawa Mountains, SW Poland101
Monika NOWAK, Wojciech STAWIKOWSKI Peridotite xenoliths in basanites from Wołek Hill, Kaczawskie Mts., SW Poland - petrological data vs microstructural observations102
Anna PIETRANIK Mixing, mingling or subsolidus interactions: which were important in the Gęsiniec intrusion?103
Maria RACKA, Grażyna BZOWSKA Preliminary geochemical and mineralogical data on the Lower Carboniferous tuffites from Kowala near Kielce (Holy Cross Mountains, Poland)

Anna ROGÓŻ, Zbigniew SAWŁOWICZ Fossilized wooly mammoth skeletal remains from the Upper Palaeolithic archeological site (Cracow Spadziasta Street (B), Southern Poland) – preliminary report
Sylwester SALWA Mineral veins from the low grade metamorphic rocks of the Łysogóry Unit (Holy Cross Mts, Central Poland)106
Sylwester SALWA Relationships between tectonics and metamorphism in phyllite from Podmą- chocice (Łysogóry Unit of the Holy Cross Mountains, central Poland)107
Ewa SŁABY, Hervé MARTIN, Michał ŚMIGIELSKI, Andrzej DOMONIK, Stanisław HAŁAS Magmatic equilibration and subsolidus re-equilibration in Archaean granites - analysis of an integrated data base108
Jacek SZCZEPAŃSKI, Sławomir ILNICKI Geochemical diversity of metabasalts from the Nove Mesto Unit and the Stronie Formation and its bearing on their origin109
Marek SZCZERBA, Mariusz ROSPONDEK Comparison of methylphenantrene distributions predicted from molecular modelling with relevant geological data110
Marek SZCZERBA, Mariusz ROSPONDEK, Kamilla MALEK, Maciej GÓRA, Leszek MARYNOWSKI Theoretical studies of phenyldibenzothiophenes in the course of maturation111
Eligiusz SZEŁĘG Native copper and cuprite from secondary Cu-mineralization in the Laskowa quarry, Góry Świętokrzyskie Mts112
Krzysztof SZOPA The same reaction but different environment: breakdown of monazite in the High Tatra granites113
Wanda WILCZYŃSKA-MICHALIK, Renata GASEK, Janusz DAŃKO, Marek MICHALIK Fly ash from coal and biomass co-combustion and its role in CO ₂ sequestration114
Beata ZYCH-HABEL, Angelika KĘDZIERSKA Accessory minerals and selected trace elements in altered granodiorite from Strzeblów (Strzegom-Sobótka Massif, SW Poland)115

FIELD SESSIONS	117
FIELD SESSION 1	119
Zdzisław M. MIGASZEWSKI, Agnieszka GAŁUSZKA, Sabina DOŁĘGO Geochemical studies in environmental monitoring and assessment – examples from the Holy Cross Mts	WSKA
STOP 1: The influence of acid mine waters on the environment in the Wiśniówka area (Holy Cross Mountains)	119
STOP 2: The use of springs for geoindication studies Zdzisław MIGASZEWSKI, Artur MICHALIK, Agnieszka GAŁUSZKA	122
FIELD SESSION 2	125
Roman WŁODYKA, Łukasz KARWOWSKI, Krzysztof SZOPA Diabase intrusions from the Bardo syncline (the Kielce region) in the Holy Cross Mts - Introduction to field trip	125
STOP 1: The Ordovician and Lower Silurian sedimentary succession in Zalesie	128
STOP 2: Diabase intrusion at Zalesie Roman WŁODYKA, Łukasz KARWOWSKI, Krzysztof SZOPA	128
STOP 3: Phyllites from Kamecznica Podmąchocicka – metamorphic rocks from in the Holy Cross Mountains Sylwester SALWA	142
FIELD SESSION 3	149
Leszek MARYNOWSKI, Maria RACKA Two different examples of the Upper Devonian – Lower Carboniferous successions in the Holy Cross Mountains, Poland	,149
STOP 1: Kowala quarry	150
STOP 2: Ostrówka quarry	151
STOP 3: The Ore Mining Museum in Miedzianka	151

FIELD SESSION 4
Józef SZAJN, Łukasz KARWOWSKI, Justyna CIESIELCZUK, Krzysztof SZOPA Deposits of clay minerals and geotouristic aspects of the Holy Cross Mts155
STOP 1: The Pałęgi deposit155
STOP 2: Gagaty Sołtykowskie – protected area160
STOP 3: Samsonów old ironworks160
STOP 4: The Oak Bartek161
AUTHOR'S INDEX

MINERALOGIA - SPECIAL PAPERS, 35, 2009 www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



VII Conference of the Mineralogical Society of Poland and XVI Meeting of the Petrology Group at Święty Krzyż, Holy Cross Mountains, 24–27 September 2009

Dear Colleagues,

The joint VIIth Conference of the Mineralogical Society of Poland and the XVIth Meeting of the Petrology Group of this Society at Święty Krzyż in the Holy Cross Mountains, 24–27 September 2009, is an unusual scientific event for at least two reasons: (1) the celebration of the 40th anniversary of the Mineralogical Society of Poland and (2) the Petrology Group annual meeting is being held, for the first time since its beginning 16 years ago, in the Holy Cross Mountains.

The Mineralogical Society of Poland was founded on 17 April 1969 thanks to the great efforts of Professor Andrzej Bolewski and his co-workes: Jan Kubisz, Leszek Stoch and Witold Żabiński. The memory of one of the initiators and founders, Professor Witold Żabiński, who died on 15 January 2007, is addressed in this volume in a special paper authored by Prof. Barbara Kwiecińska.

During its forty years, the Mineralogical Society of Poland has been a leading scientific organization in its field in Poland. And so it continues today. The Society is a very active scientific community, co-operating with the Committee on Mineralogical Sciences of the Polish Academy of Sciences and having extensive links with its international counterparts – the European Mineralogical Union and the International Mineralogical Association. Its activities contribute significantly to the development and promotion of modern trends in Earth Sciences.

The Petrology Group of the Mineralogical Society of Poland has been one of the most active sections of the Society since the Group was established 16 years ago. The annual meetings of the Group have been organized by teams from various mineralogical and geological institutions at a range of interesting venues in Poland. However, rather surprisingly, the Group has never met in the Holy Cross Mountains despite the well-known mineralogical and geological attractions and mining heritage of that region. Therefore, great thanks are due to the organizers of the joint VIIth Conference of the Mineralogical Society of Poland and XVIth Meeting of the Petrology Group at Święty Krzyż, in particular to the Chief Organizers from the Faculty of Earth Sciences of the University of Silesia and from the Jan Kochanowski University in Kielce, co-operating with colleagues from the Jagiellonian University, the Faculty of Geology of Warsaw University, the Polish Geological Institute, and the Committee on Mineralogical Sciences. They have created a great opportunity for us, the participants at this meeting, to learn what is new in the Earth and environmental research issues in the Holy Cross Mountains, and to discuss current problems in the mineralogical and related sciences.

With best wishes to all participants,

Ryszard Kryza

MINERALOGIA - SPECIAL PAPERS, 35, 2009 www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The Mineralogical Society of Poland: 40th Anniversary

Ryszard KRYZA¹, Marek MICHALIK², Piotr WYSZOMIRSKI³

¹ Institute of Geological Sciences, University of Wrocław ,ul. Cybulskiego 30, 50-205 Wrocław, Poland ² Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2a, 30-063 Kraków, Poland

³ AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland

The Mineralogical Society of Poland (MSP) was founded on the 17th April 1969, initiated by Professor Andrzej Bolewski and his co-workers: Jan Kubisz, Leszek Stoch and Witold Żabiński. The first President of the Society was Prof. Andrzej Bolewski, and the headquarters was established at the AGH University of Science and Technology in Kraków. According to the Statue of the MSP, the Society "supports the development of mineralogical sciences and propagates them in Polish society". The formation of the Society was highly anticipated by the wide Polish mineralogical community and during the first year the number of its members reached 165 (Fig. 1). A number of scientific and industrial institutions have become formal members of the MSP.

The recent activities of the MSP are, in general, a continuation of those carried out during the first decades of its history. Now, in 2009, the Society has 222 members (including 13 honorary members), affiliated in four regional branches in: Warsaw, Sosnowiec (Upper-Silesia), Wrocław (Lower-Silesia) and Kraków. Four specific scientific groups of the Society have been formally established: Clay Minerals, Geochemistry, Thermal Analysis, and Petrology groups.

The MSP organizes regular and occasional conferences, such as annual meetings of the Polish Clay Group and of the Petrology Group, as well as general meetings of the MSP every two years. The conferences are usually attended by a great number of participants, including young researchers, from Poland and from other countries, and they have become important scientific events in the field of mineralogical sciences in Central Europe.

The MSP has been a member of the International Mineralogical Association (IMA) since 1973 and of the European Mineralogical Union (EMU) since 1999. The representatives of the MSP are members of several commissions of the IMA. The MSP also co-organizes international scientific meetings, together with the EMU, IMA, Mid-European Clay Group and other societies. Since the beginning, the MSP has closely collaborated with the Commission on Mineralogical Sciences of the Polish Academy of Sciences in developing and promoting modern trends and research issues in mineralogical and related sciences.

The Mineralogical Society of Poland publishes (in English) two journals: "Mineralogia Polonica" (since 2008 "Mineralogia") and "Mineralogical Society of Poland – Special Papers" (since 2008 "Mineralogia – Special Papers"). "Mineralogia" publishes reviewed papers on the latest achievements in mineralogy, petrology and geochemistry in Poland and in other countries. "Mineralogia – Special Papers" publishes reviewed abstracts, texts of posters and oral presentations presented during conferences organized by the MSP. Over

the last few years, the MSP has co-publishesd "Elements", an International Magazine of Mineralogy, Geochemistry and Petrology, edited by the Mineralogical Society of America.

Kraków, dnia 28.V.1969 r. POLSHIE TOWARZYSTWO MINGRALOGICZNE Pismi ckólne 1 1/ De 15 maja br. zgłosiłe się 165 człenków-założycieli PTMin. 2/ W dniu 8 maja br. odbyło się pierwsze posiedzenie naukewe PTMin. zorganizewane wspólnie z Komisją Nauk Lineralegioznych O/PAN, na którym wygłoszone 3 referaty naukowe, a to: Dr X. Prochazka - "Sole kamienne ze strontem i barem ze złoża selnego Wieliczki" Dec. dr L.Stoch - "Agregaty ziarn mineralów ilastych" Mgr inż. A. Skewroński - "Wyniki rentgenograficznych badań sfalerytów ze śląske-krakowskich złóż kruszców cynku 1 ołowiu" 3/ O powstaniu PTMin. zestako poinformowanych 18 redakcji czasopism naukewych 1 haukowo-teehnicznych, a niektóre z nieh zgłosiły zamiar epublikowania materiału informacyjnego o Pelskim Towarzystwie Mineralogicznym. 4/ Zgodnie z uchwałą Walnego Zgromadzenia z dnia 17.IV.br. Prezydium wystąpiło do Sekretarza Naukowego PAN z wnioskiem o uruchomienie organu Tewarzystwa p.n. MINERALOGIA POLONICA. 5/ Rodakoja wydawnictw PT.in. nawiązała współpracę z Redakcją Przeglądu Geologicznego, która zamierza wydać zeszyt specjalny o treści mineralogicznej oraz powiększyć udział artykułów z zakreu nauk mineralogicznych. Prosimy więc o nadsykanie stosownych materiałów. 6/ Zarząd zwraca się z prośbą do ozłonków o zgłaszanie tematów referatów naukowych na posiedzenie PTMin. obowiązuje przy tym dostarozenie streszozeń o objętości nie prze raczającej 3 stron maszynopisu przeznaczonych do druku. 7/ PTMin. uzyskało zatwierdzenie preliminarza budżetowego na rok 1969 oraz dotacje PAN w wysokości zł 50.000 .-8/ Powszechna Kasa Oszczędności i O/li w Krakowie otwarła rachunek bicżący PTMin. nr 4 - 9 - 70. Zgodnie ze statutem PTMin. oraz uchwałą Malnego Zgromadzenia prawa ozłonka uzyskują tylke te osoby, które dokonają wpłaty zł 200,- /100 zł wpisowe, 100 zł składka roczna/. W związku z tym przesyłamy blankict nadawczy celem dokonania wpłaty. Sekretarz Przewodniczący mp. doc. dr Jan Eubisz mp. prof. dr inż. ... Bolewski

Fig. 1. "The first circular" about the activities of the first weeks of the Mineralogical Society of Poland. (MSP archive).



Fig. 2. Meeting on the 10th anniversary of the Mineralogical Society of Poland; participants on the excursion to Wieliczka Salt Mine. (Phot. MSP archive).

The Presidents of the Mineralogical Society of Poland:

Andrzej BOLEWSKI (1969-1980) Witold ŻABIŃSKI (1981-1994) Marian BANAŚ (1995-1998) Janusz JANECZEK (1999-2002) Piotr WYSZOMIRSKI (2003-2004) Marek MICHALIK (2005-2008) Ryszard KRYZA (2009-)

The Present Honorary Members of the Mineralogical Society of Poland:

Jiři KONTA, Czech Republic Anna LANGER-KUŹNIAROWA, Warsaw Alfred MAJEROWICZ, Wrocław Andrzej MANECKI, Kraków Wojciech NARĘBSKI, Kraków Pádhraig KENNAN, Ireland Aleksiej Nikołajewicz PŁATONOW, Ukraine Michał SACHANBIŃSKI, Wrocław Leszek STOCH, Kraków Manfred STÖRR, Germany Andrzej WIEWIÓRA, Warsaw Josef ZEMANN, Austria Jack ZUSSMAN, Great Britain

The Late Honorary Members of the Mineralogical Society of Poland:

Andrzej BOLEWSKI, Kraków, 1906-2002 Antoni GAWEŁ, Kraków, 1901-1989 Dimitr Pawlowicz GRIGORIEW, Russia, 1909-2003 Antoni ŁASZKIEWICZ, Warsaw, 1904-1980 William Scott MACKENZIE, Great Britain, 1920-2001 Kazimierz MAŚLANKIEWICZ, Wrocław, 1902-1981 Günter Harald MOH, Germany, 1929-1993 Henryk PENDIAS, Warsaw, 1921-1994 Antoni POLAŃSKI, Warsaw, 1914-2002 Paul RAMDOHR, Germany, 1980-1985 Kazimierz SMULIKOWSKI, Warsaw, 1900-1987 Tadeusz WIESER, Kraków, 1922-2005 Jean WYART, France, 1902-1992 Witold ŻABIŃSKI, Kraków, 1929-2007

Regional Branches

Kraków Branch President: Dr hab. Maciej Manecki (AGH Kraków)

Lower Silesian Branch (Wrocław) President: Dr Czesław August (University of Wrocław)

Upper Silesian Branch (Sosnowiec) President: Prof. Dr hab. Łukasz Karwowski (University of Silesia, Sosnowiec)

Warsaw Branch President: Prof. Dr hab. Anna Maliszewska (Polish Geological Institute, Warsaw)

Scientific Groups

Polish Clay Group President: Prof. Dr hab. Jan Środoń (Polish Academy of Sciences, Kraków)

Geochemistry Group President: Prof. Dr hab. Zdzisław Migaszewski (Jan Kochanowski University, Kielce)

Thermal Methods Group President: Prof. Dr hab. Anna Langier-Kuźniarowa (Polish Geological Institute, Warsaw)

Petrology Group President: Prof. Dr hab. Ewa Słaby (Warsaw University)

Board of the Mineralogical Society of Poland, 2009-2010

President

Prof. Dr hab. Ryszard Kryza (University of Wrocław)

Vice - presidents Dr hab. Marek Michalik (Jagiellonian University) Prof. Dr hab. Ewa Słaby (Warsaw University)

Secretaries

Dr Marek Awdankiewicz (University of Wrocław) Dr Tadeusz Szydłak (AGH Kraków)

Treasurer Mgr Beata Zych-Habel (Jagiellonian University)

Librarian

Dr Eng. Katarzyna Górniak (AGH Kraków)

Members of the Board

Dr Czesław August (University of Wrocław) Prof. Dr hab. Eng. Barbara Kwiecińska (AGH Kraków) Dr Eligiusz Szełęg (University of Silesia, Sosnowiec) Prof. Dr hab. Zbigniew Sawłowicz (Jagiellonian University)

Audit Commission

Prof. Dr hab. Eng. Ksenia Mochnacka (AGH Kraków) Prof. Dr hab. Łukasz Karwowski (University of Silesia, Sosnowiec) Prof. Dr hab. Eng. Tadeusz Ratajczak (AGH Kraków)

References:

MICHALIK M., WYSZOMIRSKI P., ŻABIŃSKI W., 2006: Andrzej Bolewski jako organizator Polskiego Towarzystwa Mineralogicznego. In: Profesor Andrzej Bolewski (1906-2002). Uczony, pedagog, organizator nauki, działacz. Księga pamiątkowa w 100 lecie urodzin. Wydawnictwo Naukowe AKAPIT, Kraków: 45-51.

The Mineralogical Society of Poland, homepage: http://www.ptmin.agh.edu.pl/.

MINERALOGIA - SPECIAL PAPERS, 35, 2009 www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Prof. dr hab. Witold Żabiński (1929–2007) inicjator i długoletni Prezes Polskiego Towarzystwa Mineralogicznego

Barbara KWIECIŃSKA1

¹AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland

W dniu 15 stycznia 2007 roku zmarł Profesor dr hab. Witold Żabiński, emerytowany pracownik naukowy Wydziału Geologii, Geofizyki i Ochrony Środowiska Akademii Górniczo-Hutniczej w Krakowie. Nagłe i niespodziewane odejście Profesora Żabińskiego napełniło nas wszystkich ogromnym smutkiem i żalem. Polska mineralogia utraciła jedną ze swych wiodących postaci, wybitnego uczonego, członka Polskiej Akademii Umiejętności, byłego Przewodniczącego Komitetu Nauk Mineralogicznych Polskiej Akademii Nauk, prezesa Polskiego Towarzystwa Mineralogicznego, redaktora periodyku *Mineralogia Polonica* i członka Brytyjskiego Towarzystwa Mineralogicznego.



Fig. 1. Prof. Witold Żabiński i Prof. Tadeusz Wieser - nieżyjący Członkowie Honorowi Polskiego Towarzystwa Mineralogicznego.

Fig. 1. Prof. Witold Żabiński and Prof. Tadeusz Wieser – late Honarary Members of the Mineralogical Society of Poland.

Witold Żabiński urodził się w Krakowie w dniu 17 lipca 1929 roku. W latach 1947– 1951 studiował jednocześnie geologię i chemię na Wydziale Matematyczno-Przyrodniczym w Uniwersytecie Jagiellońskim uzyskując w 1951 r. stopień magistra filozofii w zakresie geologii i paleontologii. W 1951r. podjął pracę w charakterze asystenta w Katedrze Mineralogii i Petrografii Akademii Górniczo-Hutniczej w Krakowie. W latach następnych zajmował stanowiska adiunkta (1959), docenta (1965), profesora nadzwyczajnego, po uzyskaniu tytułu Profesora Nauk o Ziemi (1973) oraz profesora zwyczajnego (1981).W 1993 roku został członkiem korespondentem Polskiej Akademii Umiejętności. Profesor Żabiński przez 10 lat był kierownikiem Zakładu Mineralogii i Geochemii (1982– 1992) a także przez kilka lat Dyrektorem Instytutu Geologii i Surowców Mineralnych (1982–1988) na Wydziale Geologii, Geofizyki i Ochrony Środowiska AGH. Przyczynił się również w znacznym stopniu do organizacji i rozwoju nauk mineralogicznych w Uniwersytecie Śląskim i Uniwersytecie Jagiellońskim, gdzie piastował funkcje kierownika zakładów: Mineralogii UŚ (1975–1979) oraz Mineralogii i Petrografii UJ (1998–2002).

Profesor Żabiński wraz z Profesorem Leszkiem Stochem i śp. Docentem Janem Kubiszem był inicjatorem i współorganizatorem Polskiego Towarzystwa Mineralogicznego (PTMin). Pomysł utworzenia odrębnego towarzystwa o charakterze czysto mineralogicznym zrodził się po powrocie W. Żabińskiego z Wielkiej Brytanii w 1966 r. W. Żabiński, przebywając w Oxfordzie na stypendium British Council, zapoznał się z działalnością Brytyjskiego Towarzystwa Mineralogicznego. Po powrocie do kraju, po wielu trudnościach natury formalnej, Polskie Towarzystwo Mineralogiczne uzyskało status prawny. Pierwszym prezesem Towarzystwa został wybrany śp. Profesor Andrzej Bolewski. W Towarzystwie tym W. Żabiński piastował funkcję prezesa przez 14 lat (1980–1994). Na walnym zgromadzeniu w listopadzie 1978 r. Towarzystwo powierzyło mu zorganizowanie Sekcji Fizyki Minerałów. Wkrótce W. Żabiński został przedstawicielem PTMin w Komisji Fizyki Minerałów w International Mineralogical Association (IMA). Od momentu utworzenia PTMin W. Żabiński stał się rzecznikiem konieczności powołania jego organu "Mineralogia Polonica" wydawanego w językach kongresowych i profilowanego na wzór podobnych, ogólnie znanych wydawnictw światowych. Został naczelnym redaktorem periodyku Mineralogia Polonica (1970-2004). Z czasopismem tym, przez całe życie W. Żabiński był niezwykle emocjonalnie zwiazany i można chyba dzisiaj powiedzieć, że było to Jego oczko w głowie. Analizując działalność redakcyjną profesora Żabińskiego należy wspomnieć, iż pełnił on również obowiązki sekretarza naukowego Wydawnictwa PAN "Prace Geologiczne" (1960–1965), a od 1965 r. do 1970 r. wydawnictwa PAN "Prace Mineralogiczne". Brał także czynny udział w pracach związanych z organizacja Komisji Nauk Mineralogicznych Oddz. PAN w Krakowie.

Pełny spis publikacji profesora Witolda Żabińskiego (213 pozycji) znajduje się w czasopiśmie *Mineralogia Polonica* (vol.38, No.1, 2007). W chronologicznym ujęciu Jego osiągnięcia naukowe przedstawiają się następująco:

W pierwszej swej pracy, wspólnej z S. Siedleckim (1953) W. Żabiński opisał osady lądowe określane przez wulkanologów jako wulkanoklastyczne lub epiklastyczne. Z dużym zastrzeżeniem przyjął nazwę – tufit melafirowy- opatrując ją znakiem cudzysłowu. W drugiej, wspólnej z S. Dżułyńskim, przypisuje pochodzenie ciemnego zabarwienia wapieni jurajskich zjawiskom epigenetycznej pirytyzacji. Kolejne prace dotyczą zagadnień petrografii skał magmowych i osadowych okolic Krakowa a także metod oznaczania pierwiastków śladowych w minerałach i skałach. Wspólnie z Z. Michałkiem prowadzi badania geochemiczne krakowskich melafirów i diabazów . Zwraca uwagę na niższą koncentrację Cu, Ni, Cr i V w tych skałach w stosunku do typowych efuzywów z rodziny

gabr. Około 1955 r. W. Żabiński skoncentrował swe zainteresowania na mineralogii i geochemii strefy utlenienia śląsko-krakowskich złóż kruszców cynku i ołowiu. Próbuje rozwikłać kontrowersyjną genezę tych złóż. Przy okazji wyjaśnia rolę kadmu w strefie utlenienia tych złóż.

Przedmiotem jego rozprawy doktorskiej było rozpoznanie składu mineralnego galmanów, zidentyfikowanie wielu nieznanych minerałów, a także prześledzenie migracji niektórych pierwiastków śladowych w różnych utworach strefy wietrzenia. Pracę o charakterze monograficznym pt. *Mineralogiczna i geochemiczna charakterystyka strefy utlenienia śląsko-krakowskich złóż kruszców cynku i ołowiu* obronił na Wydziale Geologiczno-Poszukiwawczym AGH w 1959 r. Rozprawa ta dała asumpt do dalszych prac, wiążących się z problemem galmanów. Ukazały się następne artykuły na temat hypergenicznego hydrocynkitu czy ferrogalmanu. Ostatnią nazwę autor zaproponował dla krótkiego zdefiniowania galmanów zawierających minerał monheimit. W kolejnych publikacjach autor pozostaje przy zagadnieniach dotyczących mineralogii złóż kruszców cynku i ołowiu, wyczerpująco opisując epsomity i melanteryty z Olkusza oraz jarozyty, wspólnie z J. Kubiszem. W. Żabiński zaproponował nową nazwę dla dolomitu zawierającego węglan cynku w postaci soli podwójnej a mianowicie : dolomit cynkowy.

Po uzyskaniu stopnia naukowego doktora Witold Żabiński, w poszukiwaniu tematu pracy habilitacyjnej, zainteresował się krzemianowymi minerałami grupy granatu i wezuwianu. Szczegółowo opisał granaty spessartynowo-almandynowe występujące w pegmatytach w okolicy Świdnicy oraz grossulary i wezuwiany ze skał wapiennokrzemianowych z okolic Kletna. Szczególną uwagę poświęcił grupie hydrogranatów, opublikował monograficzną pracę pt. Studium minerałów grupy hydrogranatów, na podstawie której habilitował się na Wydziale Geologiczno-Poszukiwawczym AGH w 1965 r. Wyniki tych badań spotkały się z żywym oddźwiękiem w zagranicznych ośrodkach naukowych i wielokrotnie były cytowane w literaturze światowej. Interesujące okazało się stwierdzenie, iż wiele hydrogranatów przedstawia system dwufazowy, złożony z hydrogrossularu i wezuwianu. Powstanie jego autor tłumaczył zjawiskami odmieszania w czasie rozpadu hydrogrossularu. Podkreślał istnienie rozproszonej fazy wezuwianowej. Ta grupa minerałów- zwłaszcza wnikliwe zbadanie ich struktury krystalograficznej fascynowała Profesora Żabińskiego przez wiele lat, czego dowodem są liczne publikacje i referaty wygłaszane na sympozjach i kongresach naukowych. W 1966 r. opublikował w radzieckim czasopiśmie naukowym artykuł dyskusyjny, w którym dowiódł, że opisany przez Bliskowskiego hydrogranat z Jakucji jest w rzeczywistości wezuwianem. Artykuł ten spotkał się z aprobatą mineralogów radzieckich.

Wśród artykułów i przyczynków naukowych o tematyce odmiennej znajdujemy artykuł kompilacyjny o minerałach pomagmowych granitowego masywu strzegomskiego, wspólną notatkę z K. Birkenmajerem o śladach miedzi w pienińskim pasie skałkowym, komunikat o występowaniu sepiolitu i saponitu w melafirach Rudna i Alwernii, artykuł o niektórych problemach mineralogicznej analizy fazowej i inne. Z artykułów popularno-naukowych należałoby wymienić: *Sole kwasów organicznych w świecie minerałów* oraz *Wąwozy skamieniałych drzew*.

Zagadnienia związane z nowoczesną metodyką badań minerałów i skał (zwłaszcza spektrofotometria absorpcyjna w podczerwieni, magnetyczny rezonans jądrowy, spektroskopia moesbauerowska, absorpcyjna spektroskopia optyczna) stały się kolejnym obiektem zainteresowania Witolda Żabińskiego, co znalazło swój wyraz nie tylko w artykułach naukowych pt. Spektrofotometria absorpcyjna w podczerwieni jako metoda mineralogicznej analizy fazowej i Zastosowanie spektrofotometrii absorpcyjnej w podczerwieni do badania składu mineralnego boksytów lecz również w książce pt.

Metody badań minerałów i skał (Wyd. Geol. Warszawa 1979,1988). Prof. Żabiński opracował także oryginalne skrypty do ćwiczeń z mineralogii (wspólnie z J. Kubiszem) oraz podręcznik Mineralogia ogólna (wspólnie z A. Bolewskim i J. Kubiszem), które doczekały się kilku wydań.

W latach 70-tych coraz żywsza stawała się współpraca W. Żabińskiego z różnymi instytutami Polskiej Akademii Nauk i przemysłu. W szczególności współpracował on z Zakładem Podstaw Metalurgii PAN, czego rezultatem było współautorstwo 14 prac i komunikatów naukowych dotyczących spieków boksytowych, półproduktów metalurgii cynku itp. Od 1975 r. podjął współpracę z Zakładem Katalizy i Fizykochemii Powierzchni PAN jako kierownik i współrealizator tematu węzłowego "Utylizacja sorbentów naturalnych". Badania te zmierzały do ujawnienia ich szczególnych właściwości , do optymalnego wykorzystania niektórych krajowych sorbentów ilastych, przy czym miały zarazem charakter badań podstawowych. Uwieńczeniem tych badań stała się niewątpliwie publikacja książkowa pt. *Sorbenty mineralne Polski* pod redakcją Z. Kłapyty i W. Żabińskiego, która ukazała się w 2008 r. , a w której W. Żabiński jest autorem rozdziałów o iłach montmorillonitowych z rejonów Machowa i Chmielnika, oraz współautorem rozdziałów *Iły poznańskie* i *Ziemia krzemionkowa*.

Profesor Żabiński był wyrazicielem poglądu, że bez ścisłej współpracy z nowoczesną fizyką i chemią ciała stałego mineralogia nie jest w stanie nadążać za światowym poziomem i współczesnymi tendencjami jej rozwoju. Stąd m.in. datują się jego ścisłe kontakty z fizykami i chemikami pracującymi w różnych ośrodkach naukowych w kraju i za granicą .Są to autorzy wspólnych publikacji: K. Bruckman, K. Dyrek, M. Handke, A. Jasiński, J. Kraczka, J. Nedoma, C. Paluszkiewicz, A.N. Platonov, W. Riesenkampf, E.J. Whittaker, J. Zusman, M. Żyła. W. Żabiński przebywał na krótkich stażach naukowych w następujących miastach: Budapeszt, 1959; Frieberg, 1961; Leningrad, 1961; Oxford, 1966; Praga, 1968; Nowosybirsk, 1978; Clauthal, 1980; Marburg, 1983; Orlean, 1986; Salzburg, 1989; Piza, 1994; Toronto, 1998.

Profesor Witold Żabiński prowadził początkowo ćwiczenia a później wykłady z zakresu nauk mineralogicznych na różnych wydziałach Akademii Górniczo-Hutniczej. Wypromował 14 doktorów i 22 magistrów na Wydziale Geologii, Geofizyki i Ochrony Środowiska Akademii Górniczo-Hutniczej.

W 1968 r. W. Żabiński został powołany na kierownika i organizatora Studium Podyplomowego z zakresu mineralogii i petrografii surowców mineralnych AGH. Na studium tym prowadził specjalistyczne wykłady. W studium uczestniczyło liczne grono przedstawicieli z wielu ośrodków naukowych i przemysłowych Polski.

W 1975 r. przyjął propozycję prowadzenia wykładów z mineralogii i krystalochemii na nowoutworzonym Wydziale Nauk o Ziemi Uniwersytetu Śląskiego w Sosnowcu, obejmując jednocześnie kierownictwo Zakładu Mineralogii UŚ. Równocześnie Instytut Chemii Uniwersytetu Jagiellońskiego zwrócił się do profesora Żabińskiego z prośbą o prowadzenie wykładu "Geochemia z mineralogią" dla studentów chemii. W latach późniejszych (1998–2002) został kierownikiem Zakładu Mineralogii i Petrografii UJ.

Za wszechstronną i wieloletnią działalność naukową i dydaktyczną W. Żabiński otrzymał wiele nagród, medali i odznaczeń przyznawanych przez Urzędy Miast: Krakowa i Katowic, Rektora Akademii Górniczo-Hutniczej, Ministra Szkolnictwa Wyższego i od Rady Państwa. Zaszczytne wyróżnienia RP otrzymał w 1973 r. - Krzyż Kawalerski Orderu Odrodzenia Polski i w 2000 r. - Krzyż Komandorski Orderu Odrodzenia Polski.

Na pytanie jakim był profesor Witold Żabiński przytoczę słowa napisane przez śp. Profesora Tadeusza Wiesera w recenzji opracowanej dla władz Wydziału GGiOŚ wr.1969.Cytuję: "Jest to wybitny specjalista, chętnie i umiejętnie dzielący się swym bogatym doświadczeniem. Znamionuje go bezpośredniość, systematyczność, prostota w obcowaniu, skromność i wybitne poczucie koleżeńskości i współodpowiedzialności za pracę zespołu. O wszechstronności zainteresowań i energii świadczą nie tylko osiągnięcia badawcze ale i aktywny udział w pracach redaktorskich oraz z pasją prowadzona, wieloletnia działalność dydaktyczna."

Pozwolę sobie jeszcze przytoczyć słowa Pana Dziekana Wydziału GGiOŚ, Prof. dr hab. inż. Jacka Matyszkiewicza wypowiedziane przy pożegnaniu Profesora Żabińskiego w dniu Jego pogrzebu 23 stycznia 2007 r. Oto one: "Był to wybitny uczony a przy tym Człowiek skromny, pełen dobroci, który nigdy nie zapominał, że wysoki poziom przekazywanej wiedzy jest równie ważny, jak czynienie tego z nieskazitelną, wyniesioną z domu rodzinnego kulturą. I właśnie wspomnienie tej kultury, jednakowej wobec wszystkich, tej samej i takiej samej w kontaktach z rektorami, dziekanami, jak i studentami pierwszego roku sprawia, że nagłe odejście Profesora napełnia nas wszystkich ogromnym smutkiem i żalem. Z jego odejściem tracimy pewien wzorzec osobowy. Przy ogromnej skromności i pełnej szacunku postawie, którą Profesor Żabiński okazywał wobec swoich rozmówców, klimat i poziom każdej rozmowy były po prostu uniwersyteckie, bo wprost nie sposób było zachować się inaczej w obecności Pana Profesora. Profesor Żabiński nie aspirował do bycia postacią medialną."

Na zakończenie dodam od siebie, że Profesor Witold Żabiński był dla nas niedościgłym wzorem wnikliwego i rzetelnego badacza, był wybitnym uczonym, postacią wiodącą w polskiej mineralogii, był znakomitym nauczycielem akademickim, wspaniałym Człowiekiem.

Professor dr hab. Witold Żabiński (1929 – 2007): a founding fellow and former President of the Mineralogical Society of Poland

Professor dr hab. Witold Żabiński, professor emeritus of the Faculty of Geology, Geophysics and Environment Protection of the AGH University of Science and Technology in Kraków, deceased on January 15th, 2007. His sudden and unexpected death has filled us with deep sadness and sorrow. Polish mineralogy has lost one of its leading figures, an outstanding scientist, a fellow of the Polish Academy of Arts and Sciences, a former President of the Committee on Mineralogical Sciences of the Polish Academy of Sciences, a former President of the Mineralogical Society of Poland (MSP), an editor of *Mineralogia Polonica*, and a member of the Mineralogical Society of Great Britain.

Witold Żabiński was born in Kraków on July 17th, 1929. In 1947–1951 he studied, contemporaneously, geology and chemistry on the Faculty of Mathematics and Science of the Jagiellonian University and graduated in 1951 with the degree of Master of Philosophy, in the scope of geology and palaeontology. In the same year he was employed as an assistant in the Department of Mineralogy and Petrography of the AGH Academy of Mining and Metallurgy in Kraków. In the following years, he got a position of adjunct (1959), docent (1965), associated professor (after receiving his Professorship in Earth Sciences in 1973) and, finally, full professor (1981). In 1993 he became a membercorrespondent of the Polish Academy of Arts and Sciences. For ten years (1982-1992), Witold Żabiński was the head of the Department of Mineralogy and Geochemistry, and also for several years (1982–1988), the director of the Institute of Geology and Mineral Raw Materials at the Faculty of Geology, Geophysics and Environment Protection of the AGH. He has also contributed a lot to the organization and development of mineralogical sciences at the University of Silesia and the Jagiellonian University, taking the position of the head of the Department of Mineralogy at the US (1975-1979) and of the Department of Mineralogy and Petrography at the JU (1998–2002).

Professor Witold Żabiński, together with Professor Leszek Stoch and late Docent Jan Kubisz, were the initiators and co-organizers of the Mineralogical Society of Poland. The idea of the formation of the MSP as a separate society was born after Witold Žabiński's return from his British Council scholarship in Oxford in 1966, where he got acquainted with the activities of the Mineralogical Society of Great Britain. After his return to Poland, and after overcoming a range of formal obstacles, the MSP was formed on April 17^{th} , 1969. The first President of the MSP was Professor Andrzej Bolewski. Witold Żabiński was his follower, and he kept the position of the President of the MSP for the next 14 years (1980–1994). In 1978 the General Assembly of the MSP designated him to organize a Group of Physics of Minerals, and soon afterwards Witold Zabiński was elected as the MSP representative to the Commission on Physics of Minerals of the International Mineralogical Association (IMA). Soon after the formation of the MSP, Witold Zabiński strongly opted for the creation of the society journal Mineralogia Polonica, edited in English and in an editorial form corresponding to recognized international journals. He was appointed as the editor of *Mineralogia Polonica* and kept this position for the long period of 1970-2004. Mineralogia Polonica was his "beloved child" and he was very emotionally involved in the editorial works for the journal.

Reviewing the editorial activities of Professor Witold Żabiński, one should also mention that he was the scientific secretary of *Prace Geologicze* (*Geological Papers*), 1960–1965, and *Prace Mineralogiczne* (*Mineralogical Papers*), 1965–1970, both journals edited by the

Polish Academy of Sciences (PAS). He was also involved in organizing the Kraków Branch of the Commission on Mineral Sciences of the PAS.

Professor Witold Żabiński's achievements in the field of mineralogy are impressive and the list of his publications contains 213 items. The complete list can be found in *Mineralogia Polonica*, vol. 38/1, 2007. Here, we present only a short chronological review of Professor Żabiński's most significant achievements.

The early research interests of Witold Žabiński dealt with selected problems of the mineralogy and geochemistry of sedimentary and volcanic rocks of the Kraków region. His PhD thesis on weathering processes in the zinc-lead ore deposits of the Silesia–Kraków area was defended in 1959, and was followed by a number of publications describing interesting mineral parageneses, with galmans, Zn-bearing carbonates, monheimite, hydrozincite, epsomite, melanterite, jarosite etc.

The next research projects were carried on the garnets and vesuvianite group minerals, mostly from pegmatites near Świdnica and calc-silicate rocks from Kletno in the Śnieżnik Massif in Lower Silesia. The results of these studies were summarized in a monograph *Hydrogarnets* presented as his habilitation thesis and defended at the AGH in 1965. He discovered that many hydrogarnets are in fact two-phase systems composed of hydrogrossularite and vesuvianite and this finding was widely recognized in international literature.

Further scientific interests of Professor Żabiński concentrated around novel instrumental techniques in mineralogy and petrology, in particular IR, EPR, NMR, as well as opticalabsorption, Mössbauer and Raman spectroscopies. Applications of these methods are exemplified in a number of his mineralogical case-studies, and described in the well-known Polish handbook *Methods of investigation of minerals and rocks* (Wydawnictwa Geologiczne, Warszawa, 1979, 1988). Professor Żabiński published also original academic manuals for practicals in mineralogy and the basic Polish handbook *General mineralogy* (co-authored by A. Bolewski and J. Kubisz), the latter having several editions.

Professor Witold Żabiński used to say that modern mineralogy must have intimate links with modern physics and chemistry. He co-operated closely with many well-known physicists and chemists and he applied physical and chemical methods in his studies. During his academic career, he visited many universities abroad, e.g.: Budapest, Freiberg, Leningrad, Oxford, Prague, Novosibirsk, Marburg, Orlean, Salzburg, Pisa, Toronto. He also collaborated with industry- and mining-oriented institutions and companies dealing with practical issues, such as boxites, zinc ores, natural sorbents etc.

For many years Professor Witold Żabiński was a leading lecturer in mineralogical sciences at several faculties of the AGH in Kraków, and for shorter periods also at the University of Silesia in Sosnowiec, and at the Jagiellonian University in Kraków. In 1968 he was appointed as the organizer and director of the Post-Diploma Studies in Mineralogy and Petrology at the AGH. These courses were highly recognized and attended by a great number of mineralogists from several universities and industrial companies in Poland. Professor Żabiński supervised 22 MSc and 14 PhD theses.

For his scientific and didactic achievements, Professor Witold Żabiński received many prizes and decorations, e.g. from the Rector of the AGH, from the Minister of High Education, and many other honorary medals, including the prestigious Cavalier Cross and the Commander Cross of the Polonia Restituta Order.

What kind of person was Professor Witold Żabiński ? Part of the answer could be found in a fragment of Professor Tadeusz Wieser's reference letter to the Council of the Faculty of Geology, Geophysics and Environment Protection (1969): "He is an outstanding specialist, always willingly sharing with others his great expertise. He is systematic, straightforward and natural in his relationships with others, very friendly and responsible for his team". In a similar way sound the words of Professor Jacek Matyszkiewicz, the Dean of the Faculty, at the mourning ceremony: "He was an outstanding scientist and, at the same time, a modest and very good person, who never forgot that the high level of knowledge being offered to the students is as important as doing that with impeccable high culture brought away from your home. And just remembering this culture, equal for all, the same in contacts with rectors deans, and with the first-course students, is the reason why the lost of Professor fills us with great sorrow and deep mourning. We loose a standard of great personality."

And, finally, my personal reflection: Professor Witold Żabiński was for many of us an inimitable example of a very exact and honest researcher, an outstanding scientist, and a leading figure in Polish mineralogy; He was an excellent academic teacher and a wonderful Man.

Invited lectures

MINERALOGIA - SPECIAL PAPERS, 35, 2009 www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Valuing geodiversity and its importance for abiotic nature conservation in the Holy Cross Mountains, Poland

Agnieszka GAŁUSZKA¹, Zdzisław M. MIGASZEWSKI¹

¹ Geochemistry and the Environment Division, Institute of Chemistry, Jan Kochanowski University, 15G Świętokrzyska Str., 25-406 Kielce, Poland; aggie@ujk.kielce.pl

Introduction

Geodiversity is "a natural diversification of Earth's surface including geologic, geomorphologic, soil, and surface water features and systems formed by natural (endogenic and/or exogenic) processes, in places with a different anthropogenic imprint" (Kozłowski et al., 2004a). Even a cursory glance at a geologic map of Poland gives the impression of a very high geodiversity of the Holy Cross Mountains (Świętokrzyskie Mountains). This region is known as a Mecca for geologists. Nowhere else in Poland one can observe sedimentary rocks so diversified in their origin, mineral composition and age spanning most of the Paleozoic, Mesozoic and Cenozoic. According to Wróblewski (2000), about 40% of all geologic reserves in Poland are located in this relatively small area of about 120 x 70 km². The Holy Cross Mountains have also the oldest tradition of mining, which started with flint (chert) extraction in the Paleolithic and Neolithic periods. The main mining center of that time, one of the biggest in Europe, was located in Krzemionki Opatowskie in the northeastern part of the Holy Cross Mountains. In the Roman times covering the period from the 2nd century BC to the 4th century AD, the Holy Cross Mountains were one of the largest iron mining and smelting regions in Europe and then in the 16th through 19th centuries in Poland (Old Polish Industrial Center). Since the early Medieval times until the 17th century lead and copper ores, as well as a variety of decorative stones (e.g. rose-like calcite and "Zygmuntówka" conglomerates) were also mined here. The unique geologic features of the Holy Cross Mountains give an opportunity to study the values of their geodiversity and impose an obligation to conserve it.

According to Gray (2004, 2005), the values of geodiversity may be divided into six groups: (i) intrinsic or existence; (ii) cultural; (iii) aesthetic; (iv) economic; (v) functional; (vi) scientific. In this article we apply Gray's classification in valuing geodiversity of the Holy Cross Mountains. We also aim at establishing importance of such classification in managing abiotic nature conservation in the Holy Cross Mountains.

Intrinsic value of geodiversity

Intrinsic (existence) values refer to non-utilitarian features of abiotic nature (Gray, 2004). This category has a lot in common with cultural value of geodiversity and it is very hard to objectively evaluate. Geodiversity in this approach may be considered as a source of intellectual inspiration, a stimulation of an interest in geosciences or a base for answering philosophical questions, such as these about the origin and evolution of life, relation of human to nature etc.

Abiotic nature of the Holy Cross Mountains has a great intrinsic value. Even a short Sunday walk taken in one of the four geologic reserves in Kielce, the capital city of the region, arouses imagination and stimulates studying of Earth's history recorded in rock formations. Observation of the worldwide famous overturned fold in the "Ślichowice Reserve" (Fig. 1A) or the fossil coral reef in the "Kadzielnia Reserve" (Wróblewski, 2000) may be very important for taking an active interest in geology.

Another example for intrinsic value of geodiversity in the Holy Cross Mountains is the link between geology and religion. This relation is based on spiritual value of some geologic features. One of such objects is the sacred stone circle at Mt. Holy Cross (595 m a.s.l.). In the best preserved part it is about 2 km long, 10 m wide and 2.5 m high. It was built in the 8th and 9th centuries and it is recognized as a place of worship topped with a pagan temple. Both geology and religion meet again in the Saint Rosalie Chapel which was built within the outcrop of large fissured sandstone blocks of Triassic age at the top of Mt. Perzowa (Fig. 1B). The consecutive example of spiritual value of geodiversity is a 1.5 m high sculpture of Saint Barbara, the patron saint of miners and geologists, carved in a lump of galena (PbS) that was mined in the Karczówka Hill in the early 17th century (Fig. 1C).

The legends and myths of the region have often been referred to geologic phenomena that were hard to understand by uneducated inhabitants of the Holy Cross Mountains. One of the examples is the legend of the origin of "Devil's Stone" quoted by Stankiewicz (2002). This is a nature landmark that encompasses a Cambrian quartzitic sandstone cliff located at the top of Mt. Klonówka (473 m a.s.l.). According to the legend, it was created by the devil, which was flying with a large stone taken from hell as a gift for a witch. As soon as the devil heard a church bell, he dropped the rock and it stuck in the ground forming a cliff (Fig. 1D). Many cliff groups or caves bear the name "hell". The most spectacular are Lower Jurassic sandstone cliffs named "Piekło Niekłańskie" ("Niekłań Hell") located in the northern part of the region (Fig. 2A). Another legend explains the origin of vast rock fields on the northern slopes of Mt. Holy Cross as ruins of an ancient castle (Fig. 2B). These examples may seem very naive at first sight, but they demonstrate that even uneducated people ask questions about the geologic processes they observe and experience. Geodiversity of the Holy Cross Mountains may act as an intellectual stimulation, which is certainly of intrinsic value.

Cultural value of geodiversity

These and other similar legends and myths explaining the origin of rock formations or landforms in the Holy Cross Mountains originate from folklore, which represents in this respect a cultural value of geodiversity (Gray, 2004). Another example of such value is the link between geology and archaeology (Gray, 2005). The most important archaeological mining site in this region is the Krzemionki flint mine (Fig. 2C). This mine is now an archaeological reserve and efforts are made to enter it on the UNESCO World Heritage List. The striped flint (chert) was extracted there from about 3900 to 1600 BC, but the use of this important mineral raw material dates probably back to the Mesolithic period (Bąbel, 2003). The "Paradise" cave located southwest of Kielce is famous for its beautiful dripstones and flowstones. After the cave was discovered in 1964, some stone tools used by *Homo (sapiens) neandertalensis* and bones of a cave bear, a mammoth and a wooly rhino were found.

The cultural value of geodiversity is also manifested by cultivating an ancient tradition of iron smelting from local iron ore deposits. Every August an open-air festival of ancient iron smelting is organized in Nowa Słupia – a small town situated at the foot of the Mt. Holy Cross. In addition, the guests of the "Jodłowy Dwór" hotel (near the southern entrance

to Świętokrzyski National Park) may request a private demonstration of this event. The local hematite ore was smelted in charcoal fuelled primitive furnaces of about 1.2 m high made of clay.



Fig. 1 A) Overturned fold composed of Frasnian beds in the "Ślichowice Reserve" (western part of Kielce); B) Saint Rosalie Chapel inside Triassic sandstone blocks (Mt. Perzowa); C) Sculpture of Saint Barbara carved in a lump of galena (cloister at Karczówka Hill, southwestern part of Kielce); D) "Devil's Stone" made of Cambrian quartzitic sandstones at Mt. Klonówka

Geodiversity may sometimes be an inspiration for artists, for example giving rise to a new trend in photography, the so-called "Holy Cross Mountains school of landscape" in the 20th century. Geomorphology and geology of this region were also present in literary works of many famous Polish writers and poets, for example Stefan Żeromski, Witold Gombrowicz, Adolf Dygasiński (Gralak, 1997).

The last example of cultural value of geoviversity in the Holy Cross Mountains may be a unique amphitheater built in an abandoned limestone quarry which is now a geologic reserve "Kadzielnia". Numerous cultural events, such as festivals, concerts, shows and performances are organized there in the summertime.



Fig. 2 A) Lower Jurassic sandstone cliffs named "Piekło Niekłańskie" ("Niekłań Hell"); B) Quartzite rock field on the northern slope of Mt. Holy Cross; C) Krzemionki flint mine dating back to the Mesolithic period; D) Saint Francis spring in Święta Katarzyna

Aesthetic value of geodiversity

Aestethic value of abiotic nature is reflected in various landscapes and landforms, which make up specific environment for relaxation and contemplation of the forces of nature. It is hard to objectively assess the aesthetic value of a place due to the subjectivity of such judgement, but there are some signs that may be regarded as its indicators. In relation to geodiversity, such an indicator is geotourism. Geotourism is an active way of spending free time combined with learning by visiting places linked to geologic formations or history, such as geological museums and exhibitions, caves, inanimate nature reserves, outcrops with fossil beds and minerals etc. In the definition of geotourism proposed by Newsome and Dowling, an emphasis is laid on appreciating the processes that are forming and formed geologic and geomorphologic features (Newsome, Dowling, 2006). These authors also presented the hierarchy of features of potential geotourism interest: landscape > landforms > rock outcrops > rock types > sediments > soils > crystals. All these features can be found in the Holy Cross Mountains. This region also offers to visitors many opportunities to do geological museums or exhibitions. The biggest regional geologic museum with a large mineral and rock collection is located in the building of the Polish Geological Institute in

Kielce. The National Museum has also an exhibition dedicated to geology. Occasionally, special geologic exhibitions are also organized by this museum, for example the one regarding Jurassic and Cretaceous flints. For those who are interested in local minerals, several private galleries and small exhibitions in local museums are available, for example in Święta Katarzyna, Chęciny, Pińczów and Miedzianka. In Nowa Słupia there is a museum of ancient mining and smelting. One of the main attractions for children is the Jurassic park in Bałtów with an open-air exhibition of dinosaur models. This museum also organizes some activities, including geologic and art workshops for children or panning gold. These and other geologic attractions of the Holy Cross Mountains promote tourism and have a great educational value.

Aesthetic value of geodiversity is also manifested through inspiration for artists. As mentioned above, landscapes and landforms or even smaller-scale objects, such as Saint Francis spring in Święta Katarzyna (Fig. 2D), were an inspiration for Polish photographers, writers and poets. In the last decade a striped flint became a very popular decorative stone. Artistic flint silver jewelry is manufactured in Sandomierz, where the most precious collections are exhibited in the regional museum.

Economic value of geodiversity

From the point of view of nature conservation, this category of geodiversity value may be controversial. In the Holy Cross Mountains there is a well prospering mining industry quarrying mostly for limestones, dolomites and sandstones. Mining is usually seen as a destructive activity having a negative impact on the environment, but there are many examples of nature reserves or other forms of conservation which were created in abandoned quarries. For example: thanks to limestone extraction in the western part of Kielce a unique and worldwide famous overturned fold was exposed and it is now one of the most valuable features of geodiversity in the Holy Cross Mountains (Fig. 1A). Thus mining, especially sustainable mining, should not be treated only as a threat to the environment, but also as an important human activity assuring high prosperity for modern society and sometimes as a factor influencing geodiversity (Kozłowski at al., 2004b).

Functional value of geodiversity

Functional values of geodiversity encompass all utilitarian features of abiotic nature. These values include: rocks beds that serve as a filter for permeating precipitation waters, rock formations that hold the water in subsurface aquifers, soils for their role in agriculture, forestry, soil and rock minerals as a source of micronutrients for plants, animals and humans (Gray, 2005). Gray (2004) stresses an important function of abiotic nature for providing habitats, creating and nurturing biodiversity. According to Kozłowski (2004), geodiversity in the geological past of the Earth greatly influenced its biodiversity. Different authors introduced quantitative methods for evaluating the relationship between biodiversity and geodiversity (e.g. Burnett et al., 1998; Jačková, Romportl, 2008). The biodiversity of the Holy Cross Mountains is high (Andrzejewski, Weigle, 2003). A diversity of habitats, e.g. typical for high mountains, such as Carpathian beechwood -Dentario glandulosae-Fagetum, peatbogs or xerothermic meadows occurs here in a relatively small area. The Holy Cross Mountains are famous for the largest reserve of endemic Polish larch (Mt. Chełmowa) or tree forms of yew (Cisów). At the top of Łysogóry range an endemic forest community occurs – the Holy Cross fir forest. There are plans of including about 40% of the area of the Holy Cross Mountains province to NATURA 2000 Ecological Network. Although no efforts of evaluation of the geodiversity
influence on biological diversity in the Holy Cross Mountains region have been made so far, it is obvious that these two features of the environment overlap each other.

Scientific value of geodiversity

Geodiversity of a given region also provides opportunities for research and education. The unique geology of the Holy Cross Mountains has fascinated many scientists. Among them, the most known Polish geologists: Stanisław Staszic, Jan Czarnocki, Jan Samsonowicz and Walery Goetel. Different aspects of geology: structural geology, sedimentology, tectonics, paleontology, hydrogeology, ore geology, geochemistry etc. have been studied in this region. The scientific institutions that conduct geologic studies in the Holy Cross Mountains are located in Kielce (Jan Kochanowski University, Holy Cross Mountains Branch of the Polish Geological Institute, Geological Enterprise), but many geoscientists from Poland and other countries also publish scientific articles regarding this area. These studies provide a wide understanding of the processes that shape the Earth, the knowledge about geologic history of the planet that has implications for the special educational value of the Holy Cross Mountains area.

High geodiversity of the region is invaluable for training and educating the public, school and university students, as well as professional geoscientists (Gray, 2004). Every year geology students from Warsaw, Sosnowiec and Lublin come to the Holy Cross Mountains to take part in field courses in cartography, general geology, sedimentology etc. This region is often a destiny of school children excursions. For the purpose of education of non-geologists a few geologic guidebooks and leaflets have been published (e.g. Kotański, 1968; Stupnicka, Stempień-Sałek, 2001; Jędrychowski, 2008). The Center for Geoeducation was established in the City Hall of Kielce in 2003. One form of its activities is "Club of Geology Fans" – an informal organization that gathers young people interested in geosciences. Students and adults (both geologists and non-geologists) can become a member of "Holy Cross Mountains Association of Geological Sciences' Friendships", which is a non-profit organization. Twice a year this association organizes mineralogical shows during which many interesting collections of rocks, minerals and fossils from all over the world can be admired. Geoeducation has a long and vivid tradition derived from great geodiversity of this region supported by the science and education.

Abiotic nature conservation

Nature conservation is necessary for preserving the most valuable biotic and abiotic elements of the environment. Many geoscientists claim that the idea of abiotic nature conservation (geoconservation after Gray, 2008b) is often oversimplified, especially in relation to conservation of biological resources, (e.g. Gray, 2008a, 2008b). People usually think that the wildlife is worth protection because of its fragility and do not see the real threats to geodiversity. Geologic processes that have formed landscapes are so slow in the perspective of human's life that destroying a geologic feature is usually irreversible. From this point of view, it seems that geoconservation is even more important than biological conservation. Besides, there are many ways of the active and passive ways of wildlife conservation, for example nurturing endangered species in zoos, reintroduction of locally extinct species, preserving seeds or genes in DNA banks etc. In case of abiotic nature conservation, a constant management of geodiversity elements is needed. Gray (2008b) gives some details about the methods of geoconservation management, such as: secrecy, signage, physical barriers, reburial, excavation/curation, permitting/licensing, supervision, benevolent ownership, legislation, policy, site management and education. Among all the methods mentioned, legislation plays the most important role in geoconservation in Poland. Different forms of conservation are created on the base of "Nature Conservation Act" (2004). This document distinguishes the following conservation forms: areal, individual and species. These forms can be divided into: national parks, nature reserves, landscape parks, areas of protected landscapes, NATURA 2000 protected areas, nature monuments, documentary sites, areas of ecological use, nature-landscape associations and species conservation. Documentary sites are the forms of geoconservation only. All these forms occur in the Holy Cross Mountains, many of them were established to protect geologic features. The first geologic reserve in Poland - "Ślichowice" was established in Kielce in 1952 and the first geologic landscape park in Poland "Checiny-Kielce Landscape Park" was created in 1996 in the southern part of the Holy Cross Mountains. Of the other geoconservation forms: 25 geologic reserves, 120 inanimate nature monuments, 12 documentary sites are located in the region discussed. Some protected areas which have been established for protection of wildlife may also represent a high geodiversity. The examples of such forms in the Holy Cross Mountains are: "Karczówka Landscape Reserve" with traces of historical galena mining sites, "Świętokrzyski National Park" with famous quartzitic sandstone rock fields at the top of Mt. Holy Cross, and "Milechowy Forest Reserve" with diverse forms of karstification in Jurassic limestones, including 17 m long cave

Although many efforts are made to conserve a very high geodiversity of the Holy Cross Mountains, some more actions are needed for a better management of geoconservation forms. More attention should also be paid to popularization of geotourism, geoeducation and arousing general public interests in Earth Sciences. As Murray Gray stated (2004) "the greatest threat to geodiversity is ignorance", this remarkable insight is a message to all geologists who are responsible for promotion of the idea of geodiversity to the public. The most important issue of abiotic nature conservation is to show that geodiversity is a value from which we can all benefit and thus it needs special protection.

Conclusion

The geology influences great geodiversity of the Holy Cross Mountains, which is manifested in different ways from humanistic, archeological, artistic and scientific points of view. The values of geodiversity in this region should be taken into account when establishing guidelines for the best management of geoconservation forms. Six categories of geodiversity values proposed by Gray (2004, 2005) are represented in the Holy Cross Mountains. In our opinion, the most important for geoconservation in this region are the following values: cultural, aesthetic (in relation to geotourism) and scientific.

The main conclusion of this article is that geodiversity conservation in the Holy Cross Mountains should be focused on three aspects: (i) geological heritage conservation, (ii) popularization of geological knowledge and (iii) promotion of geotourism.

References:

- ANDRZEJEWSKI R., WEIGLE A., 2003: Biological diversity of Poland (in Polish), Narodowa Fundacja Ochrony Środowiska, Warsaw, 284 pp.
- BABEL J.T., 2003: Krzemionki. Prehistoric mines of the banded flint. A guidebook, Museum of History and Archaeology, Ostrowiec Świętokrzyski, 32 pp.

BURNETT M.R., AUGUST P.V., BROWN J.H., 1998: The influence of

Geomorphological Heterogeneity on Biodiversity I. A Patch-Scale Perspective. *Conservation Biology* 12(2), 363-370

GRALAK I., 1997: The Holy Cross Mountains in Polish Literature (in Polish with English summary), KTN, Kielce, 183 pp.

- GRAY M., 2004: Geodiversity: Valuing and Conserving Abiotic Nature, Wiley, Chichester, 434 pp.
- GRAY M., 2005: Geodiversity and geoconservation: what, why, and how? *Geodiversity & Geoconservation* 22/3, 4-12.
- GRAY M., 2008a: Geodiversity: the origin and evolution of a paradigm. In: C.V. Burek, C.D. Prosser (eds.), The history of geoconservation, 300, 31-36, Geological Society of London, Special Publications, London.
- GRAY M., 2008b: Geodiversity: developing the paradigm. Proceedings of the Geologists' Association 119, 287-298.
- JAČKOVÁ K., ROMPORTL D., 2008: The relationship between geodiversity and habitat richness in Šumava National Park and Křivoklátsko pla (Czech Republic): a quantitative analysis approach. *Journal of Landscape Ecology* 1/1, 23-38.
- JĘDRYCHOWSKI J. 2008: Holy Cross Mountains geologic paradise. A guidebook for geotourists (in Polish), Perpetuum Mobile Publishing Office, Kielce, 112 pp.
- KOTAŃSKI Z., 1968: With a backpack and a hammer to the Holy Cross Mountains. Geologic guidebook for tourists (in Polish), Geological Printing Office, Warsaw, 225 pp.
- KOZŁOWSKI S., 2004: Geodiversity: the concept and scope of geodiversity. *Przegląd Geologiczny* 52, 833-837.
- KOZŁOWSKI S., MIGASZEWSKI Z.M., GAŁUSZKA A. 2004a: Geodiversity conservation – conserving our geological heritage. *Polish Geological Institute Special Papers* 13, 13-20.
- KOZŁOWSKI S., MIGASZEWSKI Z., GAŁUSZKA A., 2004b: The role of geodiversity in holistic vision of nature (in Polish). *Przegląd Geologiczny*, 52, 291-294.
- NATURE CONSERVATION ACT, 2004: Journal of the Acts (Dziennik Ustaw in Polish), 92, 880.
- NEWSOME D., DOWLING R., 2006: The scope and nature of geotourism. In: D. Newsome, R. Dowling (eds.), Geotourism: sustainability, impacts and management, 3-25, Elsevier Butterworth-Heinemann, Burlington, Minnesota.
- STANKIEWICZ J., 2002: Holy Cross Mountains legends (in Polish), Glob-Tour, Kielce, 71 pp.
- STUPNICKA E., STEMPIEŃ-SAŁEK M., 2001: Getting to know the Holy Cross Mountains. Geologic excursions (in Polish), Wydawnictwo Naukowe PWN, Warsaw, 173 pp.
- WRÓBLEWSKI T. 2000: Geodiversity Conservation in the Holy Cross Mts region, with a map of protected inanimate nature objects and areas, scale 1:300,000 (in Polish with English summary), Polish Geological Institute, Warsaw, 87 pp.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Tracking turbidity currents downslope - new models for the distal run-out of sediment gravity flows

Peter HAUGHTON¹

¹ UCD School of Geological Sciences, University College Dublin, Belfield, Dublin 4, Ireland; Peter.Haughton@ucd.ie

Turbidity currents dominate the supply of sediment to many deep-water basins. Slides and slumps on the continental slope can be remoulded into debris flows which then transform into turbidity currents. The latter may also form directly from hyperpcynal river effluent or as a result of storm stirring. Turbidity currents both erode and deposit and are responsible for much of the morphology of the deep sea floor, including canyons, deep sea fans and slope channel systems. Conventional models for the run-out of turbidity currents envisage progressive dilution due to a combination of selective sediment deposition and turbulent mixing with the ambient water. Concentrated or high-density turbidity currents that leave thick stuctureless or dewatered sands are widely thought to evolve into lowdensity flows that deposit fine grained, thin-bedded, parallel- and ripple-laminated sands distally.

Better knowledge of the distal parts of many deep-water fan systems show that the reality is quite different. The distal (and lateral) reaches of these systems are dominated by relatively thick event beds that have a distinctive structure involving: a basal clean sandstone (H1), a 'banded' division of clean and more clay-rich sandstone (H2), a clay-rich sandstone (H3), often with mud clasts and carbonaceous matter, and a relatively thin capping laminated sand (H4) fining into a graded silt- to claystone cap (H5). The bed structure is thought to reflect the passage of a longitudinally fractioned 'hybrid' flow with a turbulent front followed by a turbulence-suppressed or transitional section (producing the banding) and then a 'linked' debris flow. The event is completed by a relatively dilute tail (a low-density turbidity current). The widespread occurrence of beds of this type implies common down-dip transformation and partitioning of turbidity currents into flows with cohesive behaviour, and a role for debris flows (albeit linked) in the outermost parts of even large fan systems. The incorporation of mud clasts, their segregation in near-bed layers and their disintegration to generate dispersed clay that can dampen turbulence are inferred to be key steps in the generation of many distal hybrid flow deposits.

The recognition of hybrid event beds is important for better understanding (1) the concept of proximality in turbidite successions, (2) the geometry and connectivity of sandstones in outer fan settings, (3) reservoir quality in ultra-deep exploration plays on continental margins, (4) the ultimate repository for much of the particulate carbon that leaves the continental shelf and (5) the 'greywacke' paradox.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Mineralogy and petrology in the service of society: challenges for the 21st century

Dušan HOVORKA¹

¹ Faculty of Natural Sciences, Constantine the Philosopher University, Trieda A. Hlinku l, 949 01Nitra, Slovakia

The last two decades of the 20th century, and the first years of the 21st, have brought the realisation that:

a) the leading problems of mankind in the field of technology, e.g., the treatment of diseases (except for the new ones appearing all the time) and in the development of rapid global communications, have been already generally solved to the benefit of the whole of mankind;

b) the construction of instruments, laboratory devices, global electronic communication, but also satelites, rockets, supersonic planes and super fast automobiles, had reached their limits. Generalizing, it is clear that one of the ideas for future discoveries, and for the progress of mankind generally, will be by interdisciplinary or transectorial collaboration of individuals and institutions of all nations;

c) the solution of the problems of the 21st century (shortages of raw materials, supplies of food and drinkable water for millions), is the aim that should drive both politicians and scientists;

Today, the benefits flowing from the creation of the International Council on Applied Mineralogy (ICAM) during the 1981 IMA conference in Johanesburg are of great importance. The objectives of ICAM include the organizing of international cooperation in interdisciplinary activities involving technical mineralogy.

At the beginning of these considerations, we have to take into account that the tendency towards closer connections between the states of the Old continent is progressing rapidly.

Thus, the main problems of international dimension should be capable of solution on an international basis. In the context of these goals, efforts towards finding new vaccines to counter pandemic epidemics are worth noting; at this time, the N_1K_1 virus is rapidly spreading on all continents, in both economically developed- and underdeveloped counries. At present, the focus of mineralogy is:

-) the study of known minerals, the discovery of new minerals and the development of new applications of known minerals and rocks,

-) the study of the solid products that are a part of industrial wastes produced today and those that accumlated in the past,

-) the potential to inflence technological processes so as to minimize the output of dangerous chemicals and gases into the environment,

-) the finding of substitutes for materials already fully exploited, e.g., the manufacture of artificial diamonds for use as superhard material in industry and numerous others.

Having been honored and having had the opportunity to be a member of Slovak delegations to the last six biennial General Conferences of UNESCO in Paris, I will try, in the following few sentences, to present a general review of UNESCO as expressed in its

resolutions and of the EU Commision which deals with the geosciences, including mineralogy and petrology.

The key trends in the activities of these international bodies can be briefly expressed as follows. UNESCO and the EU Commission prefer to finnancially support international geoscientific projects:

- in which institutions and people from underdeveloped countries are included;

- which focus on the material aspects of mankinds cultural heritage (the study of raw materials used in their construction, transport routes of ready made implements and their raw materials in prehistory, their description, definition of transport routes and their role in

contacts between various tribes and races, and their conservation); - which study and use of currently produced wastes and wastes accumulated in the past;

- which study raw materials used in non-traditional applications, e.g., crushed limestone used instead of pure kaolin in the paper industry, melted basic rocks (alkali basalts, amphiolites) instead of high quality steel used for metal tubes in, e.g., the bent parts of conduit systems, and others,

- which study the solid emmisions of cement-, asbestos-, magnesite- and other producing technologie;,

- which preferably study raw materials which are used in environmental projects or projects that, by overcoming challenges, support the sustainable development of mankind.

All of the above themes could be classified as aplied mineralogy and petrology. An example (chosen by the author), which should serve as an example of a non internationally-preferred scientific project might be the study of the geochronology of the Tatra Mts granite body. There exist several tens of determined ages of the granitic cooling which have been confirmed by various methods in several laboratories. The key problem nowadays is to evaluate all existing data and to write a synthesis of the problem.

Mineralogists and petrologists should be useful in various branches of industry as well as solving general problems for 21st century mankind. As examples (excepting already mentioned ones), the following human activities should be mentioned:

petrurgy (melted basic rocks – bricks, and basaltic rock-wool used as insulation material; evaluation of basic raw materials which fundamentaly influence the quality of final products; the laboratory study of portland cement clinker; the study of the mineral composition of mortars and plasters; the mineral and chemical compositon (including trace elements) of various slags; the ceramic products (brickware, stonware), porcelain - their raw materials; the products of various types of firing; concrete deterioration – from the practical point of view the most imporant is the activity of CO_2 on concrete which leads to concrete destabilization and eventually to its collapse, and medical mineralogy. These should should serve as new challenges to mineralogists.

At present, the focus of one of the leading programmes of UNESCO is the creation of knowledge-based societies. A priority, ahead of mineralogy and petrology, or more accurately, ahead of the whole of geology, is the spreading of knowledge on the Earth among the ordinary population. Such popularization should involve all members of the geoscientific community. In our countries, we lack journalists specialized in the problems of planet Earth. Probably an interdisciplinary Ph.D study (journalistic-geosciences) would help provide a future remedy. In the majority of museums in the Slovak Republik, and further afield, though collections of minerals, fossils, rocks, ores etc. are presented, the custodians in whose charge they rest are, in the majority of cases, not trained in the geosciences.

Finally, instead of a conclusion, the following might be said to all young young geoscientists. Do not follow in the footprints of your teachers who expressed, in the past,

new goals for the geosciences. But do not forget that they did so some 20-30 years ago under quite different social, economical and political conditions, and with very different laboratory equipment, etc. These teachers have mostly been excellent, but try to find your own new specialization and try to excel at it. Your new specializations, among those mentioned above, are badly needed and will be needed by society in furure. So, dear colleagues, follow this challenge!

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Granite Rb-Sr data, aggregated, define a regional framework: why?

Pádhraig KENNAN

¹ School of Geological Sciences, University College Dublin, Ireland; padhraig.kennan@ucd.ie

Granite rocks are, for obvious reasons, a common focus for Rb-Sr whole-rock studies. However, conclusions based on such data are often deemed to be open to question. The reasons are many, e.g., loss of radiogenic Sr, incomplete homogenisation of different source materials, contamination, alteration etc. Proofs are rare. Thus, a greater confidence is afforded to, e.g., U-Pb dates on accessory zircon, monazite, etc. However, adequate wholerock samples represent the complete granite mineralogy, the granitic rock actually mapped on outcrop and petrographically examined under the microscope, in a way no accessory mineral can. Those whole rock samples suitable chosen can, perhaps, best reflect the actual complexity of a large granite intrusion, or a suite of intrusions. Perhaps, in the search for precise ages, whole-rock data is undervalued or simply incorporated into models. There may be value in geological scatter.

The ca 400 Ma Caledonian granites of Ireland and Britain, the ca 320 Ma Variscan intrusions of the western Sudetes in Poland and the ca 500 Ma granite gneisses, etc. in the same region have been extensively studied over many years. Published whole-rock data are plentiful, almost all of it obtained with the aim of dating particular intrusions. Calculated dates and initial 87Sr/86Sr ratios, often based on limited numbers of samples, are referenced. The original measured data typically remain forgotten in tables. Yet it is that experimental data that, perhaps, offers a real basis for understanding and comparing the isotopic systems of individual intrusions. Geological scatter is a real characteristic of real rocks, not just a model problem to be defined by a statistical index.

In the Irish Caledonides, the value of Rb-Sr whole-rock data in aggregate (without any omissions) is demonstrated by, for example, a clear discrimination between Iapetus-related source demains and continental-margin domains. In the Polish Sudetes, even the older data reveal ca 505 Ma and ca 320 Ma granite events, allow meaningless ages to be recognised, limits to be placed on granite sources, and enable different granite intrusions to be compared and contrasted. In the manner that individual dip-and-strike readings, aggregated, contribute to the structure revealed by a geological map, so might individual Rb-Sr whole-rock values help to reveal the architecture and origins of granitic bodies – if only individual samples were always collected with the same care and precision and stored in a uniform manner in a single database.

Regional isotopic patterns clearly reflect source. But how might they also reflect fractionation, magma mixing, contamination, hydrothermal alteration, resetting, reservoir replenishment and the many other processes that have been advanced to explain individual data sub-sets or the genesis of individual plutons? With all this potential for disturbance, why do the patterns remain essentially simple?

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The use of geochemistry for assessing environmental quality based on selected case studies in the Holy Cross Mountains (south-central Poland)

Zdzisław M. MIGASZEWSKI¹, Agnieszka GAŁUSZKA¹

¹ Geochemistry and the Environment Division, Institute of Chemistry, Jan Kochanowski University, 15G Świętokrzyska Str., 25-406 Kielce, Poland; zmig@ujk.kielce.pl, aggie@ujk.kielce.pl

Introduction

Of many geosciences, the study of geochemistry represents the most holistic approach to assessing the quality of various environmental systems. The practical aspects of geochemistry encompass not only environmental protection, but also geology, mining, agriculture, biology, medicine, etc. Environmental geochemistry is a branch of geochemistry dealing with cycling, and spatial and temporal distribution of elements and their isotopes in the Earth's outermost layers that include the uppermost lithosphere, pedosphere, hydrosphere and atmosphere. This geoscience describes the geochemical environment and interactions that take place in-between terrestrial, atmospheric, acquatic, living and anthropogenic systems. Human activity is a factor that has a great impact on the natural environment. However, the most hazardous is a chemical aspect leading to degradation and destruction of land, water, air, and biota. Knowledge of pollution sources and geochemical processes help us better understand all the potential hazards that can jeopardize a fragile nature balance (Migaszewski et al., 2001b). This article presents an overwiew of selected geochemical case studies conducted in the Holy Cross Mountains. Some of these studies were performed in close collaboration with the U.S. Geological Survey, Denver (Colorado). The obtained results have been published primarily in peerreviewed scientific journals of international stature (see references).

The scope of investigations has encompassed:

- (i) geochemical interactions in-between rock soil water plant atmosphere systems in forest ecosystems and highly protected areas;
- (ii) bioindication study of air quality using Scots pine (*Pinus sylvestris*), lichens (*Hypogymnia physodes*) and mosses (*Hylocomium splendens, Pleurozium schreberi*);
- (iii) geoindication study of environmental quality, including spring waters and soil subhorizon-Ofh;
- (iv) natural (geogenic) pollution sources, including acid rock/mine drainage (ARD/AMD);
- (v) geochemical background in various environmental systems.

The characteristic feature of these investigations was a multidisciplinary approach to the environment – the complex study of various systems (especially soils and plant bioindicators), and the use of a large variety of analytical methods. These included geochemical [atomic absorption spectrometry (AAS), inductively coupled plasma-optical

emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence spectrometry (XRF), gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography-mass spectrometry (HPLC-MS)], mineralogical [(optical microscopy, scanning electron microscopy (SEM)] and isotopic (mass spectrometry) (e.g., Migaszewski et al., 2001a, 2002, 2006, 2007b, 2008, 2009a,b; Pasławski, Migaszewski, 2006). The selected case studies are discussed in the subsequent sections.

Geochemical and biogeochemical monitoring and assessment

The complex environmental geochemical studies in the Holy Cross Mountains were initiated in 1994 by the U.S. Geological Survey and the Polish Geological Institute under the U.S. - Poland Maria Curie-Skłodowska Joint Fund II. The study area included two subareas: Świętokrzyski National Park and the remaining Holy Cross Mountains. The principal objective was to determine baselines for trace elements and organic compounds [polycyclic aromatic hydrocarbons (PAHs), phenols, polychlorinated biphenyls (PCBs), pesticides], and stable sulfur isotopes in soils, rocks, plant bioindicators [Hypogymnia physodes lichen thalli, Scots pine (Pinus sylvestris) needles, Hylocomium splendens, Pleurozium schreberi, Hypnum cupressiforme moss tissues]. The geochemical baseline results measured in this initial study also served as a reference level for comparison with subsequent monitoring activities whose purpose was to record fluctuations in the distribution pattern of elements and PAHs. The assessment of chemical and isotopic (sulfur) areal variability was derived using "barbell" cluster and ANOVA designs. This approach enabled obtaining statistically valid information using a minimum number of samples (Migaszewski, Pasławski, 1996; Migaszewski, 1998; 1999). Lichens, mosses, and pine needles showed nearly the same stable sulfur isotope pattern. The δ^{34} S values in vegetation varied from +3.2 to +5.4‰ being close to those in rain (+3.7‰) (Trembaczowski, Hałas, 1983) and snow (+5.1 to +6.8‰) (Michalik, 2008). It is interesting to note that the δ^{34} S variation pattern in topsoil (horizon-A) and bioindicators was nearly identical (Figs. 1, 2). This fact indicates that mixed local and imported SO₂ emissions underwent rapid homogenization.





Fig. 1. The δ^{34} S variation pattern in topsoil (horizon-A) from the Holy Cross Mountains



This and the next study performed in Świętokrzyski National Park in 2002 (Migaszewski et al., 2004), revealed similar concentrations of trace elements and sulfur in

topsoil (Table 1) and plant bioindicators. Moreover, the use of the same sampling, preparation and analytical methods enabled comparison of the pollution level between Świętokrzyski, Magurski and Wigierski National Parks. An assessment of chemical variability in various ecosystems was obtained through the calculation of geochemical baselines using "barbell" cluster and ANOVA designs. The results of the study in Świętokrzyski National Park showed that the largest proportion of chemical variability in the soils, and partly *P. sylvestris* needles and bark, was linked to the smaller distance increments, i.e., 0.5 and 2.5 km. The spatial distribution pattern of elements in soils and plant bioindicators displayed generally a bedrock lithology "signature" modified by geochemical and/or biogeochemical processes, with a more distinct anthropogenic imprint in Świętokrzyski and Magurski National Parks.

Table 1. Concentration of selected trace elements and S in topsoil (horizon-A) of Świętokrzyski National Park (compiled from Migaszewski, Pasławski, 1996; Migaszewski et al., 2004)

		1994	2002			
Element	mg kg ⁻¹ (ppm) [N = 14 in 1994 and N = 16 in 2002]					
	G.M.	Observed range G.M.		Observed range		
As	9	5 - 22	10	6 – 16		
Cd	0.5	< 0.5 - 1.1	< 0.5	_		
Со	3	1 - 16	3	1 - 16		
Cr	13	4 – 19	10	8 - 17		
Cu	15	5 - 29	10	4 - 32		
Fe	9100	2300 - 15,900	8962	5300 - 27300		
Hg	0.32	0.03 - 1.10	0.180	0.072 - 0.603		
Mn	351	19 – 2477	407	89 - 3693		
Ni	7	1 – 15	6	4 - 27		
Pb	77	15 - 310	89	29 - 478		
S	430	70 - 1160	468	230 - 1580		
Zn	60	12 - 109	58	32 - 119		

NOTE: N - number of samples; G.M. - geometric mean

The geochemical and biogeochemical studies also encompassed the most characteristic habitats of the Holy Cross Mountains (Migaszewski et al., 2001a; 2002; Gałuszka, 2005). Their objective was to record any trends in temporal and spatial distribution pattern of elements and PAHs as well as to determine relationships between rocks, soils and plant bioindicators. These studies showed that the variability for PAHs, trace metals and sulfur in topsoils and plant bioindicators was impacted primarily by anthropogenic factors. The influence of the bedrock lithology (limestones with Cu- and Pb-ore mineralization) is more distinct in the southwestern part of the Holy Cross Mountains. This relationship was confirmed by Pb-isotope ratios in various media at Mt. Stokówka (Table 2). These ratios indicated that lead in the Scots pine needles and soil horizons displayed values similar to those in limestones. In turn, a greater influence of atmospheric sulfur emissions was particularly notable in Scots pine needles. In contrast, the δ^{34} S values of soil horizons were relatively close to those in limestones. It should be stressed that galena from the Pb-mineralization zone revealed distinctly different Pb- and S-ratios.

The highest contents of PAHs and numerous trace elements were found in the organic horizon-O and humic horizon-A, but especially in the organic (fermentative-humic) subhorizon-Ofh of most soil types. This subhorizon may be a good geoindicator of environmental quality due to preconcentration abilities of some pollutants. However this physicochemical property needs further detailed study (Migaszewski, Gałuszka, 2008a).

The biogeochemical studies also showed that most of the lichen thalli also exhibited higher concentrations of individual hydrocarbons and some elements than their host bark. In contrast to Scots pine, common birch and common oak bark, many of *H. physodes* thalli were enriched in Fe, K, Mg, Ni, P, S, Ti and Zn and simultaneously depleted in Ba and Sr.

Table 2. Concentration and isotope ratios of Pb and S in Scots pine needles (from two trees), soil horizons, limestones and galena at Mt. Stokówka (compiled from Gałuszka, 2005)

Medium	Pb	²⁰⁴ Pb/	²⁰⁷ Pb/	²⁰⁸ Pb/	S	$\delta^{34}S$
	$(mg \cdot kg^{-1})$	²⁰⁶ Pb	²⁰⁶ Pb	²⁰⁶ Pb	(mg·kg ⁻¹)	(‰)
1-year (2000) pine needles (1)	<5	0.054	0.844	2.074	996	+4.3
1-year (2000) pine needles (2)	<5	0.054	0.852	2.084	990	+5.5
Of	139	0.054	0.848	2.089	340	+22.1
A	118	0.055	0.849	2.089	230	+16.0
BbrC	63	0.054	0.845	2.088	110	+12.4
Cca	104	0.054	0.848	2.082	100	+33.7
Limestone	26	0.054	0.848	2.082	100	+19.0
Galena (PbS) from ore vein	-	0.058	0.851	2.027	_	-8.4

NOTE: Soil horizon symbols: Of – organic fermentative, A – humic, BbrC – mixed illuvial-subsoil, C – calcareous subsoil (waste mantle)

The subsequent geochemical studies showed that mosses are better bioindicators of airborne elements and PAHs than lichens and Scots pine (Gałuszka, 2007; Migaszewski et al., 2009a). Of the various moss species, *H. splendens* and *P. schreberi* turned out to be the best biomonitors of air quality. They possess the features of a good bioindicator, including (i) common occurrence that enable conducting comparative interregional studies, (ii) ability to assess environmental contamination over a short time, and (iii) fast, unequivocal and distinct response to toxicants (Migaszewski et al., 2001a).

A recent comparative interregional study performed in Alaska and the Holy Cross Mts revealed that geogenic sources of metals were more important in Alaska. The relatively higher concentration of 3-ring aromatic hydrocarbons in the Alaskan mosses may be linked primarily to wood combustion. In contrast, the chemistry of Polish mosses indicated different anthropogenic sources of PAHs and trace elements. However, some of the pollutants can overlap (e.g., combustion of hard- and brown coals produces both PAHs and trace metals). The concentration of most trace metals in the Holy Cross Mountains dropped considerably in both moss species (*H. splendens* and *P. schreberi*) during 2001 – 2007; for example, Ba, Ca, Cd, Fe, Pb, V, Zn (from 1.5 to 3 times). Except for Cd and Pb, the mean concentrations of Cr, Ni, Fe, Hg, V, and Zn in HCM were lower than those recorded in central Europe in 2000. During the 2-year period, the concentration of hydrocarbons at some sites increased 2- to 5-fold. This may be explained by increased road traffic and partly diverse agricultural and forestry operations near these sites (Migaszewski et al., 2009a and references therein).

Like bioindicators, springs react to any changes that occur in natural ecosystems. This is the main reason why the springs belong to the best environmental geoindicators. A decrease in the number of springs or the drop in their discharge, as well as disadvantageous changes in chemistry and quality of spring waters indicate deterioration of the environment quality. The study conducted in Świętokrzyski National Park (Michalik, 2008) revealed that the chemistry of spring waters was controlled particularly by bedrock lithology and a fewmeter thick waste mantle covering the Łysogóry slopes.

Acid rock/mine drainage (ARD/AMD)

The bacterially-induced oxidation of pyrite and iron-bearing sulfides belongs to the most hazardous pollution sources of the environment. This natural process occurs in and around mineralized areas or sulfide and coal deposits and results from the complex rock-mineral-water interactions of a variety of geochemical processes (Migaszewski et al. 2007a, 2008, 2009b and references therein; Migaszewski, Gałuszka, 2007, 2008b). The AMD study, using complex chemical, mineralogical and isotopic methods, was conducted in the Wiśniówka mining area where two acidic water bodies occur, i.e., Wiśniówka Mała lake and Podwiśniówka pond. Both reservoirs occupy quarries abandoned after mining of quartzites.

The bipartite Wiśniówka Mała pit lake displays different chemistry and stable sulfurand oxygen isotope ratios within two separated ponds. The western pond is characterized by a lower pH (mean of 3.7) and higher concentrations of most elements. In addition, this part of the lake exhibits some chemical and isotopic stratification. The most interesting, however, is the Podwiśniówka pit pond showing the lowest pH with a mean of 2.6, in places (occasional puddles) reaching even 1.5. In contrast to the Wiśniówka Mała quarry, this area is characterized by the presence of an exposed pyrite zone and a small freshwater pond. This unique location enabled the following aspects of AMD to be studied: (i) mineralogy of outcropped pyrite zone and sediment, (ii) petrology of host rocks, (iii) chemistry of acidic pond water and sediment versus small pond freshwater, (iv) isotope composition of pyrite, soluble sulfates and waters, (v) pathways of pyrite oxidation, and (vi) geochemical pyrite-water-sediment interactions.

The study in the Podwiśniówka quarrry indicated that bacterial oxidation of As-rich pyrite and leaching of oxyhydroxysulfates was a source of acidic pit pond waters and various As-bearing iron precipitates. The presence of sulfates, iron(II), iron(III) and low pH favors the generation of poorly crystalline schwertmannite $[Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}]$. The periodical increases of pH may result from transformation of this mineral into ferrihydrite \sim Fe(OH)₃·1,8H₂O (pH 2,5 – 4,5) and then into more crystalline goethite α -FeOOH (pH 3 – 7). The isotopic results also suggested that the pyrite underwent bacterially-catalyzed oxidation primarily by ferric ion. The study also revealed the presence of gorceixite and related minerals (Migaszewski et al., 2007b).

Geochemical background in environmental studies

Calculation of the geochemical background in various media is a prerequisite for determining what part of a chemical species concentration is natural and what part is anthropogenic. This requires both good geochemical, mineralogical and petrological knowledge and a holistic approach to the environment. Of various methods used for assessing geochemical background, i.e., (i) direct, (ii) indirect (statistical) and (iii) integrated, the last which combines both the direct and indirect approach seems to be plausible and reliable (Gałuszka, 2007b,c). The integrated method combines both the direct and indirect approach. However, it is essential that samples be collected in relatively

pristine areas (e.g., national parks, nature reserves, forest ecosystems) from the equivalent soil horizons, rocks, plant species etc., restricting purposely the range of obtained data that are subjected to statistical analysis (mean $\pm 2\sigma$). This method enables distinguishing the background from anthropogenic and natural anomalies. The data indicated that the geochemical background was closely linked to the geologic setting and might be assessed only on a local or regional scale.

Summary

The selected geochemical and biogeochemical case studies conducted in the Holy Cross Mountains provide evidence of the unique position of geochemistry and biogeochemistry in solving various crucial environmental issues. These two studies illustrate the use of various methods and techniques borrowed from Earth sciences, primarily prospecting geochemistry, mineralogy, petrology, mineral deposit geology, hydrogeology and geophysics, as well as chemistry, physics, biology and toxicology. This multidisciplinary approach gives an impulse to the development of new hybrid research methods and fields of study. The shift toward biology, agriculture and medicine reflects the dynamism and topicality of environmental geochemistry and biogeochemistry in a rapidly changing world.

References:

- GAŁUSZKA A., 2005: The chemistry of soils, rocks and plant bioindicators in three ecosystems of the Holy Cross Mountains, Poland. *Environmental Monitoring and Assessment* 110, 55–70.
- GAŁUSZKA A., 2006: Geochemical background of selected trace elements in mosses *Pleurozium schreberi* (Brid.) Mitt. and *Hylocomium splendens* (Hedw.) B.S.G. from Wigierski National Park. *Polish Journal of Environmental Studies* 15(2A), part I, 72–77.
- GAŁUSZKA A., 2007a: Distribution patterns of PAHs and trace elements in mosses *Hylocomium splendens* (Hedw.) B.S.G. and *Pleurozium schreberi* (Brid.) Mitt. from different forest communities: a case study, south-central Poland. *Chemosphere* 67, 1415–1422.
- GAŁUSZKA A., 2007b: Different approaches in using and understanding the term "geochemical background" practical implications for environmental studies. *Polish Journal of Environmental Studies* 3, 389–395.
- GAŁUSZKA A., 2007c: A review of geochemical background concepts and an example using data from Poland. *Environmental Geology* 52, 861–870.
- MICHALIK A., 2008: The Use of Chemical and Cluster Analysis for Studying the Spring Water Quality in the Świętokrzyski National Park, South-Central Poland. *Polish Journal of Environmental Studies* 17(3), 357–362.
- MIGASZEWSKI Z.M., 1998: Geochemistry of soils and vegetation of the Holy Cross Mts between 1994 and 1996. *Geological Quarterly* 42(1), 99–110.
- MIGASZEWSKI Z.M., 1999: Determining Organic Compound Ratios in Soils and Vegetation of the Holy Cross Mts, Poland. *Water, Air, and Soil Pollution* 111, 123–138.
- MIGASZEWSKI Z.M., GAŁUSZKA A., 2007: Laboratorium przyrody przykłady z badań w Kolorado, USA. *Analityka* 3, 39–41
- MIGASZEWSKI Z.M., GAŁUSZKA A., 2008a: The soil subhorizon-Ofh a potential geoindicator of environmental pollution. *Polish Journal of Environmental Studies* 17(3), 405–410.
- MIGASZEWSKI Z.M., GAŁUSZKA A., 2008b: Koncepcja ujemnego pH dla superstężonych wód naturalnych. *Analityka* 1, 6–10.

- MIGASZEWSKI Z.M., GAŁUSZKA A., CROCK J.G., LAMOTHE P.J., DOŁĘGOWSKA S., 2009a: Interspecies and interregional comparisons of the chemistry of PAHs and trace elements in mosses *Hylocomium splendens* (Hedw.) B.S.G. and *Pleurozium schreberi* (Brid.) Mitt. from Poland and Alaska. *Atmospheric Environment* 43, 1464–1473.
- MIGASZEWSKI Z.M., GAŁUSZKA A., HAŁAS S., DĄBEK J., DOŁĘGOWSKA S., BUDZYK I., STARNAWSKA E., MICHALIK A., 2009b: Chemical and isotopic variations in the Wiśniówka Mała mine pit water, Holy Cross Mountains (South-Central Poland). *Environmental Geology* 57, 29–40.
- MIGASZEWSKI Z.M., GAŁUSZKA A., HAŁAS S., DOŁĘGOWSKA S., DĄBEK J., STARNAWSKA E., 2008: Geochemistry and stable sulfur and oxygen isotope ratios of the Podwiśniówka pit pond water generated by acid mine drainage (Holy Cross Mountains, south-central Poland). *Applied Geochemistry* 23, 3620–3634.
- MIGASZEWSKI Z.M., GAŁUSZKA A., PASŁAWSKI P., 2002: Polynuclear aromatic hydrocarbons, phenols and trace metals in selected soil profiles and plant bioindicators in the Holy Cross Mountains, south-central Poland. *Environment International* 28/4, 303–313.
- MIGASZEWSKI Z.M., GAŁUSZKA A., PASŁAWSKI P., 2004: Baseline element concentrations in soils and plant bioindicators of selected national parks of Poland. *Geological Quarterly* 48(4), 383–394.
- MIGASZEWSKI Z.M., GAŁUSZKA A., PASŁAWSKI P., STARNAWSKA E., 2007a: An influence of pyrite oxidation on generation of unique acid pit water: A case study, Podwiśniówka quarry, Holy Cross Mountains (south-central Poland). Polish Journal of Environmental Studies 16(3), 407–421.
- MIGASZEWSKI Z.M., GAŁUSZKA A., STARNAWSKA E., PASŁAWSKI P., 2006: The SEM studies and X-ray microanalysis – the key for understanding the origin and fate of airborne particulates. *Polish Journal of Environmental Studies* 15(2A), part 1, 143–149.
- MIGASZEWSKI Z.M., GAŁUSZKA A., ŚWIERCZ A., KUCHARZYK J., 2001a: Element concentrations in soils, and plants bioindicators in selected habitats of the Holy Cross Mts, Poland. *Water, Air, and Soil Pollution* 129, 369–386.
- MIGASZEWSKI Z.M., GOUGH L.P., GAŁUSZKA A., 2001b: The Role of Biogeochemistry in Environmental Studies. *Przegląd Geologiczny (Geological Review)* 49 (10/2), 960–965.
- MIGASZEWSKI Z.M., PASŁAWSKI P., 1996: Trace element and stable sulfur isotope ratios in soils and vegetation of the Holy Cross Mountains. *Geological Quarterly* 40(4), 575–594.
- MIGASZEWSKI Z.M., STARNAWSKA E., GAŁUSZKA A., 2007b: Gorceixite from the Upper Cambrian rocks of the Podwiśniówka mine pit, Holy Cross Mountains (south-central Poland). *Mineralogia Polonica* 38(2), 171–184.
- PASŁAWSKI P., MIGASZEWSKI Z.M., 2006: The quality of element determinations in plant materials by instrumental methods. *Polish Journal of Environmental Studies* 15(2a), 154–164.
- TREMBACZOWSKI A., HAŁAS S., 1983: Oxygen and sulfur isotope ratios from atmospheric precipitations. The Book of Extended Synopsis of International Symposium on Isotope Hydrology in Water Resources Development, IAEA, Vienna, 12-16 Sept. 1983, p. 147.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Late burial dolomitization of the Devonian carbonates and a tectonothermal evolution of the Holy Cross Mts area (Central Poland)

Marek NARKIEWICZ¹

¹ Polish Geological Institute-National Research Institute, Rakowiecka 4, 00-975 Warszawa, Poland; marek.narkiewicz@pgi.gov.pl

Abstract: The Middle to lower Upper Devonian crystalline dolomites of the Holy Cross Mts were formed by a replacement of platform limestones and the recrystallization of eogenetic, facies-controlled dolomicrites. Stratigraphical data, petrological observations and the results of 1-D basin modelling are consistent with late burial dolomitization during the Carboniferous (340-305 Ma) predating the main phase of Variscan deformation.

Keywords: Holy Cross Mountains, Devonian, dolomitization, burial history

Introduction

The Devonian dolomites of the HCMts have been studied for more than a century (see the historical review in Narkiewicz 1991) but their origin is still disputable. According to the present author, the origin of dolomicritic and microdolosparitic varieties was controlled by depositional and early diagenetic (eogenetic) processes, whereas fine to coarse dolosparites were formed due to late burial (mesogenetic) replacement and recrystallization (Narkiewicz 1990, 1991, Narkiewicz et al. 2006). The alternative interpretation assumed synsedimentary, submarine hydrothermal origin for all the dolomite types (Migaszewski 1990, 1991). The present paper briefly summarizes previously reported- and unpublished data and interpretations contributing to the question of dolosparites origin. The new investigations included additional field observations, petrological studies (mostly stable isotopes, SEM and CL data), and 1-D basin modelling.

Regional and stratigraphic framework

During the Devonian and Carboniferous, the Holy Cross Mts were located in the foreland of the Variscan Orogen of Central and Western Europe (Narkiewicz 2007). Following the Late Carboniferous tectonic deformations and the ensuing Early Permian uplift, they were incorporated into the Late Permian-Mesozoic Mid-Polish Trough (Kutek & Głazek 1972), striking NW-SE along the margin of the East European Platform (Fig. 1). This depocentre was uplifted at the turn of Cretaceous and Paleocene, and the resultant erosion exposed the Palaeozoic core of the HCMts. Since then, the region has formed a part of an elevated area separating the northern Carpathian basins and the Carpathian Foredeep from the Eocene to Pliocene epicontinental basins of central-northern Europe.

The Palaeozoic core is subdivided by the WNW-ESE striking Holy Cross Fault (HCF) into southern and northern (Łysogóry) regions that differ in their Early Palaeozoic tectonostratigraphic development (Dadlez et al. 1994). During the Devonian, the HCF was a distinct palaeogeographic boundary (Fig. 1). It separated the more stable Southern Region with lower subsidence and depositional rates from the northern one characterized by two to three times the thickness of sediment accumulation and generally more open and/or deeper marine facies. The development of a restricted shallow-marine carbonate shelf started in both regions near the Early-Middle Devonian boundary. This shelf soon evolved into a coral-stromatoporoid platform that was terminated in the north due to a deepening pulse and the related onlap of marly open-marine facies already in the late Eifelian. In the southern area, the carbonate platform persisted up to the earliest Frasnian when it became aerially limited to the Dyminy Reef complex developing through the middle Frasnian (Fig. 2). In the western HCMts, the Kostomłoty area (Fig. 1) displays a transitional development, with the main drowning episode in the Middle Givetian, probably related to the subsidence of a fault-controlled block (Fig. 2).



Fig. 1. Schematic palaeogeography of the Holy Cross Mts. during approximately Middle-Late Devonian transition. Indicated are key sections in which stable isotopic composition of the Devonian dolomites has been investigated. The inset map of Poland shows setting of the study area within the framework of major regional geological units.

The early stage of the Middle Devonian carbonate platform development corresponds roughly to the Eifelian in the south and to a lower part of the stage in the north. It is represented by well-bedded marly dolomicrites typically lacking open-marine fossils. The sediments are characterized by irregular microbial or parallel horizontal lamination, mudcracked surfaces and erosional levels with intraclasts. It is overlain by the Kowala Fm. (Narkiewicz et al. 1990, Narkiewicz & Narkiewicz, in print) composed mostly of coralstromatoporoid and other shallow-marine platform limestones or crystalline dolostones. The subordinate dolomicrites and dolomicrosparites mostly form the upper parts of lowerorder shallowing-upwards cycles.. In the Southern Region, the crystalline dolostones display a characteristic regional geometry in a cross-section perpendicular to the HCF (Fig. 2). Their upper boundary cross-cuts the general pattern of the depositional architecture of the Givetian to Frasnian carbonate platform and the Dyminy Reef complex. It reaches its highest stratigraphic position along the norther margin of the region, ranging up to the lowermost Frasnian while the thickness of the complex attains 300-400 m. Its top is stratigraphically lower southwards, lying in the middle and, probably also, lower Givetian. In the Kostomłoty area, the entire upper part of the Middle Devonian carbonate platform succession is developed as crystalline dolomites. In the Łysogóry Region, the crystalline dolomites tend to form thick and continuous bodies in the lower part, whereas they are irregularly interspersed with dolomicrites and limestones upwards in the sections (e.g., Narkiewicz & Narkiewicz, in print; Skompski & Szulczewski 1994).

On a meter- to decimeter-scale, the dolosparites show a complex pattern of cross-cutting and replacive relationships along the horizontal or lateral contacts with the overlying limestones (Narkiewicz 1990, 1991). In this more or less gradual replacement zone, selectively dolomitized ramose stromatoporoid (*Amphipora*) biostromes, selectively replaced micritic matrix of stromatoporoids and corals, and relatively sharp horizontal contacts of dolosparite with overlying shaly/marly beds are common.



Fig. 2. Position of the crystalline dolomites within the stratigraphic-facies framework of the Middle to Upper Devonian in a schematic south-north cross-section (western Holy Cross Mts.).

Petrology of crystalline dolostones

The crystalline dolomites include both matrix mosaic- and drusy cement varieties. The former variety is generally composed of anhedral to subhedral fine- to medium-sized low-Fe dolomite crystals with a common range of $50-300 \ \mu\text{m}$. In many cases, it shows minute ("dusty") inclusion patterns mimicking replaced limestone fabrics. This allows the recognition in thin-section of such features of replaced limestones as peloids, fossil remains or fenestral structures, as well as later structures, notably calcite veins. Matrix-type dolomite is typically non-luminescent or weakly luminescent. It is nearly stoichiometric containing $50-54 \ \text{mol}\%$ CaCO₃; an average of 30 samples is $51.2 \ \text{mol}\%$. The trace elemental composition of a carbonate fraction shows enrichment in Fe and Mn relative to replaced limestones (based on ca 40 samples). The enrichment in silica (bulk composition)



and in Fe, Mn, Sr and Na in a carbonate fraction is characteristic particularly for the upper part of the crystalline dolomites, transitional to the overlying limestones (Narkiewicz 1990; 1991).

Fig. 3. Succession of most important diagenetic phenomena and tectonic events that affected the Middle Devonian to Frasnian carbonates in the Holy Cross Mts. Grey horizontal strip highlights processes related to the main phase of pervasive dolomitization.



Fig. 4. Oxygen isotope compositions of the Middle Devonian to Frasnian dolomites in the Holy Cross Mts. (A), and interpretation of temperatures and isotopic compositions of dolomitizing fluids (B) after Land (1983). Th – range of fluid-inclusion homogenization temperatures in dolosparites. Range of δ^{18} O for a Devonian sea water – cf. van Geldern et al. (2006).

The dolosparites are commonly fractured and display irregular millimeter- to centimeter-sized vugs and, more rarely, intercrystalline porosity. The large pores can often be attributed to dissolved organic skeletons, mainly those of stromatoporoids and corals.

They are often filled with geopetal internal sediment composed of dolomite crystals, and by several generations of dolomite and calcite cements (Fig. 3). The dolomite cements include low-Fe types (mainly earlier generations) and Fe-dolomites (typically outer rims). The crystals are typically centimicron- to millimeter-sized, commonly saddle-shaped and with a complex pattern of CL zoning. Commonly, the oldest zones are non-luminescent or dull-luminescent and the intermediate zones show alternating bright and dull zones enveloped, in turn, by non-luminescent, high-Fe zones. CL studies also reveal subsequent generations of variably-luminescent original- or recrystallized cement, but their volumetric importance and regional distribution is limited.

Thin sections reveal a common recrystallization of dolomicrite which is irregularly replaced by a mosaic of fine- to medium crystalline dolomite difficult to distinguish from a product of CaCO₃ replacement. CL observations also document replacement or recrystallization of dolomite cements by later-phase irregular differently-luminescing dolomite which otherwise is not recognizable in thin section.

The dolomitization-related phenomena, outlined above, of replacement, dissolution, internal deposition, cementation and recrystallization have been related to other diagenetic and tectonic features in order to place them in the proper temporal context of the geological evolution of the Devonian strata. The paragenetic succession (Fig. 3) demonstrates that the matrix dolosparite development and dolomicrite recrystallization postdate carbonate mineral stabilization and the blocky calcite cements, including those filling tensional fractures of probable tectonic origin. They also postdate onset of chemical compaction processes as is demonstrated by a partial obliteration of horizontal residual clayey seams and stylolite sutures. On the other hand, matrix dolosparite is cross-cut by tectonic fractures attributable to Variscan (late Carboniferous) tectonism. This is consistent with the observation that geopetal dolomitic sediments in vugs are tectonically tilted together with enclosing dolosparite beds that are, in turn, truncated by a nearly horizontal Variscan unconformity in, e.g., Zachełmie Quarry (Narkiewicz & Narkiewicz, in print). Most of Fedolomite cements postdate the matrix dolomitization and ensuing tectonic features. Late calcite blocky cements and minor latest generations of dolomite cements are even younger. The post-Variscan tectonics (probably Permian to Early Triassic) is indicated by fractures, partly filled with late blocky Fe-calcite, that cross-cut late dolomite- and calcite cement generations. The widespread dedolomitization phenomena selectively affected mainly Fedolomite. They can be related to post-Variscan erosion and/or to Paleogene and later exhumation of the Palaeozoic core of the HCMts.

Oxygen and carbon isotopes have been studied in ca 150 samples from 13 sections covering broad stratigraphic intervals of Devonian dolomites throughout the entire HCMts. area (Fig. 1). In contrast to a narrow range (-1 to 1 ‰) of rather indistincive δ^{13} C signatures, three general dolomite categories are characterized by distinct δ^{18} O values. The dolomicrites (excepting a single sample) show values between -5 and -1 ‰, mostly -3 to -1 ‰ (Fig. 4A). Assuming a slightly negative δ^{18} O (-3 to -1 ‰) for Devonian sea-water (van Geldern et al. 2006), this gives a temperature range 25-45°C consistent with surface temperatures in the Devonian tropics (Fig. 4B). The δ^{18} O signature of the matrix dolosparite is predominantly between -11 and - 7 ‰ (Fig. 4A). Fluid inclusion homogenization measurements, based on 64 samples of the crystalline dolomite, gave a range of Th values between 80.5 and 117.5°C. Coupled with the above δ^{18} O range, this

allows the δ^{18} O of the dolomitizing solutions to be estimated as ca 1 ‰, thus pointing to a slightly elevated salinity relative to the Devonian sea-water.

Although δ^{18} O in dolosparite matrix displays roughly normal distribution around median values of -10 to -8 ‰, a considerable proportion of the dolosparites shows elevated values in the range -7 to -4 ‰ (Fig. 4A). These dolomites are here interpreted as recrystallized dolomicrites with an isotopic signal partly preserving the memory of the original sediments.

The δ^{18} O signatures in a few (7) investigated dolomite cements show relatively low values between -12 and -9 ‰. Assuming δ^{18} O of the dolomitizing fluids as ca. 1 ‰, the temperatures of crystallization can be estimated to lie in the upper half of the determined Th range, i.e. 100-120 °C (Fig. 4B).

The strontium isotope data are fewer (about 20 analyses) and less conclusive than the oxygen investigations (Narkiewicz et al. 2006, and unpublished data). There seems to be a good negative correlation between ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and $\delta^{18}\text{O}$ for dolosparite matrix. This would suggest a radiogenic strontium contribution increasing with increasing temperature of dolomitizing solutions. ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ in two investigated dolomite cements was found to be higher than in any matrix dolosparite; this is consistent with the depleted $\delta^{18}\text{O}$ data. Nevertheless, micrites display a wide range from expected marine values close to 0.708 to elevated radiogenic signatures of ca. 0.71, the latter found in the Łysogóry Region.



Fig. 5. Modelled burial-thermal history of the Devonian to recent time-interval based on the Janczyce I borehole section. Graph on the right shows calibration with the vitrinite reflectance (% VR) data and the best-fit curve (see the text for further explanations). Time scale after Gradstein et al. (2004).

Dolomitization and tectonothermal evolution of the area

The fluid inclusion homogenization temperatures and the palaeotemperatures derived from the oxygen-isotope composition of the crystalline dolomites were tested against an independently obtained model of the burial-thermal history for the Janczyce I borehole section (located in Fig. 1). The modelling was performed with Marta Resak and Ralf Littke in the RWTH Aachen using PetroMod 1-D software. The results of this study will be the subject of a separate publication.

The Permian to Cretaceous stratigraphic input for the modelling included sediment thickness reconstructed by Dadlez et al. (1998). The Carboniferous stratigraphy was reconstructed basing mainly on Żakowa & Migaszewski (1995). The Carboniferous evolution is particularly speculative as the existence and magnitude of tectonic phases is hypothetical due to the incompleteness of the sedimentary record. We assumed onset of uplift due to vertical block movements near the Early-Late Carboniferous boundary. The uplift continued into the Late Carboniferous, when major transpressional Variscan deformations occurred, and on through the Permian involving several phases of block movements. The modelling results are consistent with heat flow elevated to 70-80 mWm⁻² during the Late Carboniferous and progressively decreasing in the Early Permian to recent values of ca. 50 mWm⁻². Elevated Variscan heat flow was earlier postulated based on the thermal maturity pattern in the Devonian (Belka 1990; Marynowski 1999). The alternative interpretation, assuming Mesozoic thermal events (Poprawa et al. 2005) was not confirmed.

The best-fit model for the Janczyce I section is presented in Fig. 5. According to the model, the Middle Devonian carbonates attained temperatures higher than 80° C at depths of ca. 1.5 km in the Early but not the earliest Carboniferous. This is consistent with the post-Bretonian (i.e., postdating the Devonian-Carboniferous boundary) onset of dolomitization (Fig. 3). The strata remained buried at depths of ca. 1.5-2.5 km at temperatures >80°C until the Early Permian when the temperatures started to decrease in line with uplift and erosion. Paragenetic studies have shown that the upper time limit for the regional pervasive dolomitization is imposed by the late Westphalian tectonics. The temporal relationship between the Viséan/Namurian movements and dolomitization has not been established yet. The 100-120°C temperature window defined above for late Fe-dolomite cements is limited to a narrow time interval in the latest Carboniferous, post-dating the terminal Variscan transpressive tectonism.

Conclusions: a genetic model

Sedimentological characteristics as well as petrological features and stable isotope geochemistry, confirm that the dolomicrites composing the bulk of the early Middle Devonian lithofacies were formed in shallow-marine, more or less restricted depositional environments, comprising vast carbonate mud-flats and lagoons. The source of Mg was normal or slightly altered sea-water at temperatures of 25-45°C.

The crystalline matrix-type dolomites were formed by replacement of diageneticallymature Middle Devonian to lower Frasnian platform limestones and recrystallization of eogenetic dolomicrites. The temperature of the dolomitizing fluids was in the range 80-120°C based on fluid inclusion and oxygen isotope data. The relative enrichment in heavy O and Sr isotopes and in reduced Fe and Mn, suggests that the fluids were saline brines of reducing character. These were, presumably, formation waters evolved due to pressure solution processes and interactions with carbonates (including eogenetic dolostones), clay minerals and quartz. Results of 1-D basin modeling, coupled with the isotope data and reconstructed paragenetic suscession, allows constraining of the probable age of dolomitization to ca. Viséan – early Westphalian with burial depths in a range 1.5-2.5 km.

A regional subsurface fluid circulation pattern is required for a large-scale pervasive dolomitization in order to supply large amounts of Mg from relatively diluted watersolutions occurring in natural systems. Spatial correlation between the zone of elevated heat flow along the HCF on one hand, and the maximum range of dolomitization on the other, suggests thermal convection as a probable mechanism of circulation. An additional factor enhancing Mg supply could have been compaction-driven flow towards the buried northern margin of the Middle Devonian-Frasnian carbonate platform (Fig. 2). Both of these mechanisms were earlier proposed by the author (Narkiewicz 1990; 1991).

Acknowledgments: I am grateful to Dr. Magdalena Sikorska-Jaworowska (PGI Warszawa) for her kind assistance in CL investigations. The fluid inclusion data were obtained by Dr. M. Żywiecki (Warsaw University).

References:

- BELKA Z., 1990: Thermal maturation and burial history from conodont colour alteration data, Holy Cross Mountains, Poland. Courier Forschungs-Institut Senckenberg 118, 241–251.
- DADLEZ R., KOWALCZEWSKI Z. ZNOSKO J., 1994: Some key problems of the pre-Permian tectonics of Poland. Geological Quarterly 38, 169-189.
- DADLEZ R., MAREK S., POKORSKI J., 1998: Paleogeographic atlas of epicontinental Permian and Mesozoic in Poland (1:2 500 000). Polish Geological Institute, Warszawa.
- GRADSTEIN F., OGG J., SMITH A., 2004: A Geologic Time Scale 2004. Cambridge University Press, 589 pp.
- KUTEK J., GŁAZEK J., 1972: The Holy Cross area, Central Poland, in the Alpine cycle. Acta Geologica Polonica 22, 603-653.
- LAND L.S., 1983: Dolomitization. AAPG Education Course Note Series 24.
- MARYNOWSKI L., 1999: Thermal maturity of organic matter in Devonian rocks of the Holy Cross Mountains. Przegląd Geologiczny 47, 1125-1129 (in Polish with English summary).
- MIGASZEWSKI Z., 1990: Synsedymentacyjne utwory hydrotermalne dewonu srodkowego i górnego Gór Swietokrzyskich. Prace Państwowego Instytutu Geologicznego 129, 1-55.
- MIGASZEWSKI Z., 1991: Devonian dolomites from the Holy Cross Mts, Poland: A new concept of the origin of massive dolomites based on petrographic and isotopic evidence. Journal of Geology 99, 171-187.
- NARKIEWICZ M., 1990: Mesogenetic dolomitization in the Givetian to Frasnian of the Holy Cross Mountains, Poland. Bulletin of Polish Academy of Sciences, Earth Sciences 38, 101-110.
- NARKIEWICZ M., 1991: Procesy dolomityzacji mezogenetycznej na przykładzie żywetu i franu Gór Świętokrzyskich. Prace Państwowego Instytutu Geologicznego 132, 1-54.
- NARKIEWICZ M., 2007: Development and inversion of Devonian and Carboniferous basins in the eastern part of the Variscan foreland (Poland). Geological Quarterly 51, 231-256.
- NARKIEWICZ M., RACKI G., WRZOŁEK T., 1990: Litostratygrafia dewonskiej serii stromatoporoidowo-koralowcowej w Górach Swietokrzyskich. Kwartalnik Geologiczny 34, 433-456.
- NARKIEWICZ M., RACKI G., SKOMPSKI S., SZULCZEWSKI, M., 2006: Records of processes and events in the Devonian and Carboniferous of the Holy Cross Mountains. 77th Meeting of the Polish Geological Society, Conference Volume, 51-77 (in Polish).
- NARKIEWICZ K., NARKIEWICZ, M. (in print): Mid Devonian carbonate platform development in the Holy Cross Mts. area (central Poland): new constraints from the conodont *Bipennatus* fauna. Neues Jahrbuch für Geologie und Paläontologie, Abhandlungen.
- POPRAWA P., ŻYWIECKI M.M., GROTEK I., 2005: Burial and thermal history of the

Holy Cross Mts. area – preliminary results of maturity modelling. Mineralogical Society of Poland, Special Papers 26, 251-254.

- SKOMPSKI S., SZULCZEWSKI M., 1994: Tide-dominated Middle Devonian sequence from the northern part of the Holy Cross Mountains (Central Poland). Facies 30, 247-266.
- VAN GELDERN R., JOACHIMSKI M.M., DAY J., JANSEN U., ALVAREZ F., YOLKIN E.A., MA X.-P., 2006: Carbon, oxygen and strontium isotope records of Devonian brachiopod shell calcite. Palaeogeography, Palaeoclimatology, Palaeoecology 240: 47-67.
- ŻAKOWA H., MIGASZEWSKI Z., 1995: Góry Świętokrzyskie Mts. In: Zdanowski A., Żakowa H. (eds.). The Carboniferous System in Poland. Prace Państwowego Instytutu Geologicznego 148, 109-115.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Some features of the Bardo diabase intrusion (Holy Cross Mts.)

Jerzy NAWROCKI¹

¹ Polish Geological Institute-National Research Institute, Rakowiecka Str. 4, 00-975 Warszawa; jerzy.nawrocki@pgi.gov.pl

Abstract

The Bardo diabase that surrounds the Bardo syncline (S part of the Holy Cross Mts.) provided unique information about the late Silurian geomagnetic field pattern, and the tectonic regime and paleogeography of the Trans-European Suture Zone in the late Silurian/early Devonian.

The ⁴⁰Ar-³⁹Ar age spectra and geological constraints clearly point to a late Caledonian age interval (422-418 Ma) for the Bardo intrusion. The late Silurian paleomagnetic pole isolated from the Bardo diabase does not support the hypothesis of large-scale post-Caledonian dextral tectonic movements along the Trans-European Suture Zone but favours an in-situ model for the Variscan evolution of the Holy Cross Mts. It also does not indicate any paleomagnetically detectable local tectonic rotations of the investigated rocks.

Key words : paleomagnetism, magnetic survey, diabase, Holy Cross Mts.

Introduction

The most extensive magmatic intrusion of the Holy Cross Mts occurs in the Bardo syncline (Fig. 1). Their features are very important in reconstructing the tectonic regime and paleogeography of this part of central Europe. It is widely named the Bardo diabase (e.g., Czarnocki, 1919; Kowalczewski, 1974). According to Krzemiński (2004), the CIPW normative composition classifies the Bardo diabase as olivine tholeiite. It shows a strong chemical similarity to the continental flow basalts associated with extensional tectonics (op. cit.). Further discussion about the tectonic setting of the Bardo diabase needs more information about its accurate age and its spatial distribution. The diabase contains not only a geochemical record but it documents some features of the ancient geomagnetic field as well. It can provide information about its age and the geographic location of the Holy Cross Mts during emplacement of the magma. The Bardo diabase can also be considered as a potential raw material and sites for its exploitation should be investigated. The aim of this short paper is to summarize some of the geophysical and isotope features of the Bardo diabase described in my earlier works.

Stratigraphic and spatial model of the Bardo diabase

The diabase intrusion penetrates the Silurian rocks of the Bardo Syncline close to the stratigraphic boundary between Lower Ludlow graptolite shales and Upper Ludlow greywackes. The overall thickness of the intrusion varies between 20-30 m. The first magnetic survey of the Bardo Syncline was performed between 1937 and 1942. It

established an almost continuous diabase body surrounding the Bardo Syncline (Fig. 1, Czarnocki, 1958; Kowalczewski and Lisik, 1974).

The spatial image of the diabase is more complex in the western part of the syncline where the authors (op. cit.) draw more than two dykes. A new detailed magnetic survey was performed in that part of the syncline (Nawrocki et. al., 2007a). According to the geological map of Czarnocki (1958), the roots of the diabase intrusion should occur at the surface in just this area. Petromagnetic data obtained from the bore-core Zagórze PIG-1 and the results of the detailed magnetic survey enabled perform 2D magnetic modelling to be performed (Nawrocki et al., 2007a). The results show that the shape of the Bardo intrusion in the Zagórze area is not as complex as presented in the earlier works (Czarnocki, 1958; Kowalczewski and Lisik, 1974). There is one steep dyke that cuts the pre-Silurian rocks. The dyke spilled into Silurian strata. Its southern branch, observed in other parts of the Bardo Syncline, is not preserved in the Zagórze area due, most probably, to erosion. Nevertheless, it is in that part of the syncline that the Bardo diabase seems to hold most promise for exploitation. There, the diabase forms a body ca 150 m wide and > 20 m thick that is covered by no more than 10 m of Quaternary deposits. The length of this almost horizontal fragment of the diabase intrusion can be also deducted from the results of magnetic survey; it is ca 700 m long



Fig. 1. Area of detailed magnetic survey (Nawrocki et al., 2007a), sites of paleomagnetic studies (Nawrocki, 2000) and the sample location for isotope Ar-Ar age estimation (Nawrocki et al., 2007b) on a simplified geological map of the Bardo Syncline (after Czarnocki, 1958).

The age of the Bardo diabase

Preliminary tectonic and stratigraphic observations point to a Late Ludlowian -Siegenian age interval for the Bardo intrusion. The Ludlowian strata and the piercing diabases were folded and discordantly covered by Lower Devonian (Emsian) sediments, equivalent to the Old Red facies (Kowalczewski and Lisik, 1974). In the vicinity of Pragowiec, the angle of the unconformity is 30-50° (Kowalczewski and Migaszewski, 1994). Recent results of studies of the Late Silurian - Early Devonian sequences from the southern part of HCM show that the main phase of the late Caledonian movements occurred here in the latest Ludlowian (Pożaryski, 1977; Stupnicka, 1995) or Late Gedinian (Malec, 1993). Hence, the age of the Bardo diabase can be constrained to between Late Ludlowian and Early Gedinian. Przybylowicz and Stupnicka (1991) correlate the Upper Ludlowian Niewachlów greywackes with the diabase sills. In their opinion, the diabases and volcanic material in the greywackes originated from the same magmatic centre. Additionally, the close spatial correlation between the diabase sills and the locations of the maximum thicknesses of the greywackes containing subvolcanic material, points to a Late Ludlovian age for the diabases (op. cit.). A paleomagnetic study described below provides a prefolding paleomagnetic pole concordant with the Ludlow segment of the Baltic APWP (Nawrocki, 2000).

However, preliminary isotope studies did not exclude the intrusion being of Variscan age (Migaszewski, 2002). Recent ⁴⁰Ar-³⁹Ar studies (Nawrocki et al., 2007b) provide more consistent age data. Plagioclase grains from fresh core taken from the southern limb of the syncline near Zalesie village were analysed in the laboratory at the Research School of Earth Sciences, Australian National University. The sample revealed the presence of two plateaux at 432 ± 2 Ma and 425 ± 11 Ma for the low- and high-temperature steps, respectively. On the other hand, the step size weighting indicates that the section of the age spectrum from the step-heating run, from 0.4 to 0.97, is 424 ± 6 Ma. The middle Ludlow strata containing the intrusion cannot be older than 422 Ma (Gradstein et al., 2004) and it is clear that the ⁴⁰Ar-³⁹Ar age spectra and geological constraints point clearly to a late Caledonian age (422-418 Ma) for the Bardo intrusion.

Paleomagnetic and rock magnetic properties of the Bardo diabase

A paleomagnetic study of the Bardo diabase was conducted in the Paleomagnetic Laboratory of the Polish Geological Institute and described in two papers by Nawrocki (1999, 2000). Only two exposures of the intrusion were available for that study. Fortunately, the fact that they are situated on the opposite limbs of the Bardo syncline allowed a paleomagnetic fold test to be performed. Samples were collected near the village of Zalesie on the southern limb of the Bardo syncline and in the Pragowiec Ravine near the village of Bardo on the northern limb. At neither locality is the diabase-sedimentary rock contact previously described (Kowalczewski and Lisik, 1974) exposed at present. Pilot samples were subjected to both alternating field and thermal demagnetization experiments. The paleomagnetic fold test of McFadden (1990) was used to assess the origin of the characteristic component. Magnetic mineralogy was determined from isothermal remnant magnetization (IRM) techniques, thermomagnetic analyses and scanning electron microscope images. The natural remnant magnetization (NRM) intensities of diabases from Zalesie ranged between 4.2 and 10.6 A/m and those of the diabases from Pragowiec between 0.3 and 1.1 A/m. Most of the samples revealed a low-coercivity NRM component removed by alternating fields < 20 mT and temperatures of ca 520° C. After removal of the low-coercivity overprint, a > 20 mT high-coercivity component was identified. That magnetization was isolated as a straight-line segment directed towards the origin in orthogonal projection. It yielded an overall mean direction of $047^{\circ}/-25^{\circ}$, k = 3.1, α_{95} = 50.5° in situ and 042° / $-32^\circ,~k$ = 505.4, α_{95} = 3.4 $^\circ$ after bedding correction. The improvement in clustering of the site mean direction after bedding correction was significant at the 95% confidence level using the fold test of McFadden (1990). IRM experiments, and subsequent thermal demagnetization of the saturation magnetization, confirmed the predominance of magnetic carriers from the ulvospinel-magnetite solid

solution series. The demagnetization behaviour was typical for basaltic lava containing deuterically-oxidised titanomagnetite. SEM images support this interpretation. Magnetite-ilmenite intergrowths are common in the diabase rocks.

The paleopole calculated from the high-coercivity component corresponds to the Ludlovian segment of the Baltic APWP. The paleomagnetic pole calculated from the low-coercivity component fits well with the Early Carboniferous segment of the Baltic APWP after correction for the Variscan deformation. The late Silurian paleomagnetic pole isolated from the Bardo diabase does not support the hypothesis of large-scale post-Caledonian dextral tectonic movements along the Trans-European Suture Zone but favours an in-situ model for the Variscan evolution of the Holy Cross Mts (Nawrocki, 2000). Neither does it indicate any paleomagneticaly-detectable local tectonic rotations of the rocks investigated.

Magnetic susceptibility and inclination of magnetic remanence of the Bardo diabase were also studied in the core from borehole Zagórze PIG-1 (Nawrocki et al., 2007a). A new interesting paleomagnetic feature was discovered in the weathered zone of the diabase. The inclination characteristic for that zone is -67° . Such a high value indicates a Cenozoic age of exposure and weathering of the intrusion. Reversed polarity record means that the process of weathering had to be older than 783 Ma when the last normal-polarity Brunhes chron started.

Conclusions

From the scientific point of view, the Bardo diabase is one of the most fruitful magmatic rocks cropping out in the central part of the Trans-European Suture Zone. It provided unique information concerning the late-Silurian geomagnetic field features and about the tectonic regime and paleogeography of the TESZ in late Caledonian times.

Selected parts of the Bardo intrusion are promising for exploitation purposes. These can be defined by a more detailed, modern magnetic survey and subsequent magnetic modelling. In some places, the results of new magnetic studies should be verified by shallow (< 30 m deep) boreholes.

References:

- CZARNOCKI 1919: Stratygrafia i tektonika Gór Świętokrzyskich. Prace Towarzystwa Naukowego, Warszawa, t. 28, pp. 77-81.
- CZARNOCKI J. 1958: Mapa rozmieszczenia diabazów w okolicy Łagowa, Surowce mineralne w Górach Świętokrzyskich, z.3 Surowce Skalne, Inst. Geol., Prace 21.
- Gradstein, F., Ogg, J., Smith, A., 2004: A Geologic Time Scale 2004, Cambridge Univ. Press, pp. 589.
- KOWALCZEWSKI Z., 1974: Geological and structrural aspects of magmatism in the Góry Świetokrzyskie Mts. against the background of recent research. Biul. Inst. Geol., 275: 11-62.
- KOWALCZEWSKI, Z., LISIK R., 1974: New data on diabases and geological structure of the Pragowiec area in the Góry Świętokrzyskie Mts. (in Polish with English summary), Bull. Inst. Geol. 275: 114-158.
- KOWALCZEWSKI, Z. MIGASZEWSKI, Z., 1994: Excursion stop: Bardo Prągowiec Ravine, in Europrobe, Trans-European Suture Zone Workshop, Kielce, Poland, 24th September - 1st October, Excursion Guidebook: 39-45.
- KRZEMIŃSKI L. 2004: Geochemical constraints on the origin of the mid-Paleozoic diabases from the Holy Cross Mts. and Upper Silesia, southeastern Poland. Geological Quarterly, 48 (2): 147-158.

- MALEC J., 1993: Upper Silurian and Lower Devonian in the western Holy Cross Mts., Geol. Quart. 37: 501-536.
- McFADDEN, P., 1990: A new fold test for paleomagnetic studies, Geophys. J. Int. 103: 163-169.
- MIGASZEWSKI, Z.M. 2002: Datowanie diabazów i lamprofirów Świętokrzyskich metodą K-Ar i Ar-Ar. Przeg. Geolog., 50: 227-229
- NAWROCKI J., 1999: Przedfałdowa pozostałość magnetyczna intruzji diabazów z synkliny Barda w Górach Świętokrzyskich. Przeg. Geol., 47: 1101-1104.
- NAWROCKI J. 2000: Late Silurian paleomagnetic pole from the Holy Cross Mountains: constraints for the post-Caledonian tectonic activity of the Trans-European Suture Zone. Earth Planet. Sc. Lett., 179: 325-334.
- NAWROCKI J., POLECHOŃSKA O., SALWA S., 2007a: Model przestrzenny intruzji bardziańskiej w okolicach Zagórza (region kielecki Gór Świętokrzyskich) w świetle wyników nowych badań magnetycznych. Przeg. Geol., 55 (12/2): 1136-1142.
- NAWROCKI J., DUNLAP J., PECSKAY Z., KRZEMIŃSKI L., ŻYLIŃSKA A., FANNING M., KOZŁOWSKI W., SALWA S., SZCZEPANIK Z., TRELA W. 2007b: Late Neoproterozoic to Early Palaeozoic palaeogeography of the Holy Cross Mountains (Central Europe): an integrated approach. J. Geol. Soc., London, 164: 405-423.
- POŻARSKI, W., 1977: The Caledonian Epoch in the Epi-Gothian Platform and its border zone, in Geology of Poland, Tectonics, 4 : 175-206.
- PRZYBYŁOWICZ, T., STUPNICKA, E., 1991: Manifestations of volcanism in Ordovician and Silurian of the southern part of Świętokrzyskie Mts (in Polish with English summary), Archiwum Mineralog. 46: 137-154.
- STUPNICKA, E., 1995: Phases of tectonic movements in the Upper Silurian and Lower Devonian of southern part of the Holy Cross Mts (in Polish), Prz. Geol. 43: 110-112.

Contributions

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Mineralogy of saprolites in the Serra da Estrela granite massif, central Portugal; their geomorphological significance

Czesław AUGUST¹, Piotr MIGOŃ², Conçalo VIEIRA³

¹ Institute of Geological Sciences Wroclaw University, Poland

² Department of Geography and Regional Development, University of Wroclaw, Poland;

migon@geogr.uni.wroc.pl

Centro de Estudos Geográficos, University of Lisbon, Lisboa, Portugal

The Serra da Estrela massif is located in north-central Portugal at the western extremity of the Hercynian basement block of the Iberian Peninsula. It is the highest mountain massif in Portugal, built predominantly of medium- to coarse granite. Major relief features are an extensive elevated plateau, rising to 1993 m a.s.l., dissected by a few valleys of combined fluvial and glacial origin. The long-term history of its relief have not yet been fully explained and, in particular, products of granites weathering have not been explored as a potential source of information. The aim of this study is to provide mineralogical characteristics of weathering residues and to discuss their significance in the geomorphological context. Samples of saprolites have been collected at various sites, from the high-altitude plateau (1850 m a.s.l) down to the valley floors (680 m a.s.l.). The thickness of weathering mantles varies from 2 to 6 m. They belong to the category of grus (sandy) saprolites, with generally low content of fine (clay + silt) fraction. The degree of weathering varies between samples. Some show very limited decomposition, with little weathered plagioclase and biotite and minor amounts of illite, mixed layer I/S and smectite. Other samples contain illite, mixed layer I/S and smectite in larger proportions, and kaolinite or even gibbsite are recorded. A kaolinite rich fissure filling in granites on the plateau suggests the occurrence of an intensively altered granite, which has been almost completely eroded. Supporting evidence comes from the analysis of glacial deposits, which include chemically corroded quartz grains, likely derived from the same ancient saprolite. A possibility exists that this weathering crust predated late Cainozoic uplift and erosion. Samples collected on the shoulders of deeply incised valleys represent subsequent period of weathering (Pliocene-Pleistocene?) and are mineralogically immature. In places, post magmatic hydrothermal alteration facilitated high rates of weathering, accounting for both considerable thickness of saprolites and certain mineralogical features. Primary components and the distribution of secondary minerals in the saprolites suggest different stages of alteration of the Serra da Estrela granites. Products of deep weathering in the Serra da Estrela record an interplay of various factors, including parent rock geology, local relief, duration of weathering and climatic regime, all of which need to be simultaneously considered.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



A new buchwaldite-like phase from ignimbrite xenoliths in skarns of the Northern Caucasus, Russia: primary results

Kamila BANASIK¹, Radu BAILAU¹, Irina GALUSKINA¹, Viktor GAZEEV²

¹ Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec, Poland kbanasik@us.edu.pl

² Institute of Geology of Ore Deposits, Geochemistry, Mineralogy and Petrography (IGEM) RAS, Staromonetny 35, Moscow, Russia

A buchwaldite NaCa[PO₄]-like phase was discovered as an accessory mineral in the high-temperature skarn, in metasomatic rocks found as xenoliths in ignimbrites of the Upper-Chegem (Verkhniy Chegem) volcanic structure, the Northern Caucasus, Kabardino-Balkaria, Russia. Buchwaldite is a rare mineral, with an orthorhombic structure. Till now it was described only from iron meteorites. The buchwaldite-like phase is present in the contact zone between skarn and ignimbrite. Mineral association is represented by K-feldspars, alkali plagioclase, K-mica, pyroxene, calcite, monticelite, wollastonite, cuspidine, larnite. The buchwaldite-like crystals are often cracked, and form rounded lenses or elongated pillars bodies. They appear within K-feldspar and pyroxene fine-grained matrix as single grains up to 120 µm in size or within the altered K-mica rich in Fe, as small inclusions. The buchwaldite-like phase, in most cases, occurs together with hydroxyapatite replacing it from the centre of crystal to the margins. The buchwaldite-like crystals are transparent, colorless. They are characterized by simply extinction and high relief close to apatite. The microprobe analyses allowed to calculate the formula: $(Ca_{0.97}Sr_{0.01}Na_{0.01})_{\Sigma=0.99}Na_{1.00}$ [$(P_{0.99}Si_{0.01})_{\Sigma=1}O_4$]. The buchwaldite-like phase does not contain OH groups and molecular water: Raman spectra show the following bands: 431, 452, 516, 587, 593, 603, 969, 1015, 1025, 1035 1048, 2647 and 2709 cm⁻¹. The EBSD and Raman investigations indicate that the structure of the buchwaldite-like phase should have a lower symmetry corresponding to the buchwaldite orthorhombic mineral structure. Further studies are necessary to understand the structure and origin of this new mineral phase.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Mineralogical study of gothic mortars from the 'Mouse Tower' in Kruszwica (Central Poland)

Wojciech BARTZ¹, Maria RUDY²

¹ Institute of Geological Sciences, University of Wroclaw; wbar@ing.uni.wroc.pl ² Faculty of Fine Arts, N. Copernicus University; maria-rudy@wp.pl

Mineralogical characterization of historic mortars from the Mysia Wieża (Mouse Tower), a remnant of the 14th century Gothic castle, has been carried out by means of optical microscopy (OM), chemical (ICP-AES)- and sieve (ISO 565 sieves) analysis, scanning electron microscopy (SEM-EDX) and X-ray diffractometry (XRD). The main aim of our study was to identify the components of the mortars in order to design a compatible repair material, to evaluate their hydraulic properties and to shed light on the ancient technology of lime production.

All mortars comprise a calcitic binder and a fine- to medium-grained inert filler. The filler is composed of quartz, feldspars and rock grains (granitoid), which form subrounded and less common subangular grains. The granulometric analysis shows that the filler is poorly sorted, ranging from coarse or medium sand, through predominant very fine sand, to less common silt. The amount of acid-insoluble residue (i.e., filler) varies from 52-80 wt %.

Chemical analysis of the binder fraction (<0.063 mm), separated by sieving, revealed that calcium oxide is the main component and that concentration of R₂O₃ oxides is relatively low. The percentage of acid-soluble SiO₂ is also low. As the cementation index (CI) of the mortars is below 0.3, they are classified as non hydraulic.

The grains of the filler are embedded in the very fine-grained calcitic matrix. Typically the matrix contains numerous rounded lime-lumps reaching up to few mm in diameter. These binder particles are mostly composed of dark brown micrite. Their chemical composition, determined by SEM/EDS, yields at least 96% CaO, and small amounts (below 2.5%) of MgO and SiO₂. The lime-lumps frequently enclose aggregates of minerals typically rich in CaO and SiO₂. The combination of EDX analysis and the shapes of the minerals in the aggregates identified them as wollastonite (acicular, Ca/Si atomic ratio close to 49:50), and belite C_2S (equant, Ca/Si atomic ratio close to 63:35). Less common is rankinite, containing approximately 57% CaO and 40% SiO₂. Pore space between these minerals is occasionally occupied by almost pure silica (identified by XRD as cristobalite), which sporadically forms larger parts of the sparse lime lumps, together with micrite. The aggregates are rimmed by a thin zone composed of micrite and other minerals with compositions close to the melilite group (gehlenite-åkermanite).

Typically the lime lumps are interpreted as the result of dry-slaking and/or very short seasoning of the lime. However, in this particular case, occurrence of a high temperature mineral assemblage in the mortars suggests that the lime lumps should be considered as overburnt limestone chunks, formed due to presence of hot-spots locally distributed within the lime kiln. The calcium-silicate assemblage indicates that the temperature locally was in excess of 1100°C.

The EDX analysis clearly identified the presence of hydraulic phases. However their small volume had no impact on the hydraulic properties of whole sample. The applied lime was burnt from impure limestone rich in clay minerals and silica, but the temperature within the kiln was too low to produce a natural hydraulic lime.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Geochemistry of ultramafic intrusions in Albanian Ophiolites

Arjan BEQRAJ¹, Minella SHALLO¹

¹ Faculty of Geology and Mining, Tirana, Albania; ae_beqiraj@yahoo.com

Though ultramafic intrusions are widespread among Albanian ophiolites, the most abundant are found within plutonic ophiolite sequences; they occur also in the uppermost part of the mantle sequence. The best outcrops of ultramafic intrusions are found in the Puka, Kukesi and Mirdita regions in the northern ophiolite sector. Ultramafic intrusions form small-medium size discordant rarely concordant bodies of irregular, izometric or elongate shape, ranging from several m² up to 0.2-0.7 km², or relatively large sills, or thin layers (2-3 cm up to 0.3-0.5 m). Ultramafic intrusions in the western ophiolites consist mainly of poikilitic wehrlite, plagioclase wehrlite, lherzolite and plagioclase lherzolite, rare plagioclase dunite and olivine pyroxenite, whereas those within the eastern ophiolites consist of poikilitic wehrlites, lherzolites, and rare harzburgites, usually associated with pyroxenites.

With respect to major elements, they show different geochemical compositions reflecting different modal compositions; these compositions do not distinguish between the western and eastern ultramafic intrusions. TiO_2 contents, normalized to Upper Mantle (UM) abundances, range from 0.4 to 1.0 x UM and from 0.1 to 0.3 x UM for the western and eastern ultramafic intrusions, respectively. Sc and V, even though always below the Primitive Upper mantle content, are only marginally higher in western-type ultramafic intrusion. In contrast, the normalized values of the compatible elements (Cr, Ni, Co) do not show any sharp distinction between ultramafic intrusions of the two ophiolite types. The ultramafic intrusions have varying low Rare Earth Element contents and they display different spider graphics of their normalized contents. The LREE contents are higher in the eastern ultramafic intrusions, while the western ultramafic intrusions show a REE fractionation trend that is characterized by a gradual enrichment of MREE and HREE relative to LREE.

Olivine compositions that range from Fo_{85} to Fo_{91} (Table 3) do not distinguish between the western- and eastern-type intrusions – probably because of its extremely refractory nature. The clinopyroxenes from the ultramafic intrusions of the western ophiolites are higher in Ti, Na, and Fe³⁺ than those from ultramafic intrusions of the eastern ophiolites which, in contrast, are higher in tetrahedral Al. The value of Cr/(Cr+Al) in chromite ranges from 0.44-0.55 for the western intrusions and up to 0.79-0.84 for the eastern intrusions, thus characterizing them as magmatic rocks crystallized by magmas of MORB and boninite type, respectively. The high forsterite content in olivine (Fo₈₇–Fo₉₂) and high Mg values in clinopyroxene (Mg#=89–94.5) indicate that they probably crystallized from rather undifferentiated melts.
MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Behaviour of CL-activators during the hydrothermal stage of granite formation

Justyna CIESIELCZUK¹, Magdalena SIKORSKA²

¹ Faculty of Earth Sciences, University of Silesia, 60 Będzińska St., 41-200 Sosnowiec, Poland; jciesiel@wnoz.us.edu.pl ² Polish Geological Institute-National Research Institute, 4 Rakowiecka St., 00-975 Warszawa, Poland

Products of hydrothermal alteration of granites were analyzed by scanning microscopy, microprobe, optical cathodoluminescence and CL spectroscopy. Samples collected from the Strzelin, Borów and Karkonosze granitoid massifs represent three degrees of alteration of granite.

The history of the feldspar alterations is clearly revealed thanks to differences in the CL colours and emission spectra of altered and unaltered grains. Alkali feldspars and plagioclases show blue CL colours caused by structural defects due to the substitution of $A1^{+3}$ for Si⁺⁴ (450-480 nm) and activation of Ti⁺⁴ (460 nm) (Götze, 2000). Blue and pink CL colours of primary albite, and non-luminescent albitized plagioclase cores coexist with partly sericitesed K-feldspar characterized by brown CL colours. The CL spectrum of blue albite has strong emission bands at ~720 (Fe⁺³ activation) and ~450 nm whereas pink albite differs in showing a very week emission at ~450 nm. The brown CL colour of the Kfeldspars reveals that K-feldspar was affected by alteration what is confirmed by the partly sericitized K-feldspar grains and antipertites within plagioclase grains, as both are brown in CL. The CL emission spectrum of the brown-luminescing K-feldspar is dominated by the emission band of Mn²⁺ at 560 nm. In the UV range around 280 nm, there is an emission band of Tl⁺; Tl⁺ substitutes for K⁺ (Gorbets, Rogojine, 2002; Sikorska, 2005).

Accessory and newly-formed hydrothermal minerals also reflect differences in chemical composition and catodoluminescence properties.

Apatite typically occurs as small, ca 10-30 µm grains which are homogenous in CL (yellow) and BSE images. Larger grains (100 - 300 µm) show in CL a three-stage zonal growth structure. In these, the central part shows yellow CL, the subsequent zone a green CL and the outer zone a brownish CL colour. CL spectra reflect a decrease in the content of REE activators during apatite growth. Yellow apatite contains less CaO and more SiO₂ compared with the green and brownish zones.

Clinozoisite-epidote group minerals are mainly non-luminescent because of Fe^{+2} which is a CL-quencher. But parts of grains containing less iron (clinozoisite) are characterized by a dark gray CL colour; the CL spectrum confirms the presence of the activator (555 nm), probably Tb³⁺.

Prehnite is easily visible in CL because of its characteristic yellow luminescence. Two kinds of prehnite can be distinguished in CL: light-yellow and yellowish-green. The CL spectra are similar and reveal only the varying content of Mn^+ (~570 nm) as an activator.

The varying composition of titanite well seen on BSE images is confirmed by CL colours. The outer dark-olive CL-colour of titanite grains corresponds with a light-gray BSE-colour. These outer parts contain less SiO_2 , Al_2O_3 and CaO and more TiO_2 , Nb_2O_3 and V_2O_3 . CL spectra reveal a decrease in the contents of REE activators (Gaft et al., 2005) in darker zones – as in apatite.

References:

GAFT M., REISFELD R., PANCZER G., 2005: Luminescence Spectroscopy of Minerals and Materials. Springer. 1-356.

GÖTZE J., 2000: Cathodoluminescence in applied geosciences. In: Cathodoluminescence in Geosciences (Eds.: M. Pagel, V. Barbin, P. Blanc, D. Ohnenstetter): 457-478.

GOROBETS B.S., ROGOJINE A.A., 2002: Luminescent spectra of minerals. (Reference book). RPC VIMS, Moscow. 1-300.

SIKORSKA M., 2005: Badania katodoluminescencyjne minerałów. Instr. i Metody Bad. Geol. 59; 1-70.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Geochemical diversity of microgranular mafic enclaves from a composite Variscan Strzegom-Sobótka massif (SW Poland)

Justyna DOMAŃSKA-SIUDA¹, Krzysztof TURNIAK², Adam SZUSZKIEWICZ²

¹ Institute of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw; j.domanska@uw.edu.pl

² Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, 50-204, Wrocław, Poland; krzysztof.turniak@ing.uni.wroc.pl; adam.szuszkiewicz@ing.uni.wroc.pl

The Variscan Strzegom-Sobótka massif (SSM), the largest of the granitic plutons in the central part of the Fore-Sudetic Block (NE part of the European Variscan Belt), is composed of four main rock types: hornblende-biotite granite, biotite granite (W part of the massif), and two-mica granite and biotite granodiorite (E part). Mafic microgranular enclaves occur mainly in hbl-bi granite and bi granodiorite. The enclaves from the western part of SSM (EWP) display a wide spectrum of compositions ranging from monzodiorite, diorite and quartz diorite to tonalite while those of the eastern part (EEP) are mainly tonalitic. Both enclave groups are composed mainly of biotite (\pm hornblende in EWP) and plagioclase with minor alkali feldspar and quartz. Zircon, apatite, allanite, monazite and epidote occur as accessories. However they display distinct geochemical features suggesting differences in the origin and evolution of their parental melts.

EWP show a broad range of SiO₂ from 50.62 to 69.23 wt%. The Mg-number is low (0.16-0.33) and similar to that of the host granite (0.15-0.30). Na₂O/K₂O ranges between 0.72-4.92 with an average of 1.88. They are peraluminous to metalouminous with A/NCK from 0.85 to 1.22. EEP, on the other hand, display a narrower range of SiO₂ content (60.27-68.24 wt%). The Mg-number is higher (0.36-0.41) and Na₂O/K₂O between 0.76 and 2.96 with an average of 1.34. EEP are peraluminous with A/NCK ranging from 1.04 to 1.19.

For the two enclave groups, most of elements (e.g. TiO_2 , Al_2O_3 , Fe_2O_3 , MnO, MgO, CaO, P_2O_5 , Rb, Zr, Hf, Nb, Y, V, Ni) correlate negatively with SiO_2 . For EWP, K_2O and Na_2O do not show a straightforward correlation with SiO_2 ; they form curved trends. For EEP, K_2O displays a negative trend and Na_2O does not correlate with the differentiation index. EWP have higher Fe and lower Mg and Ca contents then do EEP. The REE patterns of EWP and EEP differ. EEP have less fractionated LREE ((La/Sm)_N:1.4-3.2) with absolute contents lower (83-158 X chondrite) than in EWP (103-341 X chondrite). EWP exhibit a significant fractionation of LREE ((La/Sm)_N:0.9-4.9). A negative Eu anomaly is present in both groups. HREE contents are systematically higher in EWP (123-565 X chondrite) than in EEP (85-182 X chondrite) whereas their fractionation does not show any meaningful differences between the two groups.

The geochemical differences between microgranular mafic enclaves from the W and E parts of the Strzegom-Sobótka massif are consistent with the petrological and mineralogical heterogeneity of the massif. They may also suggest a different origin and evolution of parental granitic melts.

Acknowledgement: The study was financed by the MNiSzW research grant NN 307112735

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Mineralogy of Upper Triassic clays (southern Polish Lowland) in XRD, SEM and TEM studies

Agata DUCZMAL- CZERNIKIEWICZ¹, Paulina KAPTUROWSKA¹, Jörn KASBOHM²

¹ Institute of Geology, Adam Mickiewicz University, ul. Maków Polnych 16, 61-606 Poznań, Poland;

duczer@amu.edu.pl, malachitka@tlen.pl

²Institute of Geography and Geology, Greifswald University, Friedrich-Ludwig-Jahn Str. 17a, D-17487 Greifswald, Germany; kasbohm@uni-greifswald.de

Upper Triassic clays are widely used in the ceramic industry in Poland. The best known deposits are situated in the Holy Cross Mountains and in the NE border of the Silesian-Cracow region and surroundings areas. These sediments are found also in the Southern Polish Lowland where the clays are recognized in the Zbąszyn Beds (Norian) and Wielichowo Beds (Raethian). In this work, the mineralogy, structure and chemistry of the Upper Triassic clays from deposits in Słupia – Albertów near Kępno were studied using XRD and a combination of SEM, TEM and EDS methods.

The sediments studied are typical of Triassic clays with their reddish, red or cherry colours. They constitute a monotonous interval of dark brown to reddish massive clays. In upper part, they are intercalated by green silt layers up to 1 cm thickness and display fine cross-lamination with very low slopes (about 3-5 degrees). The content of SiO₂, the main component, ranges from 73-56%. The highest content of SiO₂, and the lowest Al₂O₃, characterises the silty clays and the lowest SiO₂ contents the clayey part of the outcrops and separated clay fractions ($\phi < 0.2 \ \mu m$ and $\phi < 2\mu m$). Fe₂O₃ ranges from 8-15% and MnO from 0.03-0.58%. Na₂O and P₂O₅ occur in trace amounts.

Visual XRD patterns of randomly oriented samples indicated the presence of mica likevermiculite minerals, IS-ml and kaolinite as main clay minerals phases. The main non-clay phase is quartz. In general, there was no significant variation between the mineral compositions of the investigated $< 2 \mu m$ and $< 0.2 \mu m$ fractions. The detailed mineralogy of the sediments was established using TEM and EDS. The sediments are dominated by mixed-layer particles including end members and mixed-layer series: dioctahedral vermiculite/smectite (in the main), dioctahedral vermiculite/smectite mixed-layer, illite/smectite and beidellite. The mixed layer particles occur mainly as xenomorphic flakes, occasionally slats. Dioctahedral vermiculite/smectite minerals occur as small or very large platy crystals and xenomorphic particles. Beidellites occur as hexagonal crystals or platy xenomorphic flakes, similar to dioctahedral vermiculite/smectite. Illite-smectite particles formed platy- or irregular flakes.

The mineralogical and chemical composition suggests a terrestial origin for the clays. Beidellite is mainly a product of soil formation produced by chemical weathering and can be generally viewed as an indicator of warm and wet climate conditions. Mixed layer phases, illite/smectite and divermiculite/smectite (mica-like phase) are common components of sediments and soils that could originate due to chemical weathering from mica phases.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Calcite crystallisation in the galleries of the Rożnów Dam

Krzysztof DUDEK¹, Tadeusz RATAJCZAK¹, Adam GAWEŁ¹, Marek SIKORA¹, Sebastian KRUPCZYŃSKI²

¹ AGH – University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Al. Mickiewicza 30, 30-059 Kraków, Poland

² Zespół Elektrowni Wodnych Rożnów Spółka z o.o., Rożnów 433, 33-316 Rożnów, Poland

The Rożnów Dam and Power Station were built in the years 1936-1941 following the catastrophic flood in the Dunajec river valley in July 1934. The dam, built of 450 000 m³ of concrete, is 550 m long and 49 m high. The capacity of the power station reaches 56 MW and the annual production of energy amounts to 125 106 KWh.

The lowermost gallery of the dam, 3 m in diameter, is situated 25 m below the bottom of the Rożnów Lake. Water is percolating into the dam mostly through dilatations and technical sutures; the amount of infiltration has been at a stable, safe level below 0.5 m^3 per minute. The concrete walls of the gallery, however, have been continually covered with bright, white or yellow-brownish incrustations, in particular in the dilatation zones and in some places of more intensive water percolation. Flat incrustations covering the concrete gallery walls are the most common but small stalactites form in places.

This material crystallised on the walls of the gallery was sampled and subjected to optical and scanning microscopy, X-ray diffraction, and chemical analysis. Samples of water from the gallery and from the Rożnów Lake were also analysed.

The analyses demonstrated that the sampled material consists almost exclusively of crystalline calcite. This mineral was recognised in microscopic observation of thin slices and confirmed by the X-ray analysis (distinct peaks of 3.86, 3.04, 2.49, 2.28, 2.096 Å, as well as others, typical for calcite, in all analysed samples). The outermost, youngest parts of the incrustations are composed of fine-crystalline calcite layers, ca 0.1-0.2 mm in thickness, separated by empty spaces, up to 1 mm thick. The calcite crystals are very fine, tabular and quasi-isometric, subhedral or anhedral. In older parts of the incrustations, the originally empty spaces are fully or partly filled with relatively large, prismatic crystals up to 0.4-0.5 mm in length. SEM images enabled the recognition of the side faces of the prismatic crystals {10-10} and the faces {21-31} at their tops. Yellowish and/or bright-brownish colouration of the incrustations and stalactites is probably related to small amounts of dispersed opaque substance, presumably iron hydrooxides.

The analysed water samples proved to be basic; pH of ca 8.5 for water from the gallery, and pH = 7.6 for water from the Rożnów Lake. The cation composition (Na⁺, K⁺, Ca²⁺, Mg²⁺) was relatively diversified, whereas HCO₃⁻ predominated among the anions.

The pure-calcite incrustations, combined with the chemical composition of the waters, seem to point to the percolating water being the principal source of the calcium carbonate. This may be also indicated by a very good state of the 70-year-old concrete of the Rożnów Dam.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The Mafic/Ultramafic Rocks in Wadi El-Allaqi-area, South Eastern Desert, Egypt: implications of their geochemical and tectonic variations

Said EL NISR¹, Moghazi A. MOGHAZI¹, Mohamed M. EL SAYED¹

¹ Geology Department, Faculty of Science, Alexandria University, Egypt

The mafic plutonic rocks of the Allaqi area in the South Eastern Desert of Egypt are of 2 types: 1) a greenschist facies metagabbro which is intimately associated with serpentinites after harzburgite and, 2) intrusive metagabbro-diorite. On the basis of major and trace element chemistry, the mafic rocks are split into two magmatic groups. The first is a tholeiitic one with transitional MORB and IAT characteristics (ophiolitic) which may have developed in a back-arc setting rather than a mid-ocean ridge environment. The second is a more fractionated calc-alkaline one with volcanic arc affinities. The observed variations in major and trace element concentrations reveal that fractional crystallization was the main process in the evolution of the two gabbroic groups. However, the magnitudes of the element enrichments and depletions indicate that the arc gabbros are more fractionated than the ophiolitic varieties. Furthermore, the mineralogical composition of the fractionating assemblages in the two gabbroic varieties is different. The predicted fractionation history for the ophiolitic gabbro is Ol, Ol + Cpx and Ol + Cpx + Pl and, for the arc gabbros, Cpx + Ol and Cpx + Ol + Pl. The crystallization of the latter may have taken place under elevated water pressure.

The mafic/ultramafic suite of Wadi Allaqi may have formed in a back-arc environment and have been tectonically transported onto old continental crust during the closure of late Proterozoic ocean basin. Consequently, the oceanic assemblage had been intruded by the arc gabbros.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Investigations on tourmalines of the elbaite-schorl series

Andreas ERTL¹, Ekkehart TILLMANNS¹

¹ Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Althanstrasse 14, A-1090 Wien

Detailed chemical and structural data were obtained on samples of the elbaite-schorl series from San Diego County, California, USA. While the black core of a large crystal has the composition of an Al-rich, Mn-bearing "oxy-schorl" with ~2-4 wt% MnO, an intermediate zone can be assigned to a yellowish-green Mn-rich "fluor-elbaite" with a relatively high Mn content of ~6 wt% MnO. Nearly colourless "fluor-elbaite" has the highest Li content of all investigated samples (~1.1 apfu Li). Mössbauer studies from the different zones within a zoned crystal from a pegmatite pocket show that the relative fraction of Fe³⁺ increases continuously from the Fe-rich core to the Fe-poor near-rim zone in a large tourmaline crystal (~5 cm in diameter), reflecting increasing fugacity of oxygen in the pocket. In the outermost Fe-poor rim, the relative fraction of Fe³⁺ decreases again.

There is an inverse correlation between the $\langle Y \cdot O \rangle$ distance and the Al and Fe³⁺ content at the Y site in the investigated tourmalines of the elbaite-schorl series. Many samples contain mixed occupations of Si, Al and B at the T site. Similar to ^[4]B-bearing tourmalines from other areas, a positive correlation between Al at the Y site and ^[4]B was found in these tourmalines. Another positive correlation was found between (Mn²⁺ + Fe²⁺) and ^[4]Al.

Beryllium is very low in the Fe-rich samples (BeO ≈ 10 ppm) and increases concomitantly with the Al content. The sample with the highest Al content also has the highest Be content (BeO ≈ 80 ppm).

Our analyses indicate that some elbaites contain a mixed occupation of F, OH and O at the W site. We conclude that the assumption OH = 4 - F is only valid for elbaitic tourmalines with FeO + MnO < 8 wt%. However, for the most elbaite samples, this assumption is a good approximation for estimating the OH content.

Acknowledgement: This work was supported by Österreichischer Fonds zur Förderung der wissenschaftlichen Forschung (FWF) project no. P20509-N10.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Modification of glauconite clays and Na-X zeolites in order to receive acid gases sorbents

Wojciech FRANUS¹, Małgorzata FRANUS¹, Magdalena WDOWIN²

¹ Department of Geotechnics, Lublin University of Technology, Nadbystrzycka 40, 20-618 Lublin, Poland; w.franus@pollub.pl, m.franus@pollub.pl

² Division of Geotechnology, Mineral and Energy Economy Research Institute Polish Academy of Sciences,

J. Wybickiego 7, 31-261 Krakow, Poland; wdowin@meeri.pl

Acid gases, e.g., CO_2 , SO_2 and NO_x constitute a problem of many industrial plants such as power plants, cement mills, refineries, etc. The emission of these gases influences greenhouse-effect growth. Therefore, there exists a need to work out new, economic solutions to reduce the emission of these gases or their neutralization.

The aim of this study was the modification of the surface properties of natural and synthetic mineral resources in order to achieve acid-gas sorption. The tested materials were glauconite clays (natural material) and NaX zeolite (synthetic material).

The examined clay material was activated using 20% sulphuric acid over a period of 4-7 hours followed by calcinations at a temperature of 350°C over 4 hours. The zeolitic material, due to its lack of chemical resistance to acid, was subjected only to thermal activation at 350°C over 4 hours.

In order to define the influence of the acid and thermal activation on the analyzed material, the following surface parameters were determined: ion exchange capacity, surface area, structure and pore size distribution.

As a result of the activations, the BET surface area for the clay sample increased from 86 m²/g to 236 m²/g (after 7 hours thermal-acid activation) and from 262 m²/g to 434 m²/g (after thermal activation) for the NaX zeolite. Also, the ion exchange capacity of the clay decreased from 33 meq/100g to 15 meq/100g, whereas that of the zeolite remained nearly constant at about 218 meq/100g.

Preliminary tests of CO₂ and SO₂ sorption for the zeolite sample were conducted. Measurements of CO₂ sorption isotherms show a much greater sorption onto the activated sample (0.51 mmol/g at equilibrium pressure p/p_0 close to 0.01) than onto the natural sample (0.18 mmol/g). This result explicitly indicates the surface modification needed for this sort of material in order to achieve CO₂ sorption.

Measurements of SO₂ sorption isotherms show a much greater sorption onto the activated zeolite sample (1.76 mmol/g at equilibrium pressure p/p_0 close to 0.2) than onto the natural sample (0.46 mmol/g).

Experiments on the chemisorption of SO_2 were also conducted (sorption and desorption at 0° measurement temperature. The difference in the quantity of adsorbed SO_2 can be considered as the amount adsorbed as a result of chemisorption. This difference at a pressure of ca 0.1 p/p₀ in the case of the activated NaX was 0.72 mmol/g, that is ca 47% of the total amount adsorbed and in the case of the natural sample, the difference was 0.23 mmol/g, that is ca 57% of the total. The results explicitly indicate, for the tested materials, the degree of the surface modifications needed in order to promote acid gas sorption.

Acknowledgements: This work was financed within the scope of research and development project No R14 0013 06 and research project No N523 424837.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Hydro-fracturing by boron-rich fluid of the granitoid rocks in the Tatra Mountains

Aleksandra GAWĘDA1

¹Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec

Tourmaline is a common accessory mineral in granitoids, especially peraluminous leucogranites and their pegmatites. It crystallizes both as a magmatic mineral, as a subsolidus phase and late hydrothermal mineral, especially in the exocontact of granitoid plutons. As the presence of tourmalines is a marker of high B activity, the chemistry of tourmalines could mirror the source rocks character and might help to define the origin of B-rich parental fluid. Boron-rich fluids, released from the crystallizing granitoid magma, usually circulate in the contact aureoles and cause metasomatic reactions.

In some pegmatites in the High Tatra granite (e.g. Mnich, Mięguszowiekie Peaks, Gerlach), minerals (including first generation tourmaline occurring as crystals < 6 cm long) are intensely fractured and cemented by fine-grained tourmaline crystals. The tourmaline is schorlite-dravite in composition with the schorl component prevailing over dravite: $Ca/(Ca+Na) \sim 0.16$, *fm* = 0.578-0.595 and Al in Y in the range of 0-0.25, $c_0 = 7.187-7.183$ Å. Long-prismatic tourmaline crystals are chemically zoned with Fe enrichment at the border and are intergrown with K-feldspar ($Or_{96}Ab_2Cn_2-Or_{97}Ab_2Cn_1$) and chlorite.

In the border zone of the granite in the Western Tatra Mountains (e.g. Niżna Bysta, Kopa Kondracka, Kończysta n. Jarząbczą, Jakubina), fracture zones, 2-3 metres in length and 6-20 cm thick, anastomosing into millimetre-thick veins, are cemented by fine-grained to submicroscopic tourmaline, quartz and albite. The fracture zones, trending 174/35-160/40 are, in general, concordant both with magmatic layering and the schistosity of the metamorphic cover rocks. The tourmaline here is less calcic (Ca/(Ca+Na) = 0-0.01) and consequently shows higher c_0 (7.181-7.211 Å), less ferrous (fm = 0.495-0.535) and F in the range 0.02-0.05 a.p.f.u. Locally tourmaline is associated with xenomorphic fluor-apatite and quartz. The tourmaline-rich matrix of the fracture zones shows strong REE fractionation with a predominance of LREE (Ce_N/Yb_N = 23.91) and a flat Eu anomaly (Eu/Eu* = 0.922).

The presence of hydro-fracturing zones in the border part of the Tatra granites, and internal brecciation in granitic pegmatites, is a proof for fluid overpressures in the cooling granite magma. The predominance of tourmaline as a cementing mineral suggests the importance of boron in the fluid phase. Similarly, the presence of hydrothermal fluorapatite would also argue for the late-magmatic activity of phosphorus and fluorine. The difference in tourmaline composition in comparison with primary pegmatitic tourmaline megacrysts (secondary tourmalines are more magnesian) might be an effect of fluid evolution and/or fluid interaction with the host rocks (both granitic and metamorphic). The distribution of hydro-fractures in the granite pluton and its envelope provides a new insight into the composition and role of the fluid phase originally dissolved in the granite magma.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Alkali feldspar megacrysts from the High Tatra granite – indicators of magma mixing/mingling processes

Aleksandra GAWEDA¹, Magdalena SIKORSKA²

¹ Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec
² Polish Geological Institute-National Research Institute, 4 Rakowiecka St., 00-975 Warszawa, Poland

Alkali feldspar (Afs) megacrysts are observed in many granitoid intrusions. Their chemical patterns are indicators of magma mixing/mingling, changes in magma temperature, decompression during felsic magma ascent and/or changes of water activity in the magma. Zoned Afs phenocrysts, showing variations in celsian content, are considered to be a good monitor of chemical changes in the parent magma.

Alkali feldspar megacrysts 1-6 cm long occur in the High Tatra granite as four different types showing different geochemical and CL characteristics. Type 1 – Afs forming cumulate layers up to 0.5 thick and enclaves 0.9 m in size with normal Ba zonation (Cn = 4.8-1.2 at.% and 3.5-0.8 at.%). Type 2 – Afs in mafic microgranular enclaves (MME) showing inverted Ba zonation (Cn = 0.3-1.7 at.% and 1.2-2.2 at.%). Type 3 – Afs associated with granite layering with normal zonation (Cn = 3.9-1.9 at.% to 2.9-0.6 at.%). Type 4 – Afs with both normal and inverted zonation (Cn = 0.9-6.9 at. % and 1.4-3.6 at.%) dispersed in homogeneous granite.

Matrix alkali feldspars show either normal zonation or the irregular distribution of barium, interpreted in terms of secondary recrystallization.

Alkali feldspar megacrysts from all localities are characterised by poikilitic textures with plagioclase, quartz and biotite inclusions. The inclusion rows underline the microscopic zonation expressed by changes in Ba content. The included plagioclase crystals nucleated on the Afs growth surfaces. Late magmatic transformations, expressed as the perthite exsolutions, and interspersed with exsolution-free homogeneous domains, are evident in all Afs types.

A common feature of the Afs megacrysts is a blue luminescence of different shades, whereas the plagioclase inclusions show a green luminescence. Layers showing enhanced concentration of barium in the Afs are easily distinguishable by the dull-blue colour.

All megacrysts are carriers of Eu; they are all characterised by positive Eu anomalies. The lowest Eu/Eu* value was found in Type 2 megacrysts (Eu/Eu* = 4.8-5.5), Type 1 and Type 3 show Eu/Eu* in the range of 16.5-17.8, while Type 4 megacrysts show the highest Eu/Eu* value of 22.1.

Temperature calculations indicate the predominance of post-magmatic conditions (400-600°C) and most probably a late thermal episode related to shearing and alkali-element migration. In Type 4 Kfs megacrysts, equilibrium magmatic temperatures (T > 700°C) are preserved. In MME (Type 2), disequilibrium temperatures reach 800°C. However, in all cases, the different occurrences of the alkali feldspar megacrysts in the granite, and their Ba zonation patterns, reflect their magmatic origin.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Magmatic structures in the High Tatra Granite: a key to the model of the intrusion

Aleksandra GAWEDA¹, Krzysztof SZOPA¹

¹Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec, Poland

Magmatic layering, formerly described from mafic magmatic intrusions, and more recently found also in granitoid plutons, are interpreted in terms of the cumulate formation process. The High Tatra granite, Variscan in age, is a tongue-shape intrusion located in metamorphic host rocks. In its eastern part, the granitoid body contains many xenoliths of different size, mafic microgranular enclaves and portions of dioritic magmatic precursors. Near the contact of the granite with its host rocks, and in areas rich in larger xenoliths, magmatic layering is observed.

Layering found in the Tatra granite is defined by normal density gradation and inverse size gradation. The base of each layer is enriched in mafic minerals plus apatite, monazite and zircon, while feldspars and quartz were fractionated at the top. The mafic bases are thicker in the concave parts of the layers. Their shapes resemble the trough structures or load-casts, observed in sedimentary rocks. They are enriched in opaque minerals, apatite, monazite and zircon. Finger-like protrusions of felsic portions into the mafic bottoms of overlying layers resemble the flame structures known from sedimentary rocks and described from mafic layered intrusions. Erosion surfaces are defined by discordant contacts between the layers. Locally the layers or sets of layers are discordant. In addition, slump breccias and cumulate enclaves inside the more felsic varieties are observed. Leucocratic patches are also present and could be interpreted as the frozen portions of melt percolating upward through the crystal-mush in a `demelting` process analogous to the devolatilization of sediments during maturation and formed by filter pressing process. The layers interleave with the homogeneous equigranular monzogranite portions. Locally the Kfeldspar phenocrysts, with both normal and reversed magmatic zonation, are also concentrated near the base of the layers, pointing out the magmatic flow. K-feldspars phenocryst accumulations form layers and lenses, tens of centimetres to meters in thickness. K-feldspar megacrysts, commonly imbricated, form a closely packed framework, while the matrix is composed of biotite, muscovite, albite, quartz and accessories (apatite, zircon, monazite, xenotime). Apatite concentrations are often associated with K-feldspars.

The development of structures reflecting mechanical alignment of crystals during flow of the magma, is typical for either in situ crystallization coupled with interstitial melt removal or mechanical accumulation produced during shear flow coupled with compaction and loss of interstitial liquid by filter pressing. The slump breccias and the local presence of monzogranitic portions in leucogranite could be also understood in terms of density-current activity, stimulated by syn-magmatic faults destabilizing the accumulated crystal pile. The mixing with less viscous, mafic magma could enable the development of the sedimentarylike structures, while the presence of xenoliths, being sinks for magma heat, could act to stimulate the formation of thermal boundary layers and undercooling.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Secondary changes in schreibersite (rhabdite) and cohenite in the Morasko meteorites

Agnieszka GURDZIEL¹

¹ Uniwersytet Śląski, Wydział Nauk o Ziemi, 41-200 Sosnowiec, ul. Będzińska 60, Poland; v.agnieszka@interia.pl

Phosphides and carbides occurring in the Morasko meteorites group are resistant to weathering processes. They are represented by schreibersite (Fe,Ni,Co)₃P as well as its morphological form – rhabdite and carbide – cohenite (Fe,Ni,Co)₃C.

Many factors can be responsible for the presence and rate of development of the secondary changes in these meteorites. Disregarding environmental conditions, e.g., chemistry of soil, changes of humidity and temperature, depth of inhumation, the individual location of the studied mineral phases in the meteorites are important during weathering.

The phosphides have different forms, i.e., cracked grains for schreibersite and automorphic crystals for rhabdite. During weathering processes, the walls of rhabdite crystals initially become rougher and uneven. Based on BSE observation, secondary changes are seen as white domains in the rhabdite crystals (Fig. 1 & 2). Loss of phosphorus and increasing nickel in the marginal parts of rhabdite is evident. It is an example of a transition reaction from phosphide to a metallic phase.



Fig. 1. BSE image of lateral crosssection of weathered rhabdite crystal. Size of the crystal: $12 \mu m$. Morasko meteorite.



Fig. 2. BSE image of weathered rhabdite prism. Size of the crystal: $32 \ \mu m$. Morasko meteorite.



Fig. 3. BSE image of weathered cohenite grain associated with secondary iron hydroxide forms and graphite. Size of the crystal: $1700 \mu m$. Morasko meteorite.

Further weathering processes are responsible for morphological changes in the rhabdite crystals (Fig. 2). Phosphorus from the decomposition of rhabdite is incorporated into a new iron phosphate, mainly vivianite $Fe_3(PO_4)_2 \ge 8H_2O$. Cohenit present in the Morasko meteorites is cracked and metallic low-Ni iron in association with graphite is exuded (Fig. 3). During the weathering, the metallic iron is replaced by hydroxides which contain fragments of graphite.

Phosphates and carbides that are not normally present on the Earth's surface, in many cases, may be the only indicators of strongly weathered iron meteorites.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Petrography and geochemistry of volcanic rocks from the Niemodlin area (SW Poland)

Artur JAKUBIAK¹, Anna PIETRANIK¹, Ewelina ŁYCZEWSKA

¹ University of Wrocław, Institute of Geological Sciences, ul Cybulskiego 30, 50-205 Wrocławski, Poland; artur.jakubiak@ing.uni.wroc.pl

Tertiary volcanic rocks from the Niemodlin area (SW Poland) belong to Central European Volcanic Province (CEVP). Several quarries of basaltic rocks occur in the area including "Rutki-Ligota", "Gracze-Ameryka", "Rutki", "Gracze", "Radoszowice". In this paper we will focus on basaltoids from two active quarries: "Gracze" and "Rutki Ligota".

According to the TAS diagram, rocks from "Gracze" classify as nephelinites and those from "Rutki-Ligota" as basanites. Mineral composition is very similar in both groups of rocks. Basanite consists of olivine, clinopyroxene, nepheline, plagioclase, Ti-Fe oxide and apatite. Nephelinite consists of olivine, clinopyroxene, nepheline, Ti-Fe oxide and apatite. Phenocrysts in both groups are olivine and clinopyroxene.

Chemical compositions of minerals in the basanites and nephelinites are similar though minerals in the nephelinites are more homogenous. Olivine phenocrysts in the nephelinites show compositional variations from Fo₇₃ to Fo₈₇ (Δ Fo = 14), Ca = 100-4600 ppm and Ni = 500-4700 ppm. In contrast, olivine phenocrysts in the basanites span a wider compositional range from Fo₆₃ - Fo₈₈ (Δ Fo = 25), Ca = 1000-6350 ppm, Ni = 400-3150 ppm.

The rocks from "Rutki-Ligota" and "Gracze" are characterized by high concentrations of incompatible elements such as Ba (600-900 ppm), Sr (800-1200 ppm), Nb (70-100 ppm) and La (40-65ppm).

The similarity of mineral and chemical whole rock compositions of the rocks from "Rutki-Ligota" and "Gracze" indicate that they were derived from the same source. Slight differences in chemical composition are consistent with different degrees of differentiation and/or melting in the source. Basanite records a larger span of differentiation than nephelinite.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Crystal size distribution of olivine from the Męcinka Basalt (SW Poland)

Aleksandra JAŹWA¹, Anna PIETRANIK¹

¹ University of Wrocław, Institute of Geological Sciences, ul Cybulskiego 30, 50-205 Wrocław, Poland; aleksandra.jazwa@ing.uni.wroc.pl

Studies of crystal size distribution (CSD) can reveal the cooling histories of igneous rocks; in detail, they provide an insight into the variations in nucleation and growth rates with time. In basaltic rocks, CSD measurements of olivine phenocrysts can be used to reconstruct rates of magma crystallization from the onset of crystallization to the eruption. In this study, we calculate olivine CSD for basaltic rocks from Męcinka (SW Poland).

The basaltic rocks occurring in the vicinity of Męcinka belong to the Central European Volcanic Province extending from the Eifel Mts in Germany through the Czech Republic to Lower Silesia and the Opole Region. Volcanic activity began at the turn of the Eocene and Oligocene and lasted up to early Miocene. The basalt from Męcinka is exposed in a quarry as two lava flows interbedded with tuffs. Two types of basaltoids, differing in chemical composition occur, i.e., basalt and basanite. Both have similar mineral compositions. The matrix consists of plagioclase, diopside, Ti magnetite/ilmenite, nepheline and glass. Olivine, and rarely clinopyroxene, occur as phenocrysts. The olivine is characterized by variable degree of alteration.

The sizes of olivine phenocrysts were measured in thin sections of the Męcinka basalt. The crystal sizes were plotted against population densities. Generally, all CSD in the plots are characterized by relatively flat slopes for the largest crystals which progressively steepen towards smaller crystal sizes. This is consistent with long residence times and the slow crystallization of the largest phenocrysts. Two types of patterns with different slopes are seen for the smallest crystal fraction. One group of rocks is characterized by a steep slope which reflects both strong fractionation and short residence time. In the second group, a much flatter slope indicates slower crystallization. The difference between the two probably reflects different cooling times after eruption. Both groups probably represent different stages of eruption or different lava flows.

This preliminary results reveal different crystallization regimes in the basaltic rocks from Męcinka. Further study is necessary to address the dynamics of the magmatic system.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Preliminary study of the mineralogical and chemical composition of soils from Agnes Mine (Mpumalanga Province, South Africa)

Irena JERZYKOWSKA¹, Jolanta MESJASZ-PRZYBYŁOWICZ², Marek MICHALIK¹

¹ Jagiellonian University, Institute of Geological Sciences, Oleandry 2a, 30-063 Kraków, Poland; irena.jerzykowska@uj.edu.pl

² iThemba LABS, PO Box 722, Somerset West 7129, South Africa

The aim of the study was to determine the chemical and mineral composition of soils from an area covered by Ni-hyperaccumulating plants and to compare the results with previous studies. This work is a part of research concerning heavy-metal distribution and availability in soils. Five soil samples were collected (from a depth of ca 10 cm) near the Agnes Mine in Mpumalanga Province, the Republic of South Africa. The soils are formed on rocks of the Onverwacht Group in the Barberton Greenstone Belt. Soils in this area are shallow and rich in rock fragments. The bedrock is ultrabasic in composition (SiO₂ < 45 wt% and MgO > 30 wt%).

Soil samples and bedrock fragments were analyzed using optical microscopy, scanning electron microscopy with EDS and X-ray powder diffraction. Chemical composition was determined using IPC MS and ICP AES.

The analyzed bedrock fragments are serpentinite with a macroscopically visible weathering rim. The unweathered part of the rock is composed of rounded massive- and vein-shaped serpentine aggregates comprising serpentine that has a light brownish colour in thin section. The rock also contains chromite and Fe oxides. The weathered rim is porous and the constituent serpentines are colourless in thin section and have very variable crystal shapes. The serpentines are enriched in Fe and, in some cases, contain Cr and Ni. Cr and Ni also occur in Fe oxides. The weathered part of rock is cut by veinlets rich in Mn, Cr, Co, Ni and Fe. The soils examined are strongly enriched in MgO and depleted in SiO₂. Mean Mg/Ca is 3.22 - typical for "ultramafic soils" (> 2.5 according to McCallum, 2007). The soils have high contents of Cr (472.1-5521 ppm) and Ni (676-2525 ppm). Ni and Cr values correlate positively with Fe₂O₃ and negatively with SiO₂ in all samples. The mineral composition of the soils is very diverse. They are rich in quartz, amphibole, talc, albite, serpentine, mica and clay minerals suggesting bedrock heterogeneity (ultramafic and rocks rich in quartz). It is also possible that the quartz is allogenic (likely aeolian).

All of the soils studied have a chemical composition typical for ultramafic rocks, but mineralogical diversity probably indicates bedrock heterogeneity. For a better understanding of the weathering processes, and of the heavy metal distribution in the soils, a more detailed examination of the bedrock is needed.

McCALLUM D. A., 2007: The Ultramafic Soils of Swaziland in: Diversity and Conservation of Ultramafic Flora in Swaziland. http://hdl.handle.net/123456789/2056, 6-23.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Variety of alterations in gruses from Miłków, Karkonosze Mts.

Bartłomiej KAJDAS¹, Marek MICHALIK¹, Monika KASINA¹

¹ Institute of Geological Science, Jagiellonian University, Oleandry 2a, 30-063 Kraków; bartlomiej.kajdas@uj.edu.pl

The outcrop in Miłków is located in the Eastern part of the Karkonosze granite massif (SW Poland) at the bottom of Straconka hill. It is one of the biggest outcrops of grusified Karkonosze granite in the Jelenia Góra basin.

The variety of secondary minerals (chlorite, sulphides, epidote, prehnite, and fluorite) indicates that the whole volume of granite in the outcrop is hydrothermally altered. Three types of hydrothermally altered granites were distinguished: Ca-rich granite in the northern part of outcrop (group I), and two low-Ca granites types with and without K-feldspars (group II and III respectively).

The main differences between altered and unaltered granites relate to the mineral composition. Differences in the chemical compositions of unaltered- and altered granite are negligible.

Newly-formed phyllosilicates in the gruses were determined using X-ray diffraction. The main clay mineral in every grus sample is vermiculite (10Å after K saturation, about 14.5Å after Mg saturation and collapsing to 10Å at 330°C). In every sample, there is a small amount of kaolinite (7Å, collapsing at 550°C) and mica (10Å). In samples StrG-1 and StrG-2, a small amount of a swelling mineral (about 19Å after glycerol saturation, collapsing to 10Å at 330°C) is present.

The products of alteration of the granites in Miłków correspond to the definition of grus proposed by Migoń and Thomas (2002). The content of silt + clay fraction is even lower than in the definition (no more than 5 wt%). The chemical composition of the altered rock is rather stable and similar to unaltered granite. The chemical Index of Alteration (Nesbit, Young 1989) for the grusses is about 55-58. The main mineral formed during the grusification process is vermiculite. Kaolinite and mica crystallized in limited amounts. In addition to the clay minerals, iron oxides are present in grusified granite.

Development of grus within granite may be related to the activity of hydrothermal fluids as suggested by Evans and Bothner (1993), but not to weathering processes. The variety of hydrothermal minerals (e.g., vermiculite of high crystallinity, epidote, chlorite, prehnite, fluorite, pyrite and chalcopyrite) may support this assumption.

References:

EVANS C.V., BOTHNER W.A., 1993: Genesis of altered Conway Granite (grus) in New Hampshire, USA. Geoderma 58, 201-218.

MIGON P., THOMAS M.F., 2002: Grus weathering mantles – problems of interpretation. Catena 49, 5-24.

NESBITT, H.W., YOUNG, G.M., 1989: Formation and diagenesis of weathering profiles. Journal of Geology 97, 129–147.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Marshite – copper iodite from Miedzianka in the Holy Cross Mts

Łukasz KARWOWSKI¹

¹ Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec, Poland

A mineral sample, most probably representing rock from the lithological junction between Devonian carbonate and Triassic sandstone, was found while collecting Cu-rich ore samples in the Miedzianka mine near Chęciny. The sample was found on a local heap of ore sited on the west area of Miedzianka Mt.

The fine-grained, greenish lump has a sandy texture and is heavy. Optical investigation (reflected light) exposed a cuprite cement together with a native copper association. The presence of these minerals is responsible for the high density of the sample. The marginal parts of the sample are covered by malachite. Terrigenic material is represented dominantly by quartz, plagioclase (albite, oligoclase), K-feldspar as well as elongated clay mineral aggregates. The clastic mineral fraction is in the range from 0.15-0.0 mm.

In the cuprite grains, a new mineral phase occurs, usually in the marginal parts. The mineral is characterized by a lower reflectivity than cuprite and show internal yellowish-brownish or yellowish-pinkish reflections. BSE images reveal that the mineral is relatively lighter than cuprite and native copper. This is evidence for the occurrence of other higher relative atomic mass atoms than oxygen and copper. EMP analyses reveal that the main component besides copper is iodine; the concentrations of Cu range up to 33.35 wt% and those of I up to 66.64 wt%, respectively. The chemical composition confirms that the mineral is marshite (CuI).

The presence of marshite in association with secondary Cu-bearing mineralization in the Miedzianka area is unexpected. Up to now, the occurrence of halogens in association with primary and secondary mineral phases has not been reported from the Miedzianka deposits. The iodine origin may reflect the influence of Mesozoic sea regressions.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE

HE TOWARD ST

Phosphates in the Morasko meteorite

Łukasz KARWOWSKI¹, Andrzej MUSZYŃSKI², Ryszard KRYZA³, Katarzyna HELIOS⁴

¹ Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec, Poland

² Institute of Geology, Adam Mickiewicz University, ul. Maków Polnych 16, 60-606 Poznań, Poland

³ Institute of Geological Sciences, University of Wrocław ,ul. Cybulskiego 30, 50-205 Wrocław, Poland

⁴ Faculty of Chemistry, Wrocław University of Technology, Smoluchowskiego23, 50-370 Wrocław, Poland

In earlier literature, a range of Na, Mg, Ca, and Fe phosphates have been reported from the iron meteorites of the IAB group. In the Morasko-type meteorites of that group (Morasko, Seelasgen, Jankowo Dolne), troilite-graphite nodules are common. Silicate phases, such as winonaite, as well as oxides and, more rarely, phosphates are found in these nodules. Around some of the nodules, small aggregates (micronodules), up to 1.5 mm in diameter, can be found; they are mostly filled with anhydrous phosphates (Fig. 1). In the Morasko-type meteorites, we have identified the following phosphates: merrillite Na – $Ca_{18}Na_2Mg_2(PO_4)_{14}$, buchwaldite – NaCaPO₄, brianite – Na₂CaMg(PO₄)₂, and apatite. Buchwaldite usually occurs in the troilite-graphite nodules that are rich in silicates (albite, antiperthite, K-feldspar, diopside, kosmochlor, kosmochlor-augite, olivine and an unidentified SiO₂ phase). Locally, it is associated with a minor, also unidentified, phosphate phase of approximate formula NaFe²⁺PO₄.



Fig. 1. Phosphate micronodule in cohenite (coh) composed of graphite (graph), merrillite (merrill), apatite (ap), brianite (bria) and the new phosphate phase (nph) of formula $Na_4Ca_3Mg(PO_4)_4$

Around the troilite-graphite nodules, within cohenite-schreibersite mantles or in kamacite grains, there occur fairly large phosphate micronodules containing merrillite, brianite, apatite, and a new phosphate phase of the following formula: $Na_4Ca_3Mg(PO_4)_4$ (Fig. 1).

The phosphate nodules in the Morasko-type meteorites provide a unique natural object for crystallochemical and structural studies on rare phosphate minerals (including phases unknown to date). Preliminary results indicate that merrillite, brianite and the new phosphate phase contain significant amounts of MnO and FeO, and that the merrillite typically has an admixture of K_2O up to 0.1 wt%. Raman spectra confirm that the new phosphate has not been reported to date and that it can be considered as a candidate for recognition as a new mineral.

Acknowledgement: The study was supported by Project MNiSzW no. N N307 3533 33.

MINERALOGIA - SPECIAL PAPERS, 35, 2009 www.Mineralogia.pl MINERALOGICAL SOCIETY OF POLAND

POLSKIE TOWARZYSTWO MINERALOGICZNE



Mineral and chemical composition of slags – mobilization of elements

Monika KASINA¹, Marek MICHALIK¹, Bartłomiej KAJDAS¹

¹ Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2a, 30-063 Kraków, monika.kasina@uj.edu.pl, marek.michalik@uj.edu.pl

Slags from iron metallurgy (steel and blast furnace) are considered as important coproducts used in many fields of industry and civil-engineering. Slag is usually composed of high-temperature phases that are very reactive in the long term. They may contain harmful elements (e.g., Ni, Cu, Pb, Zn, Cr, As, Sb) that can be released into the environment during alteration or leaching processes.

The aim of the study was to determine the mineralogical and chemical composition of slag in various experimentally simulated chemical conditions. Stealmaking- and blast furnace slags, after different ageing periods, were investigated using a Soxhlet apparatus and the laboratory oven with the following solutions: distilled water (A), H₂O+NaCl (B), H₂O+CaSO₄·2H₂O (C), H₂O+MgCl₂ (E) and humic acid alkali solution (D). After the experiments, the chemical- and mineral compositions of the slag samples were studied using XRD, SEM-EDS, ICP-MS, and ICP-OES analyses. Each sample of slag was treated under hydrothermal conditions for 24 h and 120 h (experiment D was processed also for 3 months). Samples of stealmaking slag are composed of calcium ferrites (srebrodolskite, brownmillerite), larnite, but also of other Ca-Fe-Mg-Mn oxides and silicates. The blast furnace slag is composed mainly of calcium silicates (melilites - akermanite and gehlenite, rankinite, pseudowollastonite). Small amounts of sulphur (> 3 wt%) are dispersed within the calcium silicates. After all the experiments, only a few new mineral phases such as merwinite, calcium magnesium iron silicates, gypsum and calcite were formed.

The presence of the main phases remained unchanged after the experiments, but differences in XRD peak intensities may suggest that some of the slag components were partly modified. The dispalcement of XRD peaks of main mineral phases after the experiments may suggests that, though their general chemical compositions have not been changed under the influence of different solutions, their structure could be rebuilt. New phases such as merwinite, calcium magnesium iron silicates, gypsum and calcite were formed. During treatment, leaching of some elements could increase the relative contents of others. Dissolution of the main mineral phases, without recrystallization (especially in the first stage of experiment - 24h) causes relative increases in the concentrations of other elements (e.g., Co, Pb, Zn, Cu) in the residue. The mobilization of potentially harmful elements, e.g., Co, Cu, Zn, Pb, Ni, As, Cr and others is not very advanced. The overall amount of toxic elements is very low in slag and these elements are probably bound within minerals which are not subjected to easy disintegration or dissolution. It is important to appreciate that the laboratory conditions are very different from natural conditions where slags are reactive under the influence of natural long-term processes.

Acknowledgement: This research was partially financed by IROP from the EU SF in Poland

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Weathering of a slag pile produced by the smelting of Zn ores in the Katowice-Wełnowiec smelter

Jakub KIERCZAK¹, Eliza ŁOZOWSKA¹, Piotr SZNAJDER¹

¹ University of Wrocław, Institute of Geological Sciences, ul Cybulskiego 30, 50-205 Wrocław, Poland; jakub.kierczak@ing.uni.wroc.pl

Mining and smelting activities left large quantities of waste accumulated as dumps covering vast surfaces at former industrial sites of Eastern and Central Europe. Among these areas, Upper Silesia is known as a region highly polluted by heavy metals. Dumps located in Upper Silesia consist of a variety of waste materials such as barren rocks, flotation tailings and pyrometallurgical slags.

We studied pyrometallurgical slags formed during reworking of Zn-Pb ores in the former smelter located in Katowice-Wełnowiec. The objective of this study was to assess the potential environmental risk related to those wastes using mineralogical and geochemical methods.

Two main types of slag material occur at the dump in Katowice-Wełnowiec. The first is a heavy and massive slag. The second is a lighter and heavily porous slag with numerous macroscopic ellipsoidal vesicles (scoria). The chemical composition of the studied materials is dominated by SiO₂, FeO, CaO, Al₂O₃ and MgO. Some slags also contain high concentrations of Zn (< 12 wt% ZnO) and Pb (< 0.3 wt% of PbO). Primary phases identified in the materials are: melilite, pyroxene, feldspar, olivine, willemite and spinels. Most of the Zn is incorporated in willemite (< 51 wt% ZnO) and gahnite (< 33 wt% ZnO). Lead occurs mainly as Pb-Sn alloy (68 wt% PbO) but it is also present in Pb-silicate (< 42 wt% PbO). Secondary phases formed due to weathering are common at the dump and include efflorescences and encrustations of gypsum, calcite, aragonite and accumulations of jarosite, zincite, hydrozincite and Fe-oxy, hydroxides. The formation of a large variety of secondary phases (sulfates, Fe-oxy, hydroxides and carbonates) indicates dynamic changes in pH values. Zincite is the most important Zn-bearing phase and it is also the most sensitive to weathering. Low pH values may cause dissolution of this phase and the release of Zn into the surroundings.

The presence of numerous secondary phases on the dump in Katowice-Wełnowiec shows that the slags are susceptible to weathering and release of metals. Zn is, in part, trapped in secondary phases and those are very sensitive to pH conditions, therefore the slags represent a significant environmental hazard.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Metamorphic evolution of phyllites from Podmąchocice in the Łysogóry Unit of the Holy Cross Mts. (SE Poland): preliminary data from K-white mica and chlorite investigations

Joanna KOSTYLEW¹, Sylwester SALWA²

¹ Institute of Geological Sciences, University of Wrocław, ul. Cybulskiego 30, 50-205 Wrocław, Poland; joanna.kostylew@ing.uni.wroc.pl

² Polish Geological Institute, Holy Cross Mountains Branch, ul. Zgoda 21, 25-953 Kielce, Poland; sylwester.salwa@pgi.gov.pl

The metamorphic evolution of Cambrian phyllites from the Łysogóry Unit in the Holy Cross (SE Poland) has not been studied in detail to date (Salwa, 2006). To highlight that fact, we present here preliminary data from K-white mica and chlorite investigations combined with structural observations. Analyses were carried on three representative phyllite samples from the Podmachocice (Łysogóry Unit).

The values of illite (KI) and chlorite (ChC) 'crystallinity' indexes suggest that the rocks have undergone very low-grade metamorphism, at temperatures approximately 150-250°C (late diagenetic zone-low anchizone). Data from microstructural observations (ductile folding of biotite blades, deformation lamellae in quartz and translational lamellae in dolomite blasts) indicate, on the contrary, higher epizonal temperatures ranging from 250-400°C (Salwa, 2006). Chlorite geothermometer data give the most diversified results, ranging from less than 100°C up to 350°C. The results were recalculated according to four different methods (Kranidiotis, MacLean, 1987; Cathelineau, 1988; Jowett, 1991; Xie et al., 1997; vide Xie et al., 1997). The values of the K-white mica *b* cell dimension are characteristic for low- to intermediate pressure conditions, which indicates rather shallow burial, as suggested by Salwa (2006).

Phyllites from Podmąchocice have undergone multistage deformation which caused intensive recrystallization of existing mineral phases and the formation of new minerals (Salwa, 2006). We believe that evidence for epizone conditions (structural observations, chlorite geothermometers) is connected with locally deformed zones, especially shear zones, where the influence of increasing p/T was extremely strong. Evidence for likely regional-scale, very low-grade metamorphism (KI/ChC values and K-white mica *b* cell dimension) is preserved mostly in the fine-grained matrix.

References:

- SALWA S., 2006: Wstępna charakterystyka strukturalno-petrograficzna fyllitów z Podmąchocic w regionie Łysogórskim Gór Świętokrzyskich (in Polish with English abstract). Przegląd Geologiczny, 54, 513-520.
- XIE X., BYERLY G.R., FERRELL R.E., Jr., 1997: IIb trioctahedral chlorite from the Barberton greenstone belt: crystal structure and rock composition constraints with implications to geothermometry. Contribution to Mineralogy and Petrology, 126, 275-291.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



New data on the internal structure of Pacific nodules (Clarion-Clipperton Zone)

Ryszard KOTLIŃSKI¹, Justyna CIESIELCZUK², Jerzy ŻABA², Sebastian WOJTYCZKA²

¹ Interoceanmetal Joint Organization, 9 Cyryla i Metodego, 71-541 Szczecin, Poland
² Faculty of Earth Sciences, University of Silesia, 60 Będzińska St., 41-200 Sosnowiec, Poland; justyna.ciesielczuk@.us.edu.pl

Nodules formed in the deep-sea basin of the Pacific Ocean (Clarion-Clipperton Zone) were investigated by optical- and scanning microscopes, XRD and microprobe. Two generations of the nodules can be distinguished on the basis of their size: (1) a generation of smaller nodules ranging in size up to 5 cm in diameter and (2) a generation of nodules larger than 6 cm. Two nodules were chosen for further investigation. Both comprise two parts: an internal part of similar size (ca $2.2 \times 1.2 \text{ cm}$) in both populations and an external, which is twice as thick in population (2). Polymetallic nodules are difficult to investigate as they are composed of tiny amorphous mineral phases which represent the initial stages of crystallization.

In the nodules, a concentric lamination is visible even with the naked eyes. This lamination is perfectly seen using the scanning microscope where details of the structure and its chemistry can be checked with EDS. The aim of this study was to identify differences and similarities in the chemical, mineralogical and structural composition within the interiors of the nodules of the two generations.

A single nodule is composed of thousands of local, small, incipient "microconcretions". Analyzing the BSE images, many of these reveal microlamination with laminae ranging in thickness from < 1 -10 µm. They are called "*laced layers*". They are composed mainly of MnO (ca 90-100%) with little or no FeO (ca 10-0%). There is an exception – the outermost 80 µm thick nodule'layer is enriched in FeO (ca 20-30%). Apart from "*laced layers*", non-laminated areas ranging in size up to 25 µm are distinctive in that they differ in chemical composition. They are enriched in FeO (<40-50%).

Apart from iron and manganese, some trace elements, e.g., Ni, Co and Cu were detected. Cu appears in pure manganese laminae, but no interdependence was noted between lamination and the presence or quantity of Ni and Co. What is interesting is the fact that the lamination visible in BSE images is caused by the presence of carbon, probably of organic origin, accompanied by Cl and S.

Nodules contain tiny minerals of detrital origin, e.g., quartz, K-feldspars, Ca-Nafeldspars, albite and organic apatite. These are located between the micronodules, appearing to have been caught during nodule growth. The internal parts of the micronodules were expected to contain some nuclei but, in fact, any detrital particles occur in between the micronodules. Clearly, the micronodule nuclei are not detrital particles; the nuclei were probably microorganisms which are not preserved.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The Barzaman Formation in the UAE - an example of intensive alteration of ultramafic and mafic rocks in the near surface environment

Alicja ŁACIŃSKA¹, Mike STYLES¹

¹ British Geological Survey, Kingsley Dunham Centre, Keyworth, Nottingham, United Kingdom NG12 5GG alci@bgs.ac.uk, mts@bgs.ac.uk

The Barzaman Formation in the UAE comprises a series of matrix supported to locally clasts supported, polymict alluvial conglomerates. The Formation is widely exposed on the western edge of the Hajar Mountains that are a part of the large and well known Oman-UAE ophiolite.

The Formation was deposited as an ophiolite-derived conglomerate with a serpentinite and harzburgite matrix of sand, silt and clay grade constituents. It formed during a heavy, possibly seasonal rainfall that resulted in viscous, slurry-like, rapid mass movement, of diverse grain size that are called debris flows. The Formation is now typically strongly dolomite cemented and therefore stands proud as resistant outcrops of the alluvial fans that overlie a sequence of intensively altered ophiolite mantle rocks. There is a very distinctive lithological sequence below the contact, which comprises from the top downwards: silicified and carbonated serpentinite, carbonate-veined serpentinite and carbonate-veined partially serpentinised peridotite that passes downwards into the normal partially serpentinised peridotite. These units are the main source of the clasts for the Barzaman Formation. The most common lithology of the Barzaman Formation is poorly sorted, cobble to boulder conglomerate with clasts largely of harzburgite, serpentinite, silicified serpentinite, gabbro and a minor amount of metamorphic rocks, which are other components of the ophiolite thrust stack. They are cemented by dense, hard, weatheringresistant dolomite, which has precipitated from phreatic and locally vadose groundwater. A petrographical study using optical and scanning electron microscopy revealed that the cementation was preferential and it involved, firstly the complete replacement of the serpentinite and harzburgite sand and silt matrix and simultaneously or subsequently it strongly affected clasts. Both, physical erosion of clasts during transportation and exposure to various weathering conditions as well as extensive groundwater-rock interaction during diagenesis contributed to the presence of highly altered ophiolitic clasts. The mechanical erosion has created fractures and areas of enhanced weaknesses that were subsequently penetrated by groundwater leading to zonal and concentric dolomitization of clasts.

The partial dissolution of silicate minerals locally resulted in simultaneous precipitation of clay minerals and/or Fe oxides/hydroxides, leaving a ghost texture as evidence of the presence of former clasts. Clasts with diverse original composition show distinctively different alteration patterns. The susceptibility to dissolution and subsequent dolomitization of ultramafic and mafic clasts is suggested as follows: harzburgite and serpentinite are the most susceptible followed by gabbro with intermediate susceptibility, and silicified serpentinite as the least prone to alteration.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Evidence of the c. 650Ma Torellian Orogeny in SW Svalbard inferred from monazite and zircon dating

Jarosław MAJKA¹, Jerzy CZERNY², David G. GEE¹

 ¹ Uppsala University, Department of Earth Sciences, Villavägen 16, SE-752b36, Uppsala, Sweden; jaroslaw.majka@geo.uu.se
² AGH - University of Science and Technology, Faculty of Geology, Geophysics and Environment Protection,

² AGH - University of Science and Technology, Faculty of Geology, Geophysics and Environment Protection, al. Mickiewicza 30, 30-059 Kraków, Poland

The Caledonides of southwestern Spitsbergen (Wedel Jarlsberg Land) consist of Mesoto Neoproterozoic metamorphic rocks of the Isbjørnhamna, Eimfjellet, Magnethøgda and Deilegga Groups, overlain unconformably by the lower grade Neoproterozoic Sofiebogen Group, Vendian diamictites and Cambro-Ordovician formations. The Slyngfjellet conglomerates at the base of the Sofiebogen Group mark the regional scale Torellian unconformity, described by Birkenmajer in 1975.

The age of the Torellian deformation event has been much discussed previously by various authors who have claimed it to be either of early Neoproterozoic (late Grenvillian) or late Neoproterozoic age. The younger age was based on K-Ar dating of biotites from the 1960's and some structural observations; it was regarded by many authors as an unreliable cooling age.

Our recent dating of metamorphic and detrital monazite and zircon, from different lithostratigraphic units, provides strong evidence in favour of the late Neoproterozoic timing of the Torellian deformation. The amphibolite facies rocks of the Isbjørnhamna Group have yielded monazite metamorphic ages of 640-660Ma, similar to metamorphic zircons in the Magnethøgda Group. The less metamorphosed metasediments of the Deilegga Group show a spectrum of detrital monazite ages from Archean through Svecofennian to Grenvillian, and two Caledonian metamorphic maxima. The overlying Slyngfjellet conglomerate (Sofiebogen Group) shows a similar spectrum of detrital monazites and, in addition, a prominent maximum at c. 650Ma. These younger monazites are well rounded grains, with Caledonian overgrowths; they are unambiguously detrital in origin.

The new data indicate the importance of the Torellian unconformity in the Caledonides of southwestern Svalbard. The Torellian Orogeny of Wedel Jarlsberg Land occurred at c. 650Ma, simultaneously with the deposition of Neoproterozoic shallow marine successions in areas now located farther to the northeast on Svalbard (Nordaustlandet) and emphasizing the differences in the tectonic histories of these terranes.

Acknowledgements: This research was supported by the Polish research project, N30704231/3336 MNiSzW, and a Swedish polar research grant from the Ymer-80 Foundation. J. Majka was also supported by the Swedish Institute, Visby Programme.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Crustal growth and crustal recycling in the Neoproterozoic Torellian Orogen, SW Svalbard: U/Pb zircon geochronology and Hf isotopic characteristics

Jarosław MAJKA¹, Anna LADENBERGER^{1,2}, Nikolay KUZNETSOV³

¹ Uppsala University, Department of Earth Sciences, Villavägen 16, SE-752 36, Uppsala, Sweden; jaroslaw.majka@geo.uu.se

² Geological Survey of Sweden, Villavägen 18, SE-751 28 Uppsala, Sweden

³ Geological Institute, Russian Academy of Sciences, Pyzhevsky 7, 119017 Moscow, Russia

Detrital zircon dating and Hf isotopes were obtained from Gulliksenfjellet Fm. quartzites occurring within the SW Spitsbergen Pre-Devonian crystalline basement. U-Pb dating reveals 2 main groups of ages: between c. 1.7-2.05 Ga and c. 2.4-2.84 Ga.

The wide range of measured Th/U ratios in the zircons indicates a predominantly igneous source. According to the Classification and Regression Tree (CART), most of grains originate from granitoids with minor contributions from mafic rocks.

Hf isotopes show that more than 50% of the analyzed zircons have positive ϵ_{Hf} values, indicating a significant contribution of mantle-derived material in their origin. The granitic source of these rocks indicates an igneous juvenile origin for the crust (I-type magmatism) at that time without large-scale recycling and contribution of S-type granites. The widest range of ϵ_{Hf} values is seen in the population of zircons with ages 1.7-2.05 Ga, suggesting contributions from different sources (igneous and recycled). Low initial ϵ_{Hf} indicative of recycled old crust can be observed especially in 1.7 Ga Late Paleoproterozoic populations, in 2.0 Ga (Middle Paleoproterozoic) and 2.5 Ga (Early Paleoproterozoic and Neoarchean) zircon populations. This is in good agreement with Rohr et al. (2007) who reported similar trends in zircons from Cretaceous sediments in N Greenland and E Svalbard.

Zircons with ages between 2.5–2.7 Ga form a chain of recycled material for crustal values of ¹⁷⁶Lu/¹⁷⁷Hf ratios and with model age only c. 100-200 Ma older (c. 2.9 Ga) than their crystallization ages, indicating rather short crustal residence times. 2.7 Ga zircons with lower ϵ_{Hf} represent mostly recycled or remelted Archean material. Two zircons with very low ϵ_{Hf} (-14 and -8.2, respectively) and ages of 2440 Ma and 2788 Ma, lie on the crustal growth curve (¹⁷⁶Lu/¹⁷⁷Hf=0.014) with model ages of 3500 Ma, which may point to the oldest recycled source material in the area – ancient continental crust.

The events recorded by the 1.7-2.05 zircon population Ga may be related to Svecofennian orogeny. The 2.5-2.7 Ga ages are linked to the assembly of cratons, one of the major tectonic events during Earth's crust evolution (Griffin et al. 2004).

Acknowledgements: We are grateful to L.Natapov and E.A. Belousova (GEMOC Center, Macquarie University) who conducted isotopic and geochemical studies. This research was supported by a Swedish polar research grant from the Ymer-80 Foundation and RFBR (projects N 09-05-00812 and 09-05-01033) and Program N16 of Presidium RAS. J. Majka was also supported by the Swedish Institute, Visby Programme.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Mineralogy and geochemistry of pyrite ores from the Staszic mine at Rudki, the Holy Cross Mountains, Poland

Krzysztof NEJBERT¹, Paweł KRÓL², Rafał WIECZOREK¹

¹ University of Warsaw, Institute of Geochemistry, Mineralogy and Petrology, Al. Żwirki i Wigury 93, PL-02-089 Warszawa; Poland; knejbert@uw.edu.pl

² National Museum in Kielce, pl. Zamkowy 1, PL-25-010 Kielce; Poland; p.krol@mnki.pl

The abandoned Staszic Mine at Rudki, where pyrite and hematite-siderite ores have been exploited, is located in the main range of the Holy Cross Mountains, in the vicinity of Nowa Słupia. The pyrite deposit was discovered in 1922 by J. Samsonowicz, although weathered gossan ores have been mined there in Roman times. This deposit occurs in a tectonic zone associated with a N–S-striking dextral strike-slip fault (Łysogóry Fault) dipping 45-60° E. The lens-like shape of the deposit is determined by the geometry of the fault zone. The ore body is from 0.3-40 m in thickness, and extends laterally on a distance of about 600 m. It is documented to a depth of 800 m. Pyrite, siderite and a small amount of hematite ores were exploited between 1925-1971. Up to 5.5×10^6 tons of pyrite ores were mined during 46 years of exploitation.

The geometry of ore body, and the ore textures, the mineralogy, and the ore grades have been described in many papers (Kuźniar, 1933; Czarnocki, 1950; Jaskólski et al., 1953; Nieć, 1968; Szecówka, 1987). This presentation summarises all the existing data related to sulphide mineralization in the Staszic Mine at Rudki and presents the results of new EPMA and XRD studies. The investigated materials comprise samples collected by the authors from the remains of the old dumps at Rudki, and specimens hosted in the collections of the National Museum in Kielce and the University of Warsaw.

The pyrite ores, occurring mainly within dolomite and/or within black clays filling in the fault zone, are of three textural types: loose fine-grained pyrite, massive pyrite, and disseminated pyrite. The mineralogy of the pyrite ores is rather simple. They consist of marcasite and pyrite, both forming complex intergrowths with siderite. Under the reflectedlight microscope, sulphide-siderite intergrowths and aggregates show disseminated-, colomorphic- and/or crustified textures. Goethite, galena, sphalerite, chalcopyrite, covellite, tennantite, and uraninite are very rare or subordinate components of the ores. In some samples of massive pyrite and pyrite disseminated within dolomite matrix, significant amounts of Se-galena were recognised. Se-galena forms fine-grained aggregates apparently cementing earlier pyrite and marcasite grains.

The pyrite and marcasite show chemical compositions close to the stoichiometric formula. In all of the samples, significant amounts of As (from 102-339 ppm) were detected. Increased amounts of Ag (266-543 ppm), Co (162-452 ppm) and Ga (135-173 ppm) were recorded in some pyrite grains. Siderite is characterised by high amount of Mn, Mg and Ca; its chemical formula is close to $Fe_{78.79-92.08}Mn_{4.00-14.23}Mg_{1.17-3.08}Ca_{1.544.04}CO_3$. The MnO, MgO, and CaO contents in siderite vary between 2.46-8.78 wt%, 0.56-1.47 wt%, and 0.86-2.26 wt%, respectively. Se contents in the galena range from 5.83-14.43 wt%.

References

CZARNOCKI J., 1950: Geologia regionu łysogórskiego w związku z zagadnieniem złoża rud żelaza w Rudkach. Prace PIG, do użytku służbowego, 1-404.

- JASKÓLSKI S., POBORSKI C., GOERLICH E., 1953: Złoże pirytu i rud żelaznych kopalni Staszic w Górach Świętokrzyskich. Biuletyn Instytutu Geologicznego, do użytku służbowego, 1-120.
- KUŹNIAR C., 1933: Złoże syderytu i pirytu w Rudkach pod Nową Słupią. Pos. Nauk. Państw. Inst. Geol., 37, 6-8.
- NIEĆ M., 1968: Mineralizacja złoża siarczków żelaza I syderytu w Rudkach w Górach Świętokrzyskich. Prace Geologiczne PAN, 46, 1-81.
- SAMSONOWICZ J., 1922: O złożu hematytu w Rudkach pod Nową Słupią. Pos. Nauk. Państw. Inst. Geol., 4, 9-11.
- SZECÓWKA M., 1987: Mineralizacja uranowa w Rudkach koło Słupi Nowej (Góry Świętokrzyskie). Prace Geologiczne, 133, 1-69.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



New data on the Cenozoic basanite from Wołek Hill, Kaczawa Mountains, SW Poland

Monika NOWAK¹, Andrzej MUSZYŃSKI¹

¹ Institute of Geology, Adam Mickiewicz University, 61-606 Poznań, Ul. Maków Polnych 16; mnap@amu.edu.pl, anmu@amu.edu.pl

Wołek Hill is situated about 100 km south-west from Wrocław and 8 km south from Złotoryja. Multiphase volcanic activity in this area is represented by Permian trachyandesites and rhyolites which are cross-cut by a small body of Cenozoic volcanites. The best outcrop of the latter rocks is located in an abandoned quarry on the south-eastern slope of the hill. The main body is about 20 m wide and 15 m high. New mineralogical, geochemical, and isotopic data on those rocks are presented.

The studied rock was first classified as ankaratrite (Juroszek, 1985), and later as picrobasalt. Based on the new data from the whole-rock ICP-MS analyses, the rock should be reclassified as basanite.

The Wołek Hill basanite is a dark grey rock containing a large quantity of xenoliths. Recent observations reveal that it also includes rare amphibole (pargasite) megacrysts (ca 3-6 cm). The basanite texture is porphyritic to glomeroporphyritic. Olivine and clinopyroxene occur as phenocrysts. There are three types of olivine phenocrysts with differences in zonation patterns reflecting Fo content (Fo₈₂₋₉₁). There are also olivine xenocrysts with Fo ca 91%. The clinopyroxenes occur as diopside phenocrysts and are also the dominant phase in the groundmass. They show zonation with increasing Al, Ti, Fe, Ca and decreasing Si, Mg, Cr from core to rim.

The basanites from Wołek Hill are primitive mafic rocks with SiO₂ contents ca 44 wt%, MgO >7 wt%, Na₂O+K₂O ca 5 wt%, and TiO₂ ca 3 wt%. Incompatible trace elements normalized to primitive mantle show negative K, P, Rb anomalies and positive Cs, Pb, Nd anomalies. The negative K anomalies can be related with the presence of residual amphibole in the magma source (Jung et al. 2006 fide Lustrino, Wilson 2007). The Zr, Y and Nb contents are typical for intra-plate tectonic settings.

In two basanite samples strontium and neodymium ratios were measured by TIMS. The isotopic ratios from the Wołek Hill basanites have analogical values to the other Bohemian Massif localities (Ladenberger et al. 2004; Lustrino, Wilson 2007).

References:

- JUROSZEK C., 1985: Petrographic characteristics of melanocratic basaltic rock from Różana (Kaczawa Mountains) (in Polish) Kwartalnik Geologiczny 29, 713-726.
- LANDENBERGER A., PEATE D.W, TOMEK C., MICHALIK M., 2004: Isotopic characteristics of volcanic rocks from southwestern Poland and neighbouring areas in Czech Republic and Germany. Mineralogia Polonica Special Papers 24, 263-266.
- LUSTRINO M., WILSON M. 2007: The circum-Mediterranean anorogenic Cenozoic igneous province. Earth-Science Reviews 81, 1-65.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Peridotite xenoliths in basanites from Wołek Hill, Kaczawskie Mts., SW Poland - petrological data vs microstructural observations

Monika NOWAK¹, Wojciech STAWIKOWSKI¹

¹ Institute of Geology, Adam Mickiewicz University, 61-606 Poznań, ul. Maków Polnych 16 mnap@amu.edu.pl, wojst@amu.edu.pl

About 300 occurrences of Cenozoic volcanic rocks belonging to the Central European Volcanic Province are known in Lower Silesia (SW Poland). Some of them, like basanites from Wołek Hill near Różana, Kaczawskie Mts., are characterized by the high abundance of mantle xenoliths.

Eight xenoliths with variable fabrics were chosen for a petrological and microstructural investigation. They are mainly spinel harzburgites; two are spinel harzburgites rich in Cpx. The main xenolith minerals are: olivine (Ol) with Fo ca 91-92%; orthopyroxene (Opx) – En_{90-92} ; at least two generations of clinopyroxene (Cpx) (diopside, the secondary Di richer in Cr and Al) and spinel with Cr number from 44 to 69, reaching >75 for a few crystals.

The Wołek harzburgites reveal, under the microscope, a diversity of textures routinely identified in peridotites, ranging from protogranular (coarse) through porphyroclastic to granuloblastic. The majority of the samples are transitional between these various pure types. Although the studied ultrabasites more commonly display a rather random fabric, some show a discernible microstructural anisotropy expressed by the presence of aligned fine-grained olivine concentrations or by the elongate shapes of Ol grains (SPO). Those features are best seen in samples with textures close to granuloblastic. The crystals in the peridotites bear evidence of moderate deformation. Apart from common undulose extinction both in Ol and Opx, the larger Ol grains often contain deformation bands. The smaller blasts commonly lack these internal structures and often group in polygonal aggregates. Additionally, in the porphyroclastic types, small neoblasts possibly resulting from subgrain recrystallization can be observed at the margins of the large Ol crystals.

To establish the crystallographic fabrics of the Wołek peridotites (potential lattice preferred orientation, LPO) and to compare its intensity in different textural types, U-stage measurements were conducted (70-220 crystals per sample). The results reveal regularities in the orientations of the olivine axes in all samples – even those optically apparently random. The distributions of axes measurements often concentrate into distinct fields – point maxima or girdle-like patterns. The degree of preferred orientation is consistent with the textural diversity of the studied xenoltihs; the strongest LPO occurs in the granuloblastic samples.

Thermobarometric calculations based on the compositions of Opx or Opx-Cpx pairs gave results which, in several cases, correlate with the textural variabality. For the assumed P=15 kbar, the protogranular harzburgite gave a T in range of 1000-1150°C, while the granuloblastic xenoliths a distinctly lower T (av. 830-870°C). All temperatures, however, may be influenced by metasomatic changes or postmagmatic alternations in host basanites. The research was partly supported by the MNiSW grant no NN 307 040736.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Mixing, mingling or subsolidus interactions: which were important in the Gęsiniec intrusion?

Anna PIETRANIK¹

¹University of Wrocław, Institute of Geological Sciences, pl. Borna 9, 50-204 Wrocław, Poland; anna.pietranik@ing.uni.wroc.pl

Dioritic and granodioritic rocks coexisting in the Gęsiniec Intrusion in SW Poland show relationships that are typical of many mafic-felsic mingling zones worldwide, e.g., dioritic syn-plutonic dykes and microgranular enclaves hosted in granodiorite (Pietranik, Koepke, 2009). Ten samples from such a mingling zone were chosen for this study. They include massive diorite and granodiorite which were not affected by interaction with each other and a range of enclaves showing different degrees of interaction.

Massive diorites and enclaves show SiO_2 and MgO contents that are often linearly correlated with other major and trace elements. Granodiorites generally have lower MgO, FeO, TiO2, P2O5, Ni, Cr, Y, V, Sc, Nb, Ta and HREE and higher SiO2 and Th contents than the diorites. The dioritic compositions trend, more or less linearly, towards granodioritic compositions for these elements, indicating simple mixing relationships between diorites, enclaves and granodiorites. Plagioclase composition (%An, %Or and Sr content) was analyzed to check if it supports a mixing scenario.

Plagioclase zonation from granodioritic rocks suggests late-stage mixing probably with dioritic magma, whereas no magma mixing is recorded in plagioclase from dioritic rocks. Compositional zoning patterns in diorite plagioclases can be modeled by closed system fractional crystallization interrupted by resorption induced probably by decompression. The variations in chemical compositon in the diorites and enclaves seem to show effects of interaction with evolved, leucocratic melts derived from granodiorite, not with the granodioritic melt itself.

References:

PIETRANIK A., KOEPKE J. 2009: Interactions between dioritic and granodioritic magmas in mingling zones: plagioclase record of mixing, mingling and subsolidus interactions in the Gęsiniec Intrusion, NE Bohemian Massif, SW Poland. Contributions to Mineralogy and Petrology 158 (1): 17-36.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Preliminary geochemical and mineralogical data on Lower Carboniferous tuffites from Kowala near Kielce (Holy Cross Mountains, Poland)

Maria RACKA¹, Grażyna BZOWSKA¹

¹Faculty of Earth Sciences, University of Silesia, Będzińska Str. 60, 41-200 Sosnowiec, Poland (maria.racka@us.edu.pl)

The pyroclastic-rich clay-carbonate Lower Carboniferous succession was exposed in two trenches dug close to the northern border of the active Kowala quarry in 2000 and 2001. Two of the most distinct layers of tuffite were investigated. Tuffite A from the first trench, 40 cm thick, belongs to the Radlin Beds. Tuffite B from the second trench, ranges up to 60 cm thick and occurs ca 13 m higher in the section, in the basal part of black shaly-siliceous Zaręby Beds.

Mineralogical investigations were carried out by XRD and geochemical data were obtained by ICP, INAA and XRF methods. All samples (15 from the first trench and 5 from the second one) were studied by X-ray diffraction. Four samples from the first trench (2 of tuffite A and 2 of the directly adjacent claystones) and two samples of tuffite B were analysed for major and trace elements.

The mineral composition of both tuffite layers is similar and dominated by smectite with illite/smectite mixed-layer, sanidine and quartz. The amorphic matter content is 25%. Among the accessory components, anatase and apatite were identified.

The tuffites differ in their chemical composition. Tuffite B is noticeable enriched in SiO₂, Al₂O₃, and slightly enriched in Fe₂O₃, K₂O, TiO₂ and P₂O₅ relative to tuffite A. Amongst trace elements, V, Sb, As, Pb, Zn, U, Mo and Nb are significantly enriched in tuffite B in comparison with tuffite A. The discrimination diagram SiO₂/Al₂O₃-TiO₂/Al₂O₃, that differentiates volcanogenic from detrital deposits, was used to verify that both tuffites derived from volcanic ashes. The trace element content showing high concentrations of incompatible elements such as Zr (773-999 ppm), Nb (85-202 ppm) and Y (52-71 ppm) also confirm the igneous affinity of layers A and B, and of the claystone overlying tuffite A. Both tuffites plot in the field of trachyte on the Winchester and Floyd (1977) discrimination diagram for volcanic rocks based on Nb/Y versus Zr/TiO₂.

However, the deposits have suffered a high degree of physical and chemical alteration, including hypergenic processes, and the use of Y, long considered to be immobile, is now regarded as unreliable. Instead, an alternative diagram based on Zr/Nb versus Ti/Th (Batchelor et al., 2003) allows classification of the source material of tuffite A as trachitic and that of tuffite B, and of the claystone overlying tuffite A, as phonolitic.

The data suggest that the analysed pyroclastic deposits are representative of the original Lower Carboniferous, trachitic-phonolitic volcanic activity.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Fossilized wooly mammoth skeletal remains from the Upper Palaeolithic archeological site (Cracow Spadziasta Street (B), Southern Poland) – preliminary report

Anna ROGÓŻ¹, Zbigniew SAWŁOWICZ¹

¹ Institute of Geological Sciences, Oleandry 2a, 30-063 Kraków, Poland; anna.rogoz@uj.edu.pl

The materials described below belong to the woolly mammoth (*Mammuthus primigenius*) and come from the archeological site Spadzista Street (B) in Cracow. Different parts of the mammoth skeleton were analyzed in the study: long bones, sculls, ribs, vertebras, tusks, and teeth.

The samples studied are built of apatite, probably mainly carbonate hydroxyapatite. Most of the bones and teeth show the features of "normal" bones. In the bones, there are clearly visible Haversian systems (Haversian canals in the center and concentrically located lamellae with osteocyte lacunae), interstitial lamellae between them and trabeculae of spongy bone. Enamel prisms and dentine canaliculi are seen in the teeth. The bones are commonly infilled with calcite and/or carbonate sediment. These infillings are present in the Haversian canals, between bone trabeculaes in spongy bone and, in some cases, in cracks. The content of calcite increases from the exterior to the interior of the bones, being related to the higher porosity of spongy bone compared to compact bone. Locally, Fe-Mn (hydroxy)oxides are present, mostly as rims on osteocyte lacunae. In the teeth, dentine canaliculi are coated or infilled with secondary apatite whereas, in the tusks, the canaliculi are not infilled with secondary minerals. The bones and teeth are usually cracked. There are small cuts and multidirectional cracks around the Haversian canals, neither related to the histology of the bones. The cracks, in some cases, cut mineral infillings or/and occasionally are infilled with calcite or carbonate sediment. In some specimens, areas of demineralized tissue with high porosity or with large round holes are visible. Those changes are probably caused by bacterial attack. Some of these holes are also infilled with calcite. The Ca/P mole ratios in the apatites vary from 1.79 (in the tusks) to 2.30 (in the ribs). As the Ca/P mole ratio in fresh bones and teeth is 1.59-1.67 (Elliott, 2002), the higher ratios in the apatites could be due to replacement of PO₄ groups by CO₃²⁻ during diagenesis. A number of postdepositional events can be identified: transformation and recrystalization of apatites, bacterial degradation, cracking, infilling by various secondary minerals and/or sediment.

References:

ELLIOTT J.C., 2002: Calcium phosphate biominerals. In Kohn M., Rakovan J., and Hughes J.M., Eds., Phosphates: Geochemical, Geobiological and Materials Importance. Reviews in Mineralogy and Geochemistry Series, 48, 427-453. Mineralogical Society of America, Washington, D.C.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Mineral veins from the low grade metamorphic rocks of the Łysogóry Unit (Holy Cross Mts, Central Poland)

Sylwester SALWA¹

¹ Polish Geological Institute-National Research Institute, Holy Cross Mountains Branch, Zgoda 21, 25-593 Kielce, Poland; sylwester.salwa@pgi.gov.pl

Phyllites from Podmachocice are commonly cross-cut by numerous and various kinds of mineral veins with different compositions, shapes of crystals, ages and relationships to deformations. In terms of composition, several types of veins can be distinguished, including: quartz, quartz-chlorite, chlorite and siderite-dolomite veins. The most common are quartz and quartz-chlorite veins. In terms of crystal shape, the following types of veins can be recognized: antitaxial, syntaxial, stretched-crystal veins and shear veins; the stretched-crystal veins are the most common of these. In relation to the deformation stages in the area, the vein system can be divided into pre-, syn- and post-tectonic types with syntectonic veins being the most common in outcrops. These mineral veins are mostly smallscale (up to few meters long and up to few centimeters wide) except of some syntaxial quartz veins (up to a hundred meters long and a few meters wide).

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Relationships between tectonics and metamorphism in phyllite from Podmąchocice (Łysogóry Unit of the Holy Cross Mountains, central Poland)

Sylwester SALWA¹

¹ Polish Geological Institute-National Research Institute, Holy Cross Mountains Branch, Zgoda 21, 25-593 Kielce, Poland; sylwester.salwa@pgi.gov.pl

Recently, the regional metamorphism in the Holy Cross Mts phyllites has been completely documented for the first time from Podmachocice (Salwa, 2006). The phyllites are composed of quartz, white mica, chlorite, siderite, pyrite, dolomite, hematite, apatite and subordinate biotite. These rocks are intensively tectonized and metamorphism is strictly related to tectonic deformations. The growth of new minerals was controlled by deformational processes. Based on detailed mezostructural analysis and microscopic study, the stages of the progressive deformation in the phyllite were distinguished. During prefolding shortening of the multilayered rock, a slaty cleavage S_1 was formed. The growth of white mica is closely associated with this plane, whereas mica-chlorite stacks formed within microlithons. During folding and thrusting, an axial plane crenulation cleavage S_2 was produced and Fe and Fe-Mg chlorite phases grew within microlithons and cleavage domains. Simultaneously in the shear zones, quartz, chlorite and apatite were dynamically recrystallized and numerous quartz-chlorite and siderite-dolomite veins formed. During late folding, a new crenulation cleavage S3 was developed within narrow shear zones. Within these zones, σ -type porphyroblasts of chlorite with pressure shadows are observed. The older veins were deformed as is indicated by the presence of deformational lamellae and of subgrains in quartz grains. Microstructures and the composition of the phyllites suggest that they were produced at temperature of 300-350°C and a differential stress above 1.7 kbar.

References:

SALWA S., 2006: Preliminary structural petrography characteristic of phyllite from Podmachocice in the Łysogóry Unit of the Holy Cross Mts. Przegląd Geologiczny 54, 513-520 (in Polish).
MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Magmatic equilibration and subsolidus re-equilibration in Archaean granites - analysis of an integrated data base

Ewa SŁABY^{1a, b}, Hervé MARTIN², Michał ŚMIGIELSKI³, Andrzej DOMONIK⁴, Stanisław HAŁAS⁵

^{1a} Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw, Warsaw, Poland

^{1b} Institute of Geological Sciences, Polish Academy of Sciences, Warsaw, Poland

² Laboratoire Magmas et Volcans; OPGC, CNRS, Universite Blaise Pascal, Clermont Ferrand, France

³ Institute of Geology, University of Warsaw, Warsaw, Poland

⁴ Institute of Hydrogeology and Engineering Geology, University of Warsaw

⁵ Mass Spectrometry Laboratory, Institute of Physics, UMCS, Lublin, Poland

Granite petrogenesis, especially petrogenesis of Archaean granites is still highly debated. Currently published data focus on granite geochemistry and phase composition. Both are used to recognize processes responsible for magma generation and differentiation, however, of both of them, geochemistry plays an especially important role and is used as the predominant tool. It is used in determinations of magma source, in investigations of the progress of source melting, in investigations of the crystallization process, contamination, mixing, metasomatism, etc. In all of these studies the basic assumption is that whole rock composition reflects primordial geochemical relations. Under this assumption, whole rock composition constitutes the basic data set used for the modelling of all of the above processes. Granitic plutons are formed due to multi-stage processes, each of which can influence the whole system equilibrium; each is capable of resulting in a new reequilibration. Re-equilibration with volatiles, fluids, especially fluids of mixed origin has deep consequences for granite petrogenesis. The effects of magmatic and post-magmatic equilibration overlap. Effects of both are registered in the whole rock geochemistry. Thus whole rock composition cannot be used directly for the modelling of a single process. Precise analysis is needed in order to define and separate overlapping effects. Examples of multi-stage magmatic and post-magmatic equilibration system are Archaean plutons. Modelling of their origin using whole-rock geochemistry can be risky if the composition is not corrected.

The aim of the presentation is to show an example of such an analysis, separating the effects of multi-stage pluton evolution and finally including post-magmatic re-equilibration. We present new tools used for such an analysis based on an integrated data base.

Acknowledgements: Financed by BW 1847/19

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Geochemical diversity of metabasalts from the Nove Mesto Unit and the Stronie Formation and its bearing on their origin

Jacek SZCZEPAŃSKI¹, Sławomir ILNICKI²

¹ Wrocław University, Institute of Geological Sciences, Pl. Maksa Borna 9, 50-204 Wrocław, Poland,

js@ing.uni.wroc.pl² Warsaw University, Institute of Geochemistry, Mineralogy and Petrology, Al. Żwirki i Wigury 93, 02-089 Warszawa, Poland; slawomir.ilnicki@uw.edu.pl

Amphibolites in the Nove Mesto Unit (NMU) and the Orlica-Śnieżnik Massif (OSM) are both parts of metamorphosed volcano-sedimentary series. Metabasalts in the western OSM form relatively small exposures (lava flows and sills) embedded within Stronie Formation metasediments, whereas amphibolites in the NMU constitute a 30 km long and 2-3 km belt along its border with the OSM. In general, basic metavolcanics from both units are most probably of Neoproterozoic age (in the OSM possibly up to middle Cambrian). However, the age of the NMU metabasalts is only traditionally regarded as Neoproterozoic. These metavolcanics were hitherto described as MOR-type basalts that originated during Cambro-Ordovician extension and disintegration of the northern periphery of Gondwana or in a back-arc setting related to an unspecified subduction event. Thus, these inconsistencies in the origins of both groups of metabasites and the geotectonic implications are explored.

On several plots, the OSM amphibolites show mostly tholeiitic character; however, a few reveal transitional-to-alkaline affinity. In contrast, all NMU amphibolites plot as tholeiites. Trends on bivariate REE and HFSE diagrams, and ratios of transitional elements (e.g. Ni, Cr) to HFSE, suggest differences in source composition or/and its strong heterogeneity. Furthermore, on a Nb/Yb-Th/Yb plot, the samples from the NMU fall within the mantle array field while the majority of the OSM amphibolites tend to plot above it indicating their enrichment brought about by either crustal contamination or a subductionrelated component. Also, metabasalts from the OSM show more variegated REE/HFSE (e,g., Nb/La) than do the amphibolites from the NMU. Moreover, the tectonic setting discrimination is often ambiguous as the studied metabasites, particularly from the OSM, show affinities to either E-MORB-to-N-MORB or back arc basin basalts (BAB).

The diversity of geochemical features characterizing the metabasites may stem from asthenospheric source heterogeneity or/and may also reflect the introduction of a subduction-derived component into the parental magmas. The presence of this enigmatic component is more readily detectable in amphibolites from the OSM than from the NMU. It corroborates an earlier assumption of a BAB provenance, yet only with reference to the OSM metabasalts; those of the NMU with their prevailing MORB resemblance might represent a remnant of a separate ocean basin. However, several of the geochemical signatures might have originated due to crustal contamination of variable intensity, thus negating the presumed influence of a subduction zone and BAB affinity. Given the alternative, the origin of the metabasites remains equivocal.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Comparison of methylphenantrene distributions predicted from molecular modelling with relevant geological data

Marek SZCZERBA¹, Mariusz ROSPONDEK²

¹ Institute of Geological Sciences PAN, Senacka 1, 31-002 Kraków, Poland
² Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2A, 30-063 Kraków, Poland

The distributions of methylated Poly-Aromatic-Hydrocarbons (PACs) are highly variable between samples as they are controlled by the effects of source, thermal maturation and biotic- and abiotic oxidation. Phenanthrene (Phe) and methylphenanthrenes (MePhe) are major aromatic constituents of crude oils and solvent extracts of sedimentary rocks which are frequently applied in thermal maturation studies.

On the basis of calculated thermodynamic properties, the distribution of methylphenantrene isomers in equilibrium was calculated. Comparison of this result with geological data reveals that, with increasing maturity, the distribution of methylphenantrenes begins to resemble that of thermodynamic equilibrium although why 9-MePhe is able to persist to advanced stages of maturity up to 1.2% (*R*r) remains unexplained.

Therefore, the mechanism of isomerization was investigated. It was suggested that the 1,2-methyl shift is induced by protonation of the carbon atom next to the methyl group. The differences between energies for different transition structures are quite distinct. The lowest energy barrier is between the 1-2 (23.9 kcal/mol) and 3-4 isomers (23.9 kcal/mol), whilst the highest is between the 2-3 isomers (30.3 kcal/mol). There is also a possible alternative mechanism of isomerization through the 3^{rd} row atom of carbon between the 1-4 and 1-9 isomers. The energy barrier for this reaction is relatively higher (37.7 and 41.1 kcal/mol respectively) than for isomerizations through the 1,2-methyl shift. However, this mechanism can be responsible for isomerization from 9-MePhe to other isomers at elevated temperatures.

It was also suggested that dealkylation of methylphenanthrenes is induced by hydrogen radical attack at the carbon atom adjacent to the methyl group. Then after crossing the transition state, an intermediate state is attained. The CH_3 radical is liberated from the phenantrene molecule after crossing the second transition state. The height of the barrier is generally similar for all the isomers, and is relatively small (c.a. 10 kcal/mol), which means that if a substrate-hydrogen radical is formed, the methyl radical can be easily liberated from methylphenenthrene and others.

Acknowledgement: The provision, by ACK Cyfronet AGH, of computational time for quantum chemical calculation is greatly appreciated (Grant No. MNiSW/SGI3700/PAN/137/2007).

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Theoretical studies of phenyldibenzothiophenes in the course of maturation

Marek SZCZERBA¹, Mariusz ROSPONDEK², Kamila MAŁEK³, Maciej GÓRA³, Leszek MARYNOWSKI⁴

¹ Institute of Geological Sciences PAN, Senacka 1, 31-002 Kraków, Poland

² Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2A, 30-063 Kraków, Poland

³ Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-063 Kraków, Poland

⁴ Faculty of Earth Sciences, Silesian University, ul. Będzińska 60, 41-200 Sosnowiec, Poland

Evaluation of the relative thermodynamic stabilities of phenyldibenzothiophenes by means of molecular modelling led to prediction of the equilibrium mixture composition of these compounds. The calculated equilibrium composition approaches that obtained in laboratory maturation experiments and that encountered in mature geological samples (over ca. $Rr \sim 1.2\%$). Closer inspection of a suite of samples varying in maturity revealed that phenyldibenzothiophenes can isomerise and also cyclise to triphenyleno[1,12-*bcd*]thiophene. Both of these reactions are thermodynamically possible due to a relative decrease of enthalpy along the reaction paths. Changes in the phenyldibenzothiophene positional isomer distributions from kinetically- to thermodynamically-controlled mixtures are most likely achieved by acid catalysed 1,2-phenyl shift.

To validate this hypothesis, ab-initio quantum chemical calculations (DFT) were performed aiming to localise potential transition states and determine activation energies. The isomerisations have low activation energy barriers in the range of 13-18 kcal/mol. Low energy barriers for these reactions are consistent with the geological data. With increasing maturity, 1-PhDBT decays very rapidly, which is often accompanied by the appearance of triphenyleno[1,12-*bcd*]thiophene suggesting simultaneous its formation by cyclisation/oxidation. For the modelled cyclisation/oxidation, the energy barrier is ca. 48 kcal/mol, which suggests its operation at advanced stages of diagenesis/catagenesis. However, as evidenced by its low concentration in hydrothermal oil formed over 300°C in reducing conditions, thermal stress alone is not enough but must be associated with catagenetic oxidisation. This is most likely achieved in nature via thermochemical sulfate reduction (TSR).

Acknowledgement: The provision by ACK Cyfronet AGH of computational time for quantum chemical calculations is greatly appreciated. (Grant Nos. MNiSW/SGI3700/PAN/137/2007 and MNiSW/SGI4700/UJ/075/2007).

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Native copper and cuprite from secondary Cu-mineralization in the Laskowa quarry, Góry Świętokrzyskie Mts

Eligiusz SZEŁĘG1

¹ University of Silesia, Faculty of Earth Sciences, Będzińska 60, 41-200 Sosnowiec, Poland, eligiusz.szeleg@us.edu.pl

Up to now, the occurrence of native copper in the Góry Świętokrzyskie Mts has been reported only from the Miedziana Góra Cu deposit (Łaszkiewicz, 1933). It has now been found in the Laskowa quarry.

The Laskowa quarry is located about 5 km west of Kielce in the Kielce-Łagów Synclinorium belonging to the Kielce Unit in the Paleozoic core of the Góry Świętokrzyskie Mts. In this quarry, within dolomites, limestones and marls (Devonian-Givetian), calcite-dolomite-barite hydrothermal veins with chalcopyrite and pyrite occur. Goethite and malachite are typical products of the weathering of the primary sulphides here. During exploration works in the Laskowa quarry, a 4 cm thick calcite vein with Cu secondary mineralization was found within altered karst dolomites of the Stringocephallus Beds, Kowala Formation (Racki, 1992).

On the basis of observations performed using a polarizing microscope OLYMPUS (transmitted and reflected light) and an ESEM-XL 30 TMP (Philips/FEI) scanning electron microscope equipped with EDS (EDAX) detector at the Faculty of Earth Sciences, University of Silesia in Sosnowiec, the presence of chalcocite, covellite, native copper, cuprite and malachite was determined.

Chalcocite (Cu₂S) is the earliest mineral in succession. Covellite (CuS) is secondary in relation to chalcocite. Due to interaction with karst solutions, the secondary sulphides chalcocite and covellite formed at the expense of primary sulfides, e.g., chalcopyrite. Native copper (Cu) and cuprite (Cu₂O) formed as product of the weathering of secondary Cu sulphides. It forms dendritic aggregates up to 1 cm in diameter. Exceptional copper crystals reach sizes of up to 0.2 mm and cuprite crystals, up to 0.4 mm. Cuprite replaces native copper and is predominant in the dendrites. Malachite, the youngest mineral in the association, replaces all older Cu minerals.

EDS spectra and semi-quantitative analyses reveal the pure chemical composition of the native copper from the Laskowa quarry.

References:

ŁASZKIEWICZ A., 1933: O miedzi rodzimej. Archiwum Mineralogiczne 9, 1-17.

RACKI G., 1992: Brachiopod assemblages in the Devonian Kowala Formation of the Holy Cross Mountains. Acta Palaeontologica Polonica 37 (2-4), 297-357.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The same reaction but different environment: breakdown of monazite in the High Tatra granites

Krzysztof SZOPA¹

¹Faculty of Earth Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, POLAND, kszopa@us.edu.pl

Phosphates are a typical accessory minerals in the Tatra granites and their enclaves. Two samples, granite and its cumulate enclave have been studied, where phosphates are mostly represented by monazite-(Ce) and apatite-(OH,F) crystals. Cumulate enclave (G2), contains up to ~13 vol.% of apatite and crystals of monazite-(Ce) and xenotime-(Y) are also presented. Occasionally, small inclusions (up to 5 μ m in size) of thorite are noted. In the granite sample phosphates are represented by apatite (idiomorphic to xenomorphic crystals up to 400 μ m in size) and monazite-(Ce). In both cases fluid reacted with the monazite. The observed reaction connected with the monazite-(Ce) in the studied granites, according to Broska et al. (1998) is: $3Mnz + Ann + 4Pl + 3 Qtz + fluid(4Ca^{2+}/2H^+) \leftrightarrow Ap + 3All + Ms$.

Different stages of the decomposition reaction are observed in both studied samples. Sometimes "empty" inclusions after the monazite can be noted. Only the secondary minerals as REE-epidote/allanite, apatite as well as the shape of the inclusion can suggest what type of primary phase could have been there. In granite sample rhapdophane-(Ce) is found as a new product of monazite breakdown, as a vein filling cracks in apatite crystals. In the same rock sample, thorite and/or huttonite needle-shape crystals up to 15 µm in size, are presented. Epidote crystals with composition changing from epidote-(REE) (rim) to allanite (core) are overgrowing apatite. Based on the chemical analysis, the reaction for the main products of the monazite breakdown could be proposed as follow: (G2) $1 \text{ Mnz} + 3.44 \text{ } H_4SiO_4 + 2.97 \text{ } Ca^{2+} + 1.97 \text{ } Al^{3+} + 0.3 \text{ } Mg^{2+} + 0.02 \text{ } Ti^{4+} + 0.01 \text{ } Mn^{2+} + 1.46 \text{ } Fe^{3+} + 0.03 \text{ } F + 0.57 \text{ } H_2O \leftrightarrow 0.33 \text{ } Ap + 1.22 \text{ } Ep-(REE) + 0.02 \text{ } Ti^{4+} + 0.02 \text{ } F^{+} + 2.98 \text{ } H_4SiO_4 + 16.68 \text{ } Ca^{2+} + 11.46 \text{ } Al^{3+} + 0.12 \text{ } Mn^{2+} + 5.16 \text{ } Fe^{3+} + 0.02 \text{ } F^{+} + 2.98 \text{ } H_2O \leftrightarrow 0.31 \text{ } Ap + 6.0 \text{ } Ep-(REE) + 0.01 \text{ } Th^{2+}.$

According to chemical U-Th-Pb monazite dating, early Variscan ages in both samples were predominantly obtained (*ca* 360 Ma and *ca* 340 Ma). The episode dated for *ca* 260 Ma is also present. In many cases the younger ages are the result of "resetting" during metamorphic event but some grains show an older cores with a younger rim zones. It can be another proof for occurrence of younger event in the High Tatra granites. The monazite breakdown is controlled by fluid rich in Ca²⁺, OH⁻, F⁻. The various stages of the reaction are determined by concentration of the fluid reagents. Studied samples represent different hydrothermal type of systems: open and close, for interaction with post-magmatic fluid.

References:

BROSKA I., SIAMAN P., 1998: The breakdown of monazite in the West-Carpathian orthogneisses and Tatric granites. Geol. Carpath., 49, 3, p. 161-167.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Fly ash from coal and biomass co-combustion and its role in CO₂ sequestration

Wanda WILCZYŃSKA-MICHALIK¹, Renata GASEK¹, Janusz DAŃKO², Marek MICHALIK³

¹ Institute of Geography, Pedagogical University, ul. Podchorążych 2, 30-084 Kraków, Poland, wmichali@up.krakow.pl

² Power Plant E.C. KRAKOW S.A., ul. Ciepłownicza 1, Krakow, Poland

³ Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2a, 30-063 Krakow, Poland, marek.michalik@uj.edu.pl

Mineral carbonation is considered as an important method in carbon dioxide capture and storage (CCS). Ash rich in CaO obtained as a by-product of the combustion of several varieties of coal in power plants can effectively react with CO_2 forming carbonates.

The study of fly ash formed during coal and biomass co-combustion in the Kraków Power Plant indicates that it can be used in CCS. Co-combustion of coal and biomass (at <10% levels) is now commonly applied in Poland as a method for increasing the proportion of renewable energy in the overall energy production and reducing net CO₂ generation.

The chemical and mineral compositions of fly ash obtained in coal combustion and of fly ash from coal and biomass co-combustion differ. However, reliable comparison is difficult due to differences in coal characteristics used during coal firing and coal and biomass co-combustion and due to fluctuations in biomass composition. Both ashes are composed mainly of aluminosilicate glass, mullite, quartz, coaly matter and Fe oxides but fly ash from co-combustion processes contains, in addition, lime, periclase and wollastonite. Both fly ashes represent type F and low-calcium type but fly ash from co-combustion is relatively rich in CaO (content is close to the upper limit of the low-calcium type, i.e., 8%).

Higher contents of Al_2O_3 , Fe_2O_3 , CaO, MgO, and C_{tot} are noted in fly ash from biomass co-combustion compared to fly ash from coal combustion. Fly ash from biomass cocombustion is also richer in Na_2O and K_2O but the difference is negligible. The content of S is significantly lower in fly ash from biomass co-combustion. The contents of Th and U in fly ash from biomass co-combustion are similar to the contents in that obtained in coal combustion. Fly ash from biomass co-combustion is characterized by lower contents of Pb, Cd, Zn, As and Sb, but the Cu content is higher.

Two samples of fly ash from biomass co-combustion was subjected to a wetting and drying experiment (21 wetting and drying cycles; 50 g of sample with 400 ml of distilled water in each cycle; drying under infrared radiator; final washing after treatment with distilled water). The samples after wetting and drying are composed almost exclusively of quartz and calcite (with minor amount of mullite). Calcite in the samples is present as discrete crystals or aggregates of oriented crystals. The calcite is relatively rich in Mg.

Reductions in the contents of lime and periclase and the formation of abundant calcite in fly ash from biomass co-combustion in reaction with atmospheric CO_2 dissolved in water indicate that this type of fly ash can be used in CCS procedures

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Accessory minerals and selected trace elements in altered granodiorite from Strzeblów (Strzegom-Sobótka Massif, SW Poland)

Beata ZYCH-HABEL¹, Angelika KĘDZIERSKA¹

¹ Institute of Geological Science, Jagiellonian University, Oleandry 2a, Kraków, beata.zych@uj.edu.pl

Strongly altered biotite granodiorite from Strzeblów (Strzegom-Sobótka Massif, Fore Sudetic Block) consists of albite, K-feldspar, quartz and two micas. Mineral composition and rock texture indicate that albitization and episyenitization were dominant alteration processes affected the granodiorite. Based on chemical and mineral composition, three degrees (low, medium and high) of alteration were distinguished. The REE and other trace elements are mainly accumulated in accessory minerals such as monazite, xenotime, cheralite, zircon, ferrocolumbite. Some evidence suggests that REE and other HFSE (e.g., Zr, U, Nb), often considered as immobile during alteration, can be mobilized under certain conditions. The mobility of these elements was determined using the isocon (Grant, 1986).

Monazite, xenotime, apatite, zircon and Nb oxides occur as accessories in rocks showing the lowest degree of alteration. The Zr content in these rock is lower than in unaltered rocks, whereas the HREE and Y contents are higher. Xenotime, cheralite, zircon and Nb oxides occur in rocks showing medium degrees of alteration. In these rock, HREE, Y and Nb contents still increase, whereas the Zr content is almost stable as zircon resists alteration. Cheralite, gadolinite and thortveitite are accessories in rocks showing the highest degree of metasomatism. Zircon alteration is very common, and the concentrations of HREE and Y and Nb are highest in these rocks.

Y and HREE are mobilized in the early stages of albitization and their content increases with advancing metasomatism due to formation of, e.g., xenotime (low-medium degree of alteration) and gadolinite (high degree). Zr is leached during the early stages of albitization and its behavior changes slightly with the degree of alteration.

Reference:

GRANT J.A. 1986: The isocon diagram; a simple solution to Gresens' equation for metasomatic alteration. Economic Geology, v. 81/8; p. 1976-1982.

Field sessions

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Field session 1

Geochemical studies in environmental monitoring and assessment – examples from the Holy Cross Mts.

Zdzisław M. MIGASZEWSKI¹, Agnieszka GAŁUSZKA¹, Sabina DOŁĘGOWSKA¹

¹ Geochemistry and the Environment Division, Institute of Chemistry, Jan Kochanowski University, 15G Świętokrzyska Str., 25-406 Kielce, Poland; zmig@ujk.kielce.pl

Introduction

The principal objectives of environmental geochemistry studies are: (i) to establish concentration ranges (baselines), as well as spatial and temporal distribution patterns of elements in rocks, soils, sediments, surface- and groundwaters, plants, animals and man, and (ii) to assess mobility, translocation, deposition and remobilization of elements in different environmental conditions and in/between various environmental systems. Of great significance for environmental scientists is an identification of natural and anthropogenic sources of elements, especially those potentially detrimental or even toxic to the environment. To solve these problems and concerns, a variety of geochemical, mineralogical, petrological and geophysical methods has been applied. The results derived from the environmental geochemistry studies may especially be used in: (i) assessing maninduced processes in the environment, and (ii) monitoring the present state of the environment and predicting the future changes of its quality. The first approach is presented in stop 1 of the field session: "The influence of acid mine waters on the environment in the Wiśniówka area (Holy Cross Mountains)". In contrast, stop 2: "Springs as geoindicators of the environmental quality" shows the possibility of using geochemical data for environmental monitoring.

STOP 1: The influence of acid mine waters on the environment in the Wiśniówka area (Holy Cross Mountains)

Study area

The Wiśniówka mining area is located about 5 km north of Kielce (Fig. 1). It occupies the upper part of Wiśniówka Mt. taking up an area of about 3 km². The geology and tectonics of this area has been studied for decades arousing many controversial views (Żylińska et al. 2006 and references cited there). Wiśniówka Mt. makes up the southernmost part of the Łysogóry Block that is separated from the Małopolska Block by the Holy Cross Fault. The mining area lies within Upper Cambrian (Furongian) thickbedded quartzites and quartzitic sandstones with mudstone and clayey shale interbeds with rare tuffs and bentonites (Fig. 1). There are three quarries in the study area: the active Wiśniówka Duża quarry and two abandoned quarries – Wiśniówka Mała and Podwiśniówka. The basic raw materials are quartzites and quartzitic sandstones that are extracted for manufacturing crushed aggregates. The Wiśniówka Mała quarry is filled in with a large bipartite lake taking up an area of about 920×60 m reaching at least 15.6 m deep in the western pond (Migaszewski et al. 2009). In contrast, the Podwiśniówka quarry holds a much smaller pond with a varying surface area reaching 1.5 m deep. This area is characterized by the presence of an exposed pyrite zone. Both water bodies are a good example of Acid Mine Drainage (AMD), and the Podwiśniówka pit pond reveals the lowest pH compared to other reservoirs in Poland.

Wiśniówka Mała pit lake

The geochemical study conducted in two presently separated ponds of the Wiśniówka Mała lake indicated that there is a spatial and seasonal variability in concentrations of most elements, and in sulfur isotope ratios, in the water bodies examined. The water of the western pond showed a lower pH in the range of 3.0-4.4 (geometric mean of 3.7), higher conductivity (390 μ S/cm), and higher concentrations of sulfates (156 mg/l) and most cations and anions. The concentrations of Fe²⁺ and Fe³⁺ averaged 0.8 and 0.4 mg/l. In contrast, the eastern pond water revealed a higher pH (mean of 4.36), lower conductivity (293 μ S/cm), and lower sulfate (90 mg/l) and trace metal levels. Similar variations were recorded in the stable sulfur isotope ratios. The $\delta^{34}S_{V-CDT}(SO_4^{2-})$ values in the water of the western pit pond varied from -6.8 to -4.6‰ (mean of -5.6‰), whereas the water of the lake water was below 0.1 mg/l CaCO₃. No distinct difference in the $\delta^{18}O_{V-SMOW}(SO_4^{2-})$ was noted between the western and eastern pit ponds. More details on the chemistry and S and O isotope composition of soluble sulfates have been presented in the previous report (Migaszewski et al. 2009).



Fig. 1. Localization of acidic pit lake and pond on Mt. Wiśniówka

Podwiśniówka pit pond

The geochemical study of the Podwiśniówka acid pit waters, conducted during 2004-2007, revealed a seasonal variability in pH, EC, and concentrations of sulfates and ferric and ferrous ions (Migaszewski et al. 2007a, 2008). The pH varied from 2.4 to 3.5 and EC from 341 to 1656 μ S/cm. However, the pH and EC of strongly acidic intermittent puddles reached 1.5 and 14.3 mS/cm, respectively. The concentrations of sulfates in the pit pond water were in the range 55-314 mg/l and Fe(II) and Fe(III) in the range 1.4-14.8 mg/l and

0.0–23.6 mg/l. The puddles mentioned above showed the highest contents of sulfates (7750 mg/l), Fe(II) and Fe(III) (>750 and >300 mg/l). No statistically significant correlations were found between pH, EC, sulfate and iron concentrations. This variation resulted from the influence of seasonal environmental factors (influxes of meltwater and stormwater, droughts, insolation) combined with interactions between schwertmannite, ferrihydrite and goethite.

The comparison of stable sulfur isotope ratios in pyrite (mean of -25.4%), sulfate efflorescences on pyrite surfaces (-25.4%), and soluble sulfates of strongly acidic puddles (-25.4%), acidic pit pond water (-15.6%) and control small pond water (+9.2%) indicates that oxidation of pyrite and leaching of oxyhydroxysulfates generates the acidic waters of the pond and intermittent puddles and leads to the formation of various iron precipitates. Moreover, the comparison of stable oxygen isotope ratios in soluble sulfates and waters suggests that oxidation of pyrite is induced primarily by an iron oxidation path periodically influenced by dissolved atmospheric oxygen.

The study, using a scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDS), study of the rocks and sediments of Podwiśniówka and Wiśniówka enabled us report a new occurrence of gorceixite (hydrated barium aluminum phosphate of the crandallite series) in the Holy Cross Mountains (Migaszewski et al. 2007b). In the tuffs and quartzites from Podwiśniówka quarry, the related isostructural minerals Ca-Sr-Ce-bearing gorceixite or a mixture of Ce-bearing crandallite and goyazite, and Ca-Sr-bearing-florencite has been recorded in trace amounts.

The pit pond sediment near the pyrite zone reveals an increased amount of As (1111–1879 mg/kg). The source of this element is veined pyrite and pyrite-bearing clayey shales.

References:

- MIGASZEWSKI Z.M., GAŁUSZKA A., HAŁAS S., DĄBEK J., DOŁĘGOWSKA S., BUDZYK I., STARNAWSKA E., MICHALIK A., 2009: Chemical and isotopic variations in the Wiśniówka Mała mine pit water, Holy Cross Mountains (South-Central Poland). *Environmental Geology* 57, 29–40.
- MIGASZEWSKI Z.M., GAŁUSZKA A., HAŁAS S., DOŁĘGOWSKA S., DĄBEK J., STARNAWSKA E., 2008: Geochemistry and stable sulfur and oxygen isotope ratios of the Podwiśniówka pit pond water generated by acid mine drainage (Holy Cross Mountains, south-central Poland). *Applied Geochemistry* 23, 3620–3634.
- MIGASZEWSKI Z.M., GAŁUSZKA A., PASŁAWSKI P., STARNAWSKA E., 2007a: An influence of pyrite oxidation on generation of unique acid pit water: A case study, Podwiśniówka quarry, Holy Cross Mountains (south-central Poland). *Polish Journal of Environmental Studies* 16(3), 407–421.
- MIGASZEWSKI, Z.M., STARNAWSKA, E., GAŁUSZKA, A., 2007b: Gorceixite from the Upper Cambrian rocks of the Podwiśniowka mine pit, Holy Cross Mountains (south-central Poland). *Mineralogia Polonica* 38 (2), 171–184.
- ŻYLIŃSKA A., SZCZEPANIK Z., SALWA S., 2006: Cambrian of the Holy Cross Mountains, Poland: biostratigraphy of the Wiśniówka Hill succession. *Acta Geologica Polonica* 56 (4), 443–461.

STOP 2: The use of springs for geoindication studies

Zdzisław MIGASZEWSKI¹, Artur MICHALIK¹, Agnieszka GAŁUSZKA¹

¹ Geochemistry and the Environment Division, Institute of Chemistry, Jan Kochanowski University, 15G Świętokrzyska Str., 25-406 Kielce, Poland

The use of groundwater in geoindication studies

According to Berger and Iams (Berger, 2002), a geoindicator is "a magnitude, frequency, rate or trend of geological processes and phenomena that occur at or near the Earth's surface and that are significant for assessing environmental change over periods of 100 years or less". The selection of an area for geoindication studies is crucial for interpretation of the natural/anthropogenic character of changes in the environment. Welch (2003) reviewed the application of selected geoindicators to monitoring of Canadian national parks. Following this approach, we present the chemistry and quality of spring waters from Świętokrzyski National Park as an example of geoindication studies.

General characteristics of spring waters in Świętokrzyski National Park

The SNP encompasses a morphologically diversified region – from the parallel flat, wide Wilków and Dębno Valleys in the center through the Łysogóry Range in the southern part and scattered mountains (Bukowa, Psarska, Chełmowa) in the northen part (Fig. 2). The Łysogóry Range comprises Middle and Upper Cambrian quartzites and quartzitic sandstones with mud shale interbeds. The basement in the Wilków and Dębno Valleys consists of Ordovician- and Silurian clay and mud shales, and, in places, sandstones. The Bukowa, Psarska and Chełmowa Mounts are built of Lower Devonian sandstones and quartzites, in places with dolomite and limestone interbeds.



Fig. 2. Localization of springs in Świętokrzyski National Park

A 3-year (2003–2005) monitoring of springs in the SNP, conducted during hydrological droughts, enabled the identification of approximately 60 springs with continuous water

outflows (Fig. 2). Most of the springs were characterized by a low yield ($<1 \text{ m}^3/\text{h}$). The highest yield (2-4 m³/h) was recorded for springs 1, 2 and 3.

Based on chemical characteristics, two main types of spring waters can be distinguished in the area of the SNP (Michalik 2008). The first, typical for the Łysogóry Range, shows a low pH (<6.0) and a very low conductivity (<80 μ S/cm). The second type occurs in the Klonów and partly Pokrzywiański Ranges (springs 6, 7) and is characterized by a higher pH (>6.0) and a much higher conductivity (>200 μ S/cm).

The spring waters of the Łysogóry Range show very low ion concentrations in the prevalent SO_4 -Ca-Cl-Mg and SO_4 -Ca-Mg-Cl water types. In contrast, the spring water chemistry from the remaining part of SNP is characterized by the presence of hydrocarbonates prevailing over sulfates (HCO₃-Ca-Mg). Michalik (2006) indicated that only some of the trace metals (Ba, Cu, Mn and Zn) occurred in slightly higher concentrations both in the Łysogóry Range and the remaining part of SNP. The spring waters of the Klonów and Pokrzywiański Ranges are highlighted by raised levels of most metals.

The use of springs as geoindicators in the Świętokrzyski National Park

The results of detailed hydrogeochemical study indicated some fluctuations in both physicochemical parameters and chemical composition of the spring waters during two years (Michalik 2006, 2008). A minor drop in pH was observed in most springs. However, in the Saint Francis spring (no. 1), the difference reached 1.5 pH units. In 2006, conductivity was higher in all the springs examined, especially in the Saint Francis spring where the EC value more than doubled. Of the major components found in the spring waters, only sulfate and chloride ion concentrations in spring 4 showed any substantial variation. The most distinct changes were recorded in trace element concentrations, especially Al, Mn and Zn in springs 4 and 6. These two springs have partly been affected by human activity, e.g., cloister buildings and tourist infrastructure located on top of Holy Cross Mount (no. 4), nearby outbuildings (no. 6), and long-range and local emissions.

In the light of this, the chemistry and quality of spring waters in the park was linked primarily to the geologic setting (petrographic-lithologic composition of bedrock and superficial mantle rock), with a relatively minor influence by local and off-regional pollution sources. However, this issue requires long-term monitoring in terms of spring yield and chemistry.

Our view is that the springs of SNP are good geoindicators of natural changes in the environment. Hydrogeochemical monitoring in protected areas provides valuable data that could be used not only to record the trend of changes in the environment, but also to interpret their character.

References:

BERGER A.R., 2002: Tracking rapid geological change. *Episodes* 25(3), 154-159.

- MICHALIK A. 2006: The influence of factors on the chemistry of spring waters from Świętokrzyski National Park. *Doctorate thesis*, Technical University in Gdańsk (in Polish).
- MICHALIK A. 2008: The Use of Chemical and Cluster Analysis for Studying the Spring Water Quality in the Świętokrzyski National Park, South-Central Poland. *Polish Journal of Environmental Studies* 17(3), 357–362.
- WELCH D., 2003: Geoindicators for monitoring Canada's national park system. *Geoscience Canada* 30(1), 9–16.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Field session 2

Introduction to the field trip

Diabase intrusions from the Bardo syncline (the Kielce region) in the Holy Cross Mts

Roman WŁODYKA¹, Łukasz KARWOWSKI¹, Krzysztof SZOPA¹

¹ Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec

On the area of the Holy Cross Mts, igneous rocks appear in the Kielce (southern) and the Łysogóry (northern) region (the Psary-Święta Katarzyna Zone). The Bardo syncline (Fig. 1) is located in the central part of the Kielce region where diabases were discovered for the first time by J. Czarnocki in 1919. The Bardo diabase at the following localities was petrographically examined (Fig. 1): Bardo (Tokarski 1921, 1926; Morozewicz 1923, 1925; Małkowski 1954; Ryka 1957a, b; Szczepanowski 1963; Łabęcki 1969, 1970; Krzemiński 2004), Widełki (Ryka 1957a, 1959, Szczepanowski 1963), Zalesie (Kardymowicz 1957, 1967; Szczepanowski 1963), Zbelutka (Kardymowicz 1957, 1967), Zagórze (Nawrocki et al., 2007b) and Kędziorka (Ryka 1974). The diabase intrusions were emplaced in mechanically weakened zones in Silurian sediments between Lower Ludlovian graptolite shales and Upper Ludlovian greywackes (Fig. 2). The main products of the volcanic activity are shallow, subsurface sills with thicknesses varying from 16 to 30 m. Tectonic data suggests a late Ludlow-Siegenian (Kowalczewski, Lisik, 1974) or late Ludlow-early Gedinnian age for the Bardo diabase (Nawrocki 2000). Przybyłowicz and Stupnicka (1991) revealed that the diabases, and volcanic material from the greywackes, originated from the same magmatic source. The spatial relationship between the occurrence of the diabase sills and the locations of maximum greywacke thicknesses points to their Late Ludlovian age. Radiometric data give inconsistent results. Migaszewski (2002) suggests multi-stage magmatic processes (lower Devonian-upper Permian) whereas Nawrocki et al., (2007a) data point clearly to a Silurian age for the Bardo intrusion $(426 \pm 6 \text{ Ma})$.

Krzemiński (2004) showed that the Bardo diabases represent tholeiitic melts generated by interaction of upwelling thermal plumes with dry, subcontinental lithospheric mantle. Primary, MgO-rich melts of picritic composition generated by different degrees of partial melting underwent low-pressure fractional crystallization of plagioclase + clinopyroxene \pm olivine at shallower crustal levels. The Holy Cross diabases have the signature of anorogenic magmatites typical of continental extensional settings; they may record the detachment of the Małopolska Block from the Baltica margin during late Ludlow-Emsian times (Krzemiński 2004).

Basing on chemical analyses of the Bardo diabases given in Ryka (1957b, 1959, and 1974), Kardymowicz (1957, 1967) Krzemiński (2004) and Małkowski (1954), the authors prepared two graphs: AFM (Fig. 3) and TAS (Fig. 4) illustrating their relatively evolved compositions. On the AFM diagram, most of the projected compositions lie along the curve

of iron enrichment and above the line disciminating the tholeiitic and calc-alkaline suites. Increasing in Fe/(Fe + Mg) in mafic (augite, Ti-magnetite) minerals concurrent with an increase in the proportion of felsic (plagioclase) minerals gives rise to the trend of the residual liquid composition shown (Fig. 3). The more evolved Bardo diabases comes from Kędziorki (Ryka 1974). These are plagioclase diabases without pyroxenes forming veins not more than 3 m thick. The CIPW calculation shows that the amount of normative quartz changes in the range 3 (Bardo) to 28 % (Kędziorka), while mg-numbers and MgO content drops from 57 to 33 and 5.5 to 1% respectively. On the TAS and K₂O-SiO₂ classification diagrams (Fig. 4), the diabase rocks lie below the alkaline-subalkaline discrimination line, mainly within the subalkaline basalt field. Samples from Kędziorki plot in the basaltic andesite- and andesite fields. So, from a geochemical point of view, the diabase sills are subalkaline and show a typical tholeiitic evolution from tholeiite diabases to tholeiite andesites.



Fig. 1. Geological sketch map of the Bardo syncline after Czarnocki (1958).



Fig. 2. Simplified geological section through the Bardo synkline after Nawrocki (2000).

Hydrothermal alterations of Bardo diabase are common. The albitization of plagioclase and the replacement of olivine, glass and pyroxene by phyllosilicates suggest spilitization as a main alteration process. The secondary components in the diabases include albite, epidote, amphibole, chlorite, hydromica, kaolinite, titanite, pyrite, calcite, siderite, ankerite, fluorite and chalcedony (Ryka 1959). The magma injections caused contact metamorphism of the Silurian sediments. The thicknesses of the metamorphosed zones of the Bardo sills do not exceed 0.4 m (Kardymowicz 1967); metamorphic temperatures were below 400°C (Ryka 1959; Suchý et al. 2004).



Fig. 3. AFM diagram of whole-rock and igneous mineral compositions of

the Bardo diabases.



Fig. 4. TAS classification diagram for the compositions of the diabase rocks from the Bardo syncline. Rock analyses by Ryka (1957b, 1959, and 1974), Kardymowicz (1957, 1967), Krzemiński (2004) and Małkowski (1954) are included.

STOP 1: The Ordovician and Lower Silurian sedimentary succession in Zalesie

Wiesław TRELA¹

¹ Polish Geological Institute-National Research Institute, Holy Cross Mountains Branch, Zgoda 21, 25-593 Kielce, Poland

The Lower Palaeozoic succession in Zalesie near Łagów is represented by the Ordovician-Silurian rocks outcropped in unnamed ravine. The entire Ordovician section is up to 38 m thick and includes the upper Tramadocian to upper Hirnantian rocks (Fig. 5). This succession rests upon the Lower Cambrian shales along the unconformity produced by the Sandomierz tectonic phase (Czarnocki 1939; Kowalczewski 2000).



Fig. 5. Lithology and stratigraphy of the Ordovician succession in Zalesie nearby Łagów. A - system, B - series, C - stages, D - lithostratigraphy.



Fig. 6. Alternating sandstones/siltstones, mudstones and cherts of the Wysoczki Formation (upper Tremadocian) in Zalesie nearby Łagów.

The lowermost Ordovician is represented by the Wysoczki Formation (Dzik and Pisera 1994; Trela 2006a) referring to as alternation of glaucony-rich thin- to medium-bedded siltstones/sandstones, mudstones and cherts (Figs. 5, 6). The age of this unit was determined on the basis of conodonts (Paltodus deltifer zone), acritarchs and inarticulate brachiopods (Górka 1969; Bednarczyk 1971, 1981, 1999; Szaniawski 1980; Dzik 1994; Holmer and Biernat 2000). A distinctive feature of mudstone layers is presence of the pyroclastic material, represented by well preserved plagioclases, unaltered biotite, abundant montmorillonite and pyrogenic quartz (Chlebowski 1971). Cherts occur either as thin beds revealing sharp boundaries with accompanied siliciclastic sediment or nodules with more or less visible boundaries; however, the composite beds made up of alternating cherts and sandstones/siltstones occur as well (Fig. 7). The load structures are common at the boundary between the chert and sandstone/siltstone beds. Silica fabrics within cherts include: 1) equigranular microcrystalline quartz, 2) chalcedonic overlay lining clastic and biogenic detritus in the form of isopachous rims, 3) spherulitic chalcedony, and subordinate 4) detrital quartz grains. Moreover, the chert beds and nodules contain admixture of amorphous organic matter, glaucony grains, muscovite flakes, fragments of phosphate brachiopods and graptolites as well as rare sponge spicules and acritarchs. The sedimentary environment of these deposits was dominated by intermittent deposition of mudstones and cherts in low-energy conditions punctuated by rapid accumulation of sandstones and siltstones due to tractional processes associated with storm currents, which is supported by

biogenic escape structures (Trela 2001). Furthermore, the biogenic activity is indicated by bioturbation of mudstone beds and hypichnial trace fossils in the sandstone layers (Trela 2001). An overall coarsening-upward trend is recorded in the overlying glaucony-bearing sandstones of the Międzygórz Formation (Fig. 5; Trela 2006b), which seems to be produced by fall of the relative sea-level between Tremadocian and Floian.

The most part of the Middle and lower Upper Ordovician sedimentary record is hidden under thin Quaternary clay cover and includes: 1) grey to yellow sandstones of the Bukówka Formation, 2) dolostones and marls of the Mokradle Formation, 3) grey and red shales of the Stawy Formation (Trela 2006a) with thin K-bentonite beds (Chlebowski 1971) – Fig. 5. Dolostones of the Modrzewina Formationa (up to 2 m) and overlying marly mudstones of the Zalesie Formation (up to 7 m), form the uppermost part of Ordovician in Zalesie (Trela 2006a) – Fig. 5. This sedimentary record is coeval with the upper Katian and Hirnatian stages, which is supported by trilobite specimen of *Mucronaspis* and brachiopods of *Hirnantia* fauna found in the Zalesie Formation (Kielan 1956; Temple 1965).



Fig. 7. Composite bed showing alternation of cherts and laminated sandstone, the Wysoczki Formation (upper Tremadocian), Zalesie near Łagów.

The Zalesie Formation passes upward into pale-brown shales (80 cm; Fig. 5) with graptolites of the uppermost Ordovician *persculptus* zone (Kielan 1956; Masiak et al., 2003). The overlying Rhuddanian black radiolarian cherts and shales (Fig. 5) are poorly exposed because of the Quaternary clay cover. In nearby Bardo Stawy, the radiolarian chert unit forms the Rembów Member, which belongs to the Bardo Formation, up to 13 m thick (Trela and Salwa 2007). Numerous graptolites of the *ascensus/acuminatus* to *cyphus* zones were identified in the shale intercalations of this unit (Bednarczyk and Tomczyk 1981; Masiak et al., 2003). The chert beds reveal, more or less regular, sub-millimetric horizontal

lamination (well enhanced on the weathered surfaces) with rare white laminae (up to 10 cm long) and lens-like nodules (up to 0.8 mm thick). The white laminae/nodules are composed of cryptocrystalline quartz, some organic matter, degraded acanthomorphic acritarchs, graptolites, chitinozoans, radiolarians and phosphate sediment (Kremer 2005). In turn, cherts are made up of numerous radiolarian ghosts filled by the microcrystalline quartz with subordinate fine spherulitic chalcedony, some admixture of muscovite, rare scolecodonts, chitinozoans as well as sponge spicules (Kremer 2005). Moreover, they contain an amorphous organic matter and aggregates/clusters of very small globular bodies (1.5-3.5 µm in diameter) interpreted as remnants of degraded coccoid cyanobacteria forming benthic microbial mats (Kremer and Kaźmierczak 2005). The Rhuddanian black radiolarian cherts and shales are interpreted as transgressive deposits related to the marine flooding that was initiated in the latest Hirnantian (persculptus zone). It is postulated that accumulation of this succession was influenced by upwelling system generated by the SE trade winds along the submarine paleohigh located in the central Holy Cross Mountains (Trela and Salwa 2007; Trela 2009). These conditions generated large blooms preserved as white laminae and nodules within the chert beds (Kremer 2005).

The overlying sedimentary record is dominated by grey graptolite shales and green/grey marly claystones extending upward to the diabase intrusion, which separates the shale succession from the upper Ludlow greywacke sandstones (Tomczyk and Tomczykowa 1962; Ryka and Rubinowski 1962).

References:

BEDNARCZYK W., 1971: Stratigraphy and paleogeography of the Ordovician in the HolCross Mountains. Acta Geologica Polonica, 21, 574–616.

BEDNARCZYK W., 1981: Stratygrafia ordowiku Gór Świętokrzyskich. In: Żakowa H. (ed.), Przewodnik LIII Zjazdu Polskiego Towarzystwa Geologicznego, Kielce, 35–41.

BEDNARCZYK W., 1999: Significance of the genus Tysanotos Mickwitz 1986 for the Ordovician stratigraphy of East-Central Europe. Polish Academy of Sciences, Bulletin, 47, 15–25.

BEDNARCZYK W. & TOMCZYK H., 1981: Wybrane problemy stratygrafii, litologii i tektoniki wendu i starszego paleozoiku Gór Świętokrzyskich oraz niecki miechowskiej. Punkt 4: Bardo Stawy. In: H. Żakowa (ed.), Przewodnik LIII Zjazdu Polskiego Towarzystwa Geologicznego, Kielce, 139–143.

CHLEBOWSKI R., 1971: Petrografia utworów ordowiku rejonu synkliny bardziańskiej w południowej części Gór Świętokrzyskich. Archiwum Mineralogiczne, 29, 193-304.

CZARNOCKI J., 1939: Sprawozdanie z badań terenowych wykonanych w Górach Świętokrzyskich w 1938 r. Biuletyn Państw. Inst. Geol., 15, 1–41.

DZIK J., 1994: Conodonts of the Mójcza Limestone. Palaeontologia Polonica, 53, 43-128.

DZIK J., PISERA A., 1994: Sedimentation and fossils of the Mójcza Limestones. Palaeontologia Polonica, 53, 5–41.

GÓRKA H., 1969: Mikroorganismes de l'Ordovician de Pologne. Paleontologia Polonica, 22, 1–102.

HOLMER L.E., & BIERNAT G., 2002: Lingulate brachiopods from Lower Ordovician (Tremadoc) chalcedonites, Holy Cross Mountains, Poland. Acta Palaeontologica Polonica, 47,141–156

KIELAN Z., 1956: Stratygrafia górnego ordowiku w Górach Świętokrzyskich. Acta Geologica Polonica, 6, 253–271.

KOWALCZEWSKI Z., 2000: Litostratygrafia, paleogeografia, facje i tektonika kambru świętokrzysko-nidziańskiego (zagadnienia podstawowe i stan ich znajomości). Pr. Inst. Geogr. WSP w Kielcach, 4, 7–66.

KREMER B., 2005: Mazuelloids: product of post-mortem phosphatization of acanthomorphic acritarchs. Palaios, 20, 27–36.

KREMER B., KAŹMIERCZAK J., 2005: Cyanobacterial mats from Silurian black radiolarian cherts: phototrophic life at the edge of darkness? Journal of Sedimentary Research, 75, 897–906.

MASIAK M., PODHALAŃSKA T., STEMPIEŃ-SAŁEK M., 2003: Ordovician-Silurian boundary in the Bardo Syncline (Holy Cross Mountains) – new data on fossil assemblages and sedimentary succession. Geological Quarterly, 47, 311–329.

RYKA W., RUBINOWSKI Z., 1962: Wycieczka IB2. Trasa: Kielce – Zalesie pod Łagowem – Bardo – Prągowiec – Łagów – Daleszyce (Góra Salkowa) – Kielce. In: H. Żakowa (ed.), Przewodnik XXXV Zjazdu PTG, Kielce 16-19 wcześnie 1962, 116–125.

SZANIAWSKI H., 1980: Conodonts from the Tremadocian chalcedony beds, Holy Cross Mountains (Poland). Acta Geologica Polonica, 25, 101–121.

TEMPLE J.T., 1965: Upper Ordovician brachiopods from Poland and Britain. Acta Palaeontologica Polonica, 10, 379–450.

TOMCZYK H., TOMCZYKOWA E., 1962: Wycieczka IB1. Trasa: Kielce – Zalesie pod Łagowem – Bardo – Prągowiec – Międzygórz – Kilece. In: H. Żakowa (ed.), Przewodnik XXXV Zjazdu PTG, Kielce 16-19 wcześnie 1962, 100–115.

TRELA W., 2001: Sedimentary record of changing hydrodynamic conditions in the upper Tremadoc deposits of the Holy Cross Mountains, Poland. Geological Quarterly, 45, 131–142.

TRELA W., 2006a: Litostratygrafia ordowiku w Górach Świętokrzyskich. Przegląd Geologiczny, 54, 622–631.

TRELA W., 2006b: Ordowik w Górach Świętokrzyskich: zapis stratygraficzny i sedymentacyjny. In: S. Skompski & A. Żylińska (eds), Procesy i Zdarzenia w Historii Geologicznej Gór Świętokrzyskich – LXXVII Zjazd Naukowy Polskiego Towarzystwa Geologicznego, 28–35.

TRELA W., 2009: Rhuddanian black shales in the Holy Cross Mountains (Poland): sedimentary record of the anoxic/dysoxic event in early Silurian. In: G. Haczewski (ed.), 6th Annual Conference of SEPM-CES, Sediment 2009, Kraków, 24-25 June, 2009. Abstracts and Field Guide, 40.

TRELA W., SALWA S., 2007: Litostratygrafia dolnego syluru w odsłonięciu Bardo Stawy (południowa część Gór Świętokrzyskich): związek ze zmianami poziomu morza i cyrkulacją oceaniczną. Przegląd Geologiczny, 55, 971–978.

STOP 2: Diabase intrusion at Zalesie

Roman WŁODYKA¹, Łukasz KARWOWSKI¹, Krzysztof SZOPA¹

¹ Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec

The diabase sill near Zalesie village crops out in the bed of the unnamed stream where very fresh rock exhibits columnar jointing (Fig. 8) on one bank and disintegrated rock on the other. Its thickness amounts to about 18 m (Kardymowicz 1967). It intrudes Silurian graptolite shales with greywacke bands. In the stream section, the contacts between sill and sediments are not visible. A full vertical section is well-known from a borehole at Zalesie (Kardymowicz 1957, 1967). Systematic variation of textures across its width is a result of large cooling rates and the degree of magma supercooling. The Zalesie sill shows a symmetrical pattern consisting of spilitic diabases at the upper (0.35 m thick)- and lower (0.2 m) chilled margins which grade, over ca 0.5-1 m, through fine- to medium-grained varieties in the central part. This part of the sill is only visible in the bed of the stream. The rock exposed here shows the smallest grain size when compared to other sills from the Bardo syncline; macroscopically the rock looks like basalt. According to Kardymowicz (1957, 1967), graptolite shales in contact with diabase have been transformed into hornfelses. The thicknesses of the metamorphosed zones, upper and lower, vary between 0.3-0.4 m. Many veins (< 15 mm thick) of chalcedony, calcite and quartz intersect the entire sill. Thus, within the profile of the Zalesie sill, one can distinguish: 1) a calcite-albite (spilitic) diabase with hyaloophitic, intersertal and microlithic texture in the chilled margins (invisible) and 2) an augite-plagioclase tholeiite diabase with intersertal and subophitic texture from the central parts of the sill. The chemistry the latter tholeiite diabase is as follows (wt %): SiO₂(49.90), TiO₂(2.20), Al₂O₃(12.80), Fe₂O₃(5.01), FeO(8.33), MnO(0.25), MgO(4.73), CaO(8.93), Na₂O(2.09), K₂O(0.75), P₂O₅(0.42), H₂O⁺(1.82), H₂O⁻ (2.06), SO₃(0.45), $\Sigma(99.74)$ (Kardymowicz 1957, Table 1, an. 3)



Fig. 8. The outcrop of the diabase sill in the bed of the unnamed stream near Zalesie village.



Fig. 9. Diabase from the central parts of the Zalesie sill, crossed nicols.



Fig. 10. Glassy inclusion in network plagioclase and spiky ("swallow-tail" microlite) plagioclase crystal.



Fig. 11. Skeletal and acicular microlites of feldspars and dendritic crystal of titanomagnetite (opague).

Fig. 12. Skeletal crystals of clinopyroxene, dendritic Ti-magnetite among branching feldspars microlites; reflected light.

Under the microscope (Fig. 9), samples from the central parts of the sill comprise a random network of relatively large plagioclase laths, up to 0.8 mm in length, anhedral grains of pyroxene and a late crystallized matrix occupying the spaces between them. Small-scale fragmentation of the network feldspars has been observed (Kardymowicz 1957); plagioclase laths and pyroxene grains with glassy inclusions (*sieve texture*) are also visible (Fig. 10). The fine-grained groundmass contains spiky ("swallow-tail" microlites (Fig. 10), skeletal- (Fig. 11) and branching (Fig. 12) non-equilibrium plagioclase microcryst morphologies attributed to supercooling, and hence rapid growth. In addition, the mesostasis contains elongated skeletal augite crystals (Fig. 12) that, in some cases, have grown in clustered, fan-like aggregates, dendritic crystals of titanomagnetite and acicular (needle-like) microlites of amphibole and apatite.

X-ray diffraction patterns of hand-picked samples of the mesostasis (Fig. 13) show a broad hump (arrow 1), typical of amorphous substances, distinct broad (arrow 2)- and

narrow peaks (symbols a, p, q, m); these last are attributed to the crystallized phases mentioned immediately above. This means that the interstitial material between the plagioclase laths may have also been quenched and replaced by palagonite (Ryka 1957b). According to Stroncik and Schmincke (2001), palagonitization is a continuous process of glass dissolution and palagonite formation when the glass reacts with surrounding fluids and crystallizes to smectite. They use the term palagonite only for the amorphous alteration products of mafic glasses. An X-ray pattern indicates that palagonite evolves from amorphous, metastable material (arrow 1) to a mainly crystalline product (arrow 2 a, b, c).



Fig. 13 a- X-ray diffraction pattern of mesostasis material from Zalesie sill; b-X-ray pattern of trioctahedral smectite from Dębowiec near Ziębice.



Fig. 14. Palagonitization of volcanic glass from Bardo syncline sills; symbols: ppalagonite, s-smectite, q- quartz and ccarbonates (ankerite).



Fig. 15. The in situ replacement of microcrystalline interstitial material between plagioclase network by fibrous smectite.



Fig. 16. Two morphological forms of saponite: fibrous (left) and lamellar (right).

It shows strong peaks at 15.5 (2a - 001), 4.50 (2b - 020) and 2.56 (2c - 110) Å. The position of the 060 peak (1.53Å, trioctahedral), and the results of microprobe analysis (Table 1, an. 1-3), indicate that saponitic smectite is the final product of palagonite evolution. The transformation of palagonite to smectite is shown on Fig. 14. Palagonite

formation is accompanied by loss of Si, Al, Mg, Ca, Na and K which is linked to the precipitation of quartz and carbonates (ankerite). The results of our own chemical analyses of the palagonitization of volcanic glass from the Bardo sills, and of analyses from the literature, are summarizing in Table 1. The in situ replacement of microcrystalline, interstitial material lying between plagioclase laths by more thermodynamically stable smectite is shown on Fig. 15. On Fig. 16, two morphological forms of saponite are shown. One is fibrous, the other lamellar, brownish-reddish and strongly anisotropic.



Fig. 17. The evolution trend of clinopyroxene composition from Zalesie sill.



Fig. 18. Ternary feldspars compositions.

	smectite			palagonite			
	1	2	3	4	5	6	7
SiO ₂	47.17	46.10	44.99	39.78	35.73	38.79	38.36
TiO ₂	0.09	0.13	0.07	2.14	0.30	0.00	-
Al_2O_3	3.61	4.39	4.17	8.20	5.09	5.26	5.54
Cr ₂ O ₃	0.02	0.03	0.03	0.18	0.13	0.00	-
MgO	12.99	12.01	10.96	6.18	4.01	4.89	9.41
CaO	1.20	1.56	1.51	7.17	1.66	2.29	0.73
MnO	0.09	0.08	0.14	0.44	0.22	0.03	-
FeO [#]	22.92	23.49	24.43	21.49	22.56	24.31	19.53
Na ₂ O	0.04	0.04	0.05	1.55	0.60	0.09	0.46
K ₂ O	0.14	0.14	0.13	1.65	0.65	0.42	4.67
Total	88.26	87.95	86.47	88.78	70.95	76.08	78.70

Table 1. Chemical analyses of palagonitization products of volcanic glass from Bardo syncline sills; an. 4 from Ryka (1957b), an.5-6 from Krzemiński (2004) and an. 7 from Morozewicz (1923).

Table 2. Microprobe analyses of feldspars.

		Co	ore	Rim			
	1	2	3	4	5	6	7
SiO ₂	52.32	53.29	54.69	56.63	59.06	62.24	63.79
Al_2O_3	29.50	28.50	28.28	26.71	25.02	23.80	22.55
CaO	13.26	12.27	11.83	9.83	7.44	5.67	4.36
FeO	0.55	0.84	0.64	0.55	0.48	0.53	0.52
BaO	0.00	0.04	0.04	0.00	0.03	0.11	0.21
Na ₂ O	4.23	4.78	5.01	5.94	7.13	8.04	8.86
K ₂ O	0.20	0.21	0.21	0.32	0.57	0.79	0.90
Total	100.06	99.93	100.70	99.98	99.73	101.18	101.20
Si	2.382	2.428	2.464	2.553	2.654	2.745	2.807
Al	1.583	1.530	1.501	1.419	1.325	1.237	1.169
Ca	0.647	0.599	0.571	0.475	0.358	0.268	0.206
Fe	0.021	0.032	0.024	0.021	0.018	0.020	0.019
Ba	0.000	0.001	0.001	0.000	0.001	0.002	0.004
Na	0.373	0.422	0.437	0.519	0.621	0.688	0.756
K	0.011	0.012	0.012	0.018	0.033	0.045	0.051
Total	5.017	5.024	5.010	5.005	5.010	5.005	5.012
An	62.8	58.0	56.0	46.9	35.4	26.8	20.3
Ab	36.2	40.9	42.8	51.3	61.4	68.7	74.6
Or	1.1	1.2	1.2	1.8	3.3	4.5	5.0

		Amphibole				
	Core			Ri	m	Core
	1	2	3	4	5	6
SiO ₂	51.49	50.32	50.31	49.76	50.93	48.37
TiO ₂	0.84	0.99	0.90	0.69	0.57	0.81
Al ₂ O ₃	1.65	1.79	1.21	1.07	0.84	3.99
Cr ₂ O ₃	0.04	0.08	0.00	0.01	0.00	0.00
MgO	15.00	12.91	11.44	9.56	12.72	9.47
CaO	18.60	18.14	17.33	16.41	14.76	9.55
MnO	0.29	0.36	0.45	0.59	0.55	0.53
FeO [#]	10.92	14.64	17.86	20.84	19.28	22.69
NiO	0.00	0.02	0.00	0.00	0.04	0.00
Na ₂ O	0.25	0.27	0.25	0.21	0.20	2.37
K ₂ O	0.00	0.00	0.00	0.01	0.01	0.77
Total	99.07	99.51	99.75	99.15	99.90	98.55
Si	1.939	1.917	1.938	1.957	1.956	7.209
Ti	0.024	0.028	0.026	0.020	0.016	0.091
Al	0.073	0.080	0.055	0.050	0.038	0.701
Cr	0.001	0.002	0.000	0.000	0.000	0.000
Fe ³⁺	0.019	0.047	0.036	0.012	0.033	0.806
Mg	0.842	0.733	0.657	0.560	0.728	2.105
Ca	0.750	0.740	0.715	0.691	0.607	1.524
Mn	0.009	0.011	0.015	0.020	0.018	0.067
Fe ²⁺	0.325	0.420	0.540	0.673	0.586	2.022
Ni	0.000	0.001	0.000	0.000	0.001	0.000
Na	0.018	0.020	0.019	0.016	0.015	0.685
Κ	0.000	0.000	0.000	0.000	0.001	0.146
Total	4.000	3.999	4.001	3.999	3.999	15.634

Table 3. Representative pyroxene (augite) and amphibole (magnesiohornblende) analyses.

The igneous minerals were originally augite and plagioclase as major components and titanomagnetite, ilmenite, apatite and magnesiohornblende as accessories. Olivine was not etected in the diabase from the Bardo syncline. In the Łysogóry (northern) region, Krzemiński (2004) found a small amount of fresh olivine (Fo₇₁₋₅₈) in the Milejowice-Janowice diabase. Augite (Fig. 17, Table 2) evolves along the path $Wo_{39}En_{44}Fs_{17} \Rightarrow Wo_{32}En_{30}Fs_{38}$, as is characteristic for clinopyroxenes from tholeiitic, silica-saturated rocks. Ryka (1959) detected, in addition, orthopyroxenes (enstatite) in diabase from Widełki and Łabęcki (1969) found secondary aegerine in spilitic diabase from Bardo. Representative

analyses of plagioclase feldspar are given in Table 2 and compsitional ranges are shown in Fig. 18. Opaque phases are ilmenite and titanomagnetite (Table 4). Highly acicular apatites in the matrix are typical of those found in rapidly crystallized rocks. Magnesiohornblende occurs as a late magmatic phase mainly in the groundmass (Table 3).

		Magnetite		Ilmenite			
	1	2	3	1	2	3	
SiO ₂	0.09	0.04	0.09	0.00	0.01	0.00	
TiO ₂	24.54	23.79	21.70	50.79	50.02	50.04	
Al ₂ O ₃	1.68	1.60	1.20	0.01	0.00	0.00	
FeO [#]	67.26	67.69	69.81	46.70	46.29	47.64	
MnO	1.61	1.64	1.63	1.20	0.65	0.61	
MgO	0.15	0.16	0.03	1.20	0.49	0.45	
CaO	0.00	0.00	0.05	0.01	0.01	0.02	
Na ₂ O	0.00	0.03	0.03	0.00	0.00	0.00	
Cr ₂ O ₃	0.04	0.06	0.02	0.00	0.00	0.04	
ZnO	0.01	0.16	0.05	0.00	0.08	0.00	
V_2O_3	0.70	0.74	0.25	0.36	0.39	0.45	
NiO	0.07	0.00	0.02	0.00	0.00	0.01	
Nb ₂ O ₃	0.00	0.00	0.02	0.00	0.00	0.00	
Total	96.15	95.91	94.89	99.70	97.94	99.26	
Si	0.004	0.002	0.003	0.000	0.000	0.000	
Ti	0.701	0.681	0.628	0.957	0.965	0.952	
Al	0.075	0.072	0.055	0.000	0.000	0.000	
Fe ³⁺	0.492	0.538	0.673	0.080	0.062	0.086	
Fe ²⁺	1.644	1.616	1.573	0.898	0.931	0.921	
Mn	0.052	0.053	0.053	0.014	0.014	0.013	
Mg	0.008	0.009	0.001	0.045	0.019	0.017	
Ca	0.000	0.000	0.002	0.000	0.000	0.001	
Na	0.000	0.002	0.002	0.000	0.000	0.000	
Cr	0.001	0.002	0.001	0.000	0.000	0.001	
Zn	0.000	0.004	0.001	0.000	0.002	0.000	
V	0.021	0.023	0.008	0.007	0.008	0.009	
Ni	0.002	0.000	0.001	0.000	0.000	0.000	
Nb	0.000	0.000	0.001	0.000	0.000	0.000	
Total	3.001	3.001	3.001	2.000	2.000	2.000	

Table 4. Representative microprobe oxide analyses.

References:

CZARNOCKI J., 1919: Stratygrafia i tektonika Gór Świętokrzyskich. Pr. Tow. Nauk. wa, 28, 1-172.

KARDYMOWICZ I., 1957: Z petrografii diabazów Gór Świętokrzyskich. Kwart. Geol., 1 (1), 139-154.

KARDYMOWICZ I., 1967: Intruzje mniejsze Gór Świętokrzyskich. Biul. Inst. Geol., 197, 329-412.

KOWALCZEWSKI Z., LISIK R., 1974: Nowe dane o diabazach i budowie geologicznej okolic Prągowca w Górach Świętokrzyskich. Biul. Inst. Geol., 275, 113-158.

- KRZEMIŃSKI L., 2004: Geochemical constraints on the origin of the mid-Palaeozic diabases from the Holy Cross Mts. And Upper Silesia, southeastern Poland. Geol. Quart., 48 (2), 147-158.
- ŁABĘCKI J., 1969: Nowe dane o petrografii diabazów bardziańskich. Kwart. Geol., 13 (4), 944-945.
- ŁABĘCKI J., 1970: Petrochemiczna charakterystyka diabazów i lamprofirów świętokrzyskich w świetle nowych badań. Kwart. Geol., 14 (4), 944-945.
- MAŁKOWSKI S., 1954: O przejawach wulkanizmu w dziejach geologicznych Gór Świętokrzyskich. Acta Geol. Pol., 4, 1-52.
- MOROZEWICZ J., 1923: O bardolicie, pirogenicznym minerale chlorytowym. Spraw. Państw. Inst. Geol., 2 (3/4), 217-224.
- MOROZEWICZ J., 1925: O diabazie Gór Świętokrzyskich. Spraw. Państw. Inst. Geol., 3 (1/2), 1-14.
- MIGASZEWSKI Z. M., 2002: Datowanie diabazów i lamprofirów świętokrzyskich metodą K-Ar i Ar-Ar. Prz. Geol., 50, 227-229.
- NAWROCKI J., 1999: Przedfałdowa pozostałość magnetyczna intruzji diabazów z synkliny Barda w Górach Świętokrzyskich. Prz. Geol., 47, 1101-1104.
- NAWROCKI J., 2000: Late Silurian paleomagnetic pole from the Holy Cross Mountains: constraints for the post-Caledonian tectonic activity of the Trans-European Suture Zone. Earth Planet. Sci. Lett., 179, 325-334.
- NAWROCKI J., DUNLAP J., PECSKAY Z., KRZEMIŃSKI L., ŻYLIŃSKA A., FANNING M., KOZŁOWSKI W., SALWA S., SZCZEPANIK Z., TRELA W., 2007a: Late Neoproterozoic to Early Palaeozoic palaeogeography of the Holy Cross Mountains (Central Europe): an integrated approach. J. Geol. Soc., 164, 405-423.
- NAWROCKI J., POLECHOŃSKA O., SALWA S., 2007b: Model przestrzenny intruzji bardziańskiej w okolicach Zagórza (region kielecki Gór Świętokrzyskich) w świetle wyników nowych badań magnetycznych. Prz. Geol., 55, 1136-1142.
- PRZYBYŁOWICZ T., STUPNICKA E., 1991: Przejawy wulkanizmu w ordowiku i sylurze południowej części Gór Świętokrzyskich. Arch. Miner., 47, 137-154.
- RYKA W., 1957a: O intruzji diabazowej w zachodniej części niecki bardziańskiej. Kwart. Geol., 1 (1), 155-161.
- RYKA W., 1957b: Nowe spostrzeżenia dotyczące diabazu z Barda (Góry Świętokrzyskie). Kwart. Geol., 1 (2), 229-352.
- RYKA W., 1959: Przeobrażenia diabazu i skał otaczających w Widełkach (Góry Świętokrzyskie). Kwart. Geol., 3 (1), 160-196.
- RYKA W., 1974: Brekcje, kataklazyty i mylonity diabazu z Kędziorki w Górach Świętokrzyskich. Biul. Inst. Geol., 275, 159-169.
- STRONCIK N. A., SCHMINCKE H. U., 2001: Evolution of palagonite: Crystallization, chemical changes, and element budget. Geochem. Geophys. Geosyst., 2, paper number 2000GC000102.

- SUCHÝ V., ŠAFANDA J., SÝKOROVÁ I., STEJSKAL M., MACHOVIČ V., MELKA K., 2004: Contact metamorphism of Silurian black shales by a basalt sill: geological evidence and thermal modeling in the Barrandian Basin. Bull. Geosciences, 79 (3), 133-145.
- SZCZEPANOWSKI W. J., 1963: Badania geochemiczne wulkanitów Gór Świętokrzyskich. Cz. II - diabazy. Kwart. Geol., 7 (1), 53-62.
- TOKARSKI J., 1921: O skale magmatycznej odkrytej w Górach Świętokrzyskich. Kosmos, 46 (4), 625-638.
- TOKARSKI J., 1926: Uwagi w sprawie skały magmatycznej odkrytej w Górach Świętokrzyskich. Arch. Tow. Nauk. we Lwowie. 4 (2), 11-20.

STOP 3: Phyllites from Kamecznica Podmąchocicka – metamorphic rocks from in the Holy Cross Mountains

Sylwester SALWA

¹ Polish Geological Institute-National Research Institute, Holy Cross Mountains Branch, Zgoda 21, 25-593 Kielce, Poland; sylwester.salwa@pgi.gov.pl

The presence of metamorphic rocks in the Holy Cross Mountains (HCM) was mentioned first by Czarnocki (1919). On the basis of chemical composition, Sedlak (1985) called them "phyllite rocks from Dalionka stream". However, the first well documented example of metamorphic rocks in the HCM was described by Salwa (2005, 2006a,b) in Kamecznica Podmąchocicka, along deep unnamed ravine in the central part of the Lysogóry Region (Fig. 19). We can see there outcrops of the Middle Cambrian rocks of the Pepper Mountains Formation (Orłowski 1975), which occur in walls and bottom of the stream valley (Fig. 19.d, 20). This section is composed of three different lithological parts. The lowermost portion is dominated by claystones and mudstones overlain by sandstones and mudstones of the middle complex, which builds also the main part of a ravine. The uppermost part of the Kamecznica Podmąchocicka section is made up of mudstones and claystones intercalated by sandstones.

Petrographic and petrotectonic investigations indicate that this succession refers to the very low grade and low grade metamorphic rocks (Salwa 2005, 2006a,b). The most intensively metamorphosed zones include phyllites called "phyllites from Podmąchocice" (Salwa 2006a). A conspicuous relationship between metamorphism and tectonic deformations has been identified within the considered herein section. Phyllites appear always above thrust fault plains within strong tectonically deformed (folded and thrusted) zones (Fig. 19.d, 20, 21). New minerals grew along cleavage plains (Fig. 22) and within microlithons (Fig. 23.a-c). Quartz, white mica, chlorites and siderite are main components of phyllites, and they are accompanied by subordinate dolomite, piryte, hematite, apatite and biotite.

Basing on detailed mesostructural analysis, a few events of structural evolution of metamorphic rocks were distinguished (Salwa 2005, 2006a,b). The older stage D_1 took place in the Cambrian and originated from earthquakes. The first generation of cleavage was formed during D_2 stage. The white mica (Fig. 23.b) accompanied by mica-chlorite stacks (mostly biotite-chlorite stacks) within its planes (fig 23.a) occurs along planes of the low-angle slaty cleavage 2S_1 (Fig. 22.a). Detrical biotite crystals were plastically folded during formation of the cleavage (Fig. 23.a). Diffused in clay matrix detrical quartz was resolving bay hot fluids (Fig. 23.a). At the end of this stage the first generation of syntaxial quartz-chlorite veins 1V_1 arose. During the D_3 stage numerous thrust faults 3U_1 , 3U_2 (Fig. 19) and related folds 3F_2 (Fig. 20, 21) with axial plane crenulation cleavage 3S_2 (Fig. 22b) were formed. The crenulation cleavage 3S_2 deformed both sedimentary and slaty cleavage 2S_1 planes (Fig. 22.b). The Fe and Fe-Mg chlorites (Fig. 24, 25) and siderites with rarely preserved zones predominate within microlithos (separating cleavage domains to one another) are common. The composition of the inner part of chlorites suggests their formation from chloritized biotites (Fig. 23.c – central part of the chlorite). Moreover, porphiroclasts of Fe-rich chlorites with pressure shadows were reported within thrust fault related to shear zones. In some samples apatite and biotite are present.



Fig. 19. Location of the study area (a) in relation to the main structural units of Poland (b), Paleozoic core (c) of the Holy Cross Mountains (after Czarnocki 1950, Kowalczewski 1975, Dadlez, Kowalczewski & Znosko 1994 – modified) and tectonics sketch of Kamecznica Podmąchocicka (d).




Fig. 20. Outcrop of the folded phyllites from Podmąchocice.

Fig. 21. Symilar folds ${}^{3}F_{2}$ in the phyllite.

The commonly occurring quartz-chlorite (Fig. 23.d) and siderite veins ${}^{3}V_{2}$ were produced at the end stage of the metamorphism-related deformation processes. They are mostly represented by the antitaxial and stretched crystal veins. The latter type occurs commonly within horizontal and low-angle shear zones and achieves notable sizes (Fig. 26), which is characteristic for very low grade and low grade metamorphic areas (Jessell, Willman 1994).

The D_4 tectonic stage is represented by thrust faults 4U_3 , folds 4F_3 and crenulation cleavage 4S_3 . These mesostructures are restricted to narrow, intensively deformed shear zones cutting older faults, folds and cleavages. At the end of this stage the youngest, weakly widespread generation of quartz-chlorite veins 4V_3 was formed.



Fig. 22. Various kinds of cleavage and their relationship in phyllite from Podmąchocice: a – low-angle slaty cleavage ${}^{2}S_{1}$ defining the first generation of the foliation, b – axial plane crenulation cleavage ${}^{3}S_{2}$.

The described above tectonic mesostructures resulted from the progressive deformation produced by the tectonic compression directed from E (stage D_2), NE (stage D_3) and then

NNE (stage D_4) direction. Deformations and composition of minerals suggest that phyllites from Podmachocice correspond to the green facies metamorphism. The presence of ductile folded biotite blades (Fig. 23.a), subgrains and deformation lamellaes within quartz (Fig. 27) and translational lamellaes in dolomite crystals indicates that the temperature ranging from 300°C to 350°C (Passchier, 1996) and differential stress above 1.7 kbar (Koch, Christie 1981).



Fig. 23. Various types of chlorite occurrences in phyllites from Podmąchocice: a – micachlorite stacks, b - idioblasts of chlorites, c – chlorite crystals with zonal shape, d – chlorites in veins. Chl – chlorite, Q – quartz, M – mica.



Fig. 24. Energy dispersive spectroscopic spectra of studied chlorites.



Fig. 25. Chlorite compositions projected onto the Hey's diagram.



Fig. 26. Dynamically recrystalized quartz and chlorites within shear zone (a). (b) Detail from picture a microscopic view. Q – quartz, Chl – chlorites, arrows – sense of displacement The precise age of deformations and metamorphism is difficult to decipher, but combined tectonic and mineralogical data suggest that these processes took place after the Late Cambrian. It is supported by close association of the quartz-chlorite veins with the Cambrian and Tremadocian rocks (Salwa 2006a). On the other hand, the presence of pebbles of the Cambrian quartzitic sandstones in the Międziana Góra conglomerate (Czarnocki, 1926; Kowalczewski and Dadlez, 1996) suggests the pre-Devonian age of metamorphism and related-deformations.



Fig. 27. Subgrains (a) and two generations of the deformational lamellae (La) in quartz (b).

References:

- CZARNOCKI J., 1919: Stratygrafia i tektonika Gór Świętokrzyskich. Pr. Tow. Nauk. Warszawa, 28: 1-172.
- CZARNOCKI J., 1950: Geologia regionu łysogórskiego w związku z zagadnieniem złoża rud żelaza w Rudkach. Prace Instytutu Geologicznego, 6a.
- DADLEZ R., KOWALCZEWSKI Z., ZNOSKO J., 1994: Some key problems of the pre-Permian tectonics of Poland. Geological Quarterly, 38: 169-190.
- JESSELL M.W., WILLMAN C.E., GRAY D.R., 1994: Bedding parallel veins and their relationship to folding. Journal of Structural Geology, 16: 753-767.
- KOCH P.S., CHRISTIE J.M., 1981: Spacing of deformation lamellae as a paleopiezometr. Abstracts Transactions of American Geophysical Union, 62: 1030.
- KOWALCZEWSKI Z., 1975: Tektonika i tektogeneza paleozoiku i mezozoiku Gór Świętokrzyskich. Studium strukturalne Pasma Masłowskiego i Klonowskiego. Archiwum Państwowego Instytutu Geologicznego, Kielce.
- ORŁOWSKI S., 1975 Jednostki stratygraficzne kambru i górnego prekambru Gór Świętokrzyskich. Acta Geologica Polonica, 25: 431-448.
- PASSCHIER C.W., TROUV R.A.J., 1996: Microtectonics. Springer Verlag, Berlin.
- SALWA S., 2005 Metamorfizm i jego miejsce w procesie deformacji skał kambryjskich jednostki łysogórskiej w Górach Świętokrzyskich. Posiedzenia Naukowe Państwowego Instytutu Geologicznego, 60: 55-56.
- SALWA S., 2006a: Wstępna charakterystyka strukturalno-petrograficzna fyllitów z Podmąchocic w regionie łysogórskim Gór Świętokrzyskich. Przegląd Geologiczny, 54: 513-520.
- SALWA S., 2006b: Stanowisko 1: Kamecznica Podmąchocicka fyllity występujące wśród skał środkowego kambru. In: Skompski S., Żylińska A., (eds.) – Procesy i

zdarzenia w historii geologicznej Gór Świętokrzyskich. Przewodnik 77 Zjazdu Polskiego Towarzystwa Geologicznego, wycieczka W1: 155-159. SEDLAK W., 1985: Z dziejów odkrycia śladów kambryjskiego życia w kwarcytach łysogórskich. Rocznik Świętokrzyski, 12: 31-47.

MINERALOGIA - SPECIAL PAPERS, 35, 2009 www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Field session 3

Two different examples of the Upper Devonian – Lower Carboniferous successions in the Holy Cross Mountains, Poland

Leszek MARYNOWSKI¹, Maria RACKA¹

¹ University of Silesia, Faculty of Earth Sciences, Będzińska Str. 60, 41-200 Sosnowiec, Poland leszek.marynowski@us.edu.pl; maria.racka@us.edu.pl

Introduction

Two key Upper Devonian to Lower Carboniferous sedimentary successions from the southern Holy Cross Mountains are presented to show contrasting palaeogeographic settings of the Laurussian carbonate shelf. Stratigraphically extended Kowala section represents continuous deepening-upward transition from the Dyminy reef complex to the Chęciny-Zbrza intrashelf basin. On the other hand, despite generally similar facies evolution, the partly condensed Gałęzice succession is marked by stratigraphic gaps, typical for a pelagic swell. The carbonate shelf drowning was finalized with Visean sedimentation of black siliceous shales in the starved basin.



Fig. 1. Simplified geological map of the western and central part of the Holy Cross Mountains with location of the Kowala and Ostrówka quarries.

STOP 1: Kowala quarry

The whole of the Upper Devonian sedimentary succession, more than 350 m thick, is exposed in the well-known Kowala (formerly Wola) active quarry near Kielce (Fig. 1). The immense exposure is geologically located in the southern part of the Kielce Region, in the gently dipping southern limb of the Gałęzice Syncline.

In this excursion, we will focus on the extended Famennian part (ca. 180 m thick) of the continuous section that corresponds to the post-reef phase of carbonate shelf evolution (i.e., to the oxygen-depleted Chęciny-Zbrza basin; Szulczewski, 1995; Racki et al., 2002). Within the rhythmic, dark to black, clayey-calcareous bituminous deposits with abundant early-diagenetic pyrite, recurrent anoxic pulses of worldwide range are perfectly recorded, mostly as distinguishing horizons of bituminous shales. Studies of exceptionally immature organic matter provided evidence for the episodic occurrence of isorenieratane and gammacerane indicating water column anoxia, reaching the photic zone during Famennian global anoxic events (Joachimski et al., 2001; Marynowski and Filipiak, 2007).

The following five lithologically specific levels, representing the diversity of sedimentary phenomena, are presented with reference to the results of multidisciplinary event-stratigraphic studies involving biomarkers, trace elements and pyrite framboid diameter as a proxy of redox conditions:

- Frasnian-Famennian (**F-F**) boundary beds, corresponding to the mass extinction event (Joachimski et al., 2001; Racki et al., 2002; Bond et al., 2004). This level is marked by an abrupt lithologic change from thin-bedded fossil-rich marly deposits to uniquely thick-bedded and cherty limestones which is accompanied by a biotic switch from a diverse calcareous to a limited siliceous biota (sponges and radiolarians). Dark chert bands from the F-F boundary yielded abundant pyrite framboids with a size-frequency distribution characteristic of euxinic deposition, but this interval is characterized by rather fluctuating redox conditions in near-bottom settings.
- Middle Famennian pyritized fauna horizon (Marynowski et al., 2007). Numerous pyrite concretions and pyritized fossils, mostly ammonoid shells, occur in dark marly shales, interbedded with thin limestone layers and carbonate nodules. The majority of the framboids have larger diameters, characteristic of formation within the sediments, below a dysoxic water column.
- Basal Upper Famennian Annulata black shale (**ABS**; Bond and Zatoń, 2003; Racka and Marynowski, 2008). The oldest of several Famennian global anoxic events paired with a bloom of specially adapted biota. The spectacular bipartite black shale horizon (TOC up to 23 wt.%), 1.1 m thick in total, with intercalated thin nodular-marly and black limestone layers. Bottom-water conditions were dysoxic during the lower ABS, whereas the upper horizon originated in a strictly anoxic, most probable euxinic sedimentary regime.
- Topmost Famennian Hangenberg black shale (**HBS**; Marynowski and Filipiak, 2007; Trela and Malec, 2007). This level represents a large-scale biotic crisis recorded in a 0.9 m thick bituminous shale (TOC up to 22.5 wt.%) within grey to brownish fossil-rich calcareous succession with shale partings displaying corrosional surfaces (Woclumeria limestone). The Devonian-Carboniferous boundary is identified palynostratigraphically ca 2 m above. Greenish intercalations of tuffite occur below and above the HBS. The presence of high concentrations of peri-condensed polycyclic aromatic hydrocarbons and large

amounts of small charcoal particles indicates the occurrence of wildfires due to concomitant volcanic activity.

• Lower Tournaisian volcaniclastics (Kozłowski, 1981; Dzik, 1997). Increased explosive Eovariscan volcanic activity is indicated by greenish claystones with several thin black shale partings within a dominantly gray and cherry-coloured clayey succession with limestone intercalations (Radlin Beds), capped by black shales and radiolarites (Zaręby Beds, not exposed in the quarry). The Lower Carboniferous strata are strongly altered surficially (up to 2 m) by pre-Zechstein weathering processes, as perfectly exposed recently (August 2009) on the northern wall of the Kowala quarry.

STOP 2: Ostrówka quarry

Ostrówka quarry is located between Miedzianka hill and Gałęzice village on the NW limb of the Chęciny Anticline (Fig. 1). The exposed section illustrates drowning of a small fragment (seamount) of the Givetian-Frasnian carbonate platform which submerged during Late Devonian and Early Carboniferous times (Szulczewski et al., 1996a). The section in the Ostrówka quarry displays a wide stratigraphic range from the Middle/Upper Devonian to Carboniferous and is characterised by the following stratigraphic and lithologic sequences:

- The main part of the quarry exposes the light-creamy shallow-water Frasnian amphiporoid limestones interbedded with microbial laminites (Kowala Formation). They are interpreted as lagoonal facies with peritidal sediments (Szulczewski et al., 1996a). The upper part of the Frasnian section is characterised by the presence of Lofer-type cyclothems with regolithic and paleosol units (Skompski and Szulczewski, 2000).
- Discontinuous, 20-200 cm thick and highly-condensed Famennian pelagic limestones overlying Frasnian amphiporoid limestones. These dark-grey carbonates are remarkably fossiliferous with crinoids and cephalopods dominating. The associated fauna consist of corals, trilobites, brachiopods, gastropods and fish remains (Szulczewski et al., 1996b). These beds are interpreted as storm deposits, with crinoid debris at the bottom and cephalopods in their upper part (Szulczewski et al., 1996b).
- The next unit comprises the limestones, marls and clays of the Radlin Beds. In the lower part of the unit, pyroclastic layers have also been described (Migaszewski, 1995). The basal part of the unit belongs to the upper Tournaisian which suggests a significant stratigraphic gap between the Famennian and Lower Carboniferous (Szulczewski et al., 1996b). This sequence is moderately fossiliferous, yielding corals associated with trilobites, goniatites and fish remains (Szulczewski et al., 1996b).
- Also outcropping in the Ostrówka quarry is a unit of Lower to Upper (?) Visean black siliceous and marly shales. This unit with cherts and phosphatic nodules belongs to the clastic Zaręby Beds (Szulczewski et al., 1996b). Phosphatic concretions consist mainly of Al-rich carbonate-fluoroapatite as well as some rare phosphates, e.g., crandallite, plumbogummite and Fe-phosphates (Olszewska-Nejbert and Nejbert, 2005).
- Upper Visean bioclastic limestones outcrop in both Ostrówka quarry and an old trench on Todowa Grząba hill. The thickness of this unit does not exceed 35 m, but layers are laterally discontinuous and the unit is developed as a few lenticular

bodies (Szulczewski et al., 1996b). The extremely fossiliferous limestones contain an abundant benthic fauna of crinoids, corals and brachiopods (Szulczewski et al., 1996b). The unit is interpreted as a carbonate submarine fan deposited in a deep basin (Szulczewski et al., 1996a).

• The highest Carboniferous unit belongs to the Uppermost Visean and is represented by a clastic series (Lechówek Beds). These are mainly shales with siliceous intercalations, phosphatic concretions and tephra. Towards the top of the succession, the most significant are sandstone/greywacke intercalations with flora debris. Fauna is represented by goniatites, nautiloids and other pelagic forms. Recently, in the eastern part of the Ostrówka quarry, a relatively large section of these beds was exposed. The most interesting part of this section is a ca 30 cm thick highly fossiliferous limestone with corals and crinoid debris which is similar to that in the upper Visean. Several layers were macroscopically identified as tuffites. Some layers contain a great quantity of phosphatic concretions.

STOP 3: The Ore Mining Museum in Miedzianka

The museum is located in an old mine building in Miedzianka village. The museum contains minerals, rock samples and fossils from the Holy Cross Region.

References:

- BOND D., ZATOŃ M. 2003: Gamma-ray spectrometry across the Upper Devonian basin succession at Kowala in the Holy Cross Mountains (Poland). Acta Geol. Pol., 53, 93– 99.
- BOND D., WIGNALL P.B., RACKI G. 2004: Extent and duration of marine anoxia during the Frasnian-Famennian (Late Devonian) mass extinction in Poland, Germany, Austria and France. Geol. Mag., 141, 173–193.
- DZIK J. 1997: Emergence and succession of Carboniferous conodont and ammonoid communities in the Polish part of the Variscan sea. Acta Palaeont. Pol., 42, 57–170.
- JOACHIMSKI M.M., OSTERTAG-HENNING C., PANCOST R.D., STRAUSS H., FREEMAN K.H., LITTKE R., SINNINGHE DAMSTÉ, J.S., RACKI G. 2001: Water column anoxia, enhanced productivity and concomitant changes in δ13C and δ34S across the Frasnian-Famennian boundary (Kowala – Holy Cross Mountains/Poland). Chem. Geol., 175, 109–131.
- KOZŁOWSKI A. 1981: Melt inclusions in pyroclastic quartz from the Carboniferous deposits of the Holy Cross Mts., and the problem of magmatic corrosion. Acta Geol. Pol., 31, 273–284.
- MARYNOWSKI L., FILIPIAK P. 2007: Water column euxinia and wildfire evidence during deposition of the Upper Famennian Hangenberg event horizon from the Holy Cross Mountains (central Poland). Geol. Mag., 144, 569–595.
- MARYNOWSKI L., RAKOCIŃSKI M., ZATOŃ M. 2007: Middle Famennian (Late Devonian) interval with pyritized fauna from the Holy Cross Mountains (Poland): organic geochemistry and pyrite framboid diameter study. Geochem. J., 41, 187–200.
- MIGASZEWSKI, Z. 1995: Occurrence of pyroclastic rocks in the Lower Carboniferous of the Holy Cross Mountains (Central Poland). (English summary). Prz. Geol. 43, 7–11.
- OLSZEWSKA-NEJBERT, D., NEJBERT, K. 2005: Mineralogy and petrography of the phosphate concretions from Visean radiolarian shales near Gałęzice, Holy Cross Mountains, Poland. Pol. Tow. Mineral. Prace Spec. 25, 158–161.

- RACKA, M., MARYNOWSKI, L., 2008: Geochemical record of the late Famennian Annulata event at the Kowala quarry, Holy Cross Mountains, Poland (in Polish). Pierwszy Polski Kongres Geologiczny, June 26-28, 2008, Abstract, Polskie Towarzystwo Geologiczne, Kraków 95.
- RACKI G., RACKA M., MATYJA H., DEVLEESCHOUWER X. 2002: The Frasnian/Famennian boundary interval in the South Polish-Moravian shelf basins: integrated event-stratigraphical approach. Palaeogeogr., Palaeoclimatol., Palaeoecol., 181, 251–297.
- SKOMPSKI S., SZULCZEWSKI, M., 2000: Lofer-type cyclothems in the Upper Devonian of the Holy Cross Mts. (central Poland). Acta Geol. Pol. 50, 393-406.
- SZULCZEWSKI M. 1995: Depositional evolution of the Holy Cross Mts. (Poland) in the Devonian and Carboniferous a review. Geol. Quart., 39, 471–88.
- SZULCZEWSKI, M., BELKA, Z., SKOMPSKI S. 1996a: The drowning of a carbonate platform: an example from the Devonian-Carboniferous of the southwestern Holy Cross Mountains, Poland. Sed. Geol., 106, 21–49.
- SZULCZEWSKI, M., BELKA, Z., SKOMPSKI S. 1996b: Stop 6. Ostrówka quarry. Sixth European Conodont Symphosium ECOS VI. Excursion Guide (Szulczewski M., and Skompski S. eds.), 42-49.
- TRELA W., MALEC J. 2007: Carbon isotope record in sediments of the Devonian-Carboniferous boundary in the southern Holy Cross Mountains (in Polish with English summary). Przegl. Geol., 55, 411–415.

MINERALOGIA - SPECIAL PAPERS, 35, 2009 www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Field session 4

Deposits of clay minerals and geotouristic aspects of the Holy Cross Mts.

Józef SZAJN¹, Łukasz KARWOWSKI², Justyna CIESIELCZUK², Krzysztof SZOPA²

¹ Geol-Min. Sp. z o.o., 25-656 Kielce, Skrzetlewska 4 Str., Poland

² Faculty of Earth Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland

Introduction

This study shows the natural and geological features of the Holy Cross Region against the background of the geology of the orogen. The Holy Cross Mts are characterized by a high degree of geodiversity. To-date, in the region, a total number of 250 special areas (e.g., parks, landscape areas) and single elements (e.g., nature monuments, ecological usage areas) have been protected by law. This helps to make the area one of the most interesting in central Poland.

STOP 1: The Pałęgi deposit

The Pałęgi deposit in the western part of the *świętokrzyski* (Holy Cross) region (Fig. 1) is one of a number of deposits of clay raw materials prospected and documented in the years 2000-2004. Geological research on it started in 1997, primarily for the purpose of ensuring the raw material base for a ceramic roof tile production plant starting up at that time. After analyzing a variety of geological data, it was decided to concentrate on the Lower Triassic layers between *Radoszyce* and *Mniów*. This was despite a negative evaluation of the raw material possibilities of that area following research carried out there in the 1980s. The assumption was that terrigenous sediments from before the Middle Triassic marine transgression are generally free of carbonates and sulphates, unlike the Upper Triassic clays excavated in a number of places in the region.

At present, two documented deposits – "Pałęgi" and "Kozów" – are being fully exploited and a third mine – "Gosciniec" – is at a starting-up stage. The sediments forming these deposits represent a quite substantial part of the Lower Triassic profile on the western margin of the Holy Cross Mountains – "Pałęgi" and "Gosciniec" in the Middle *Buntsandstein (Mottled Sandstone)*, and "Kozów" in its uppermost part – *Röt* (traditional subdivision of *German type Triassic;* Fig. 2). In general, all of these deposits comprise similar silty-clayey sediments with insertions of sandstones of very variable thickness. In a typical profile exposed in the "Pałęgi" mine pit, a quite diverse suit of layers can be observed. Horizontal and vertical variability reflects both the interlayering and wedging out of layers as well as gradual sedimentary transitions within particular layers. Despite the variation on the small scale of particular layers, the silty-clayey series as a whole is quite homogeneous – no clearly different zones or horizons can be distinguished. The main dominating types are red and brown clayey mudstones (siltstones) that transition into both silty claystones and sandy mudstones. Mudstones and claystones show clear evidence of diagenesis, mostly a tabular separateness or shaly texture.



Fig. 1. Fragment of geological map, sheet Radoszyce 1:50 000

In places, mudstones are massive or, in some cases, show a brecciated or granular structure. Many mudstone- and sandy-mudstone bedding planes are characterized by large quantities of muscovite lamellae (< 1 mm).

Within the red and brown mudstones and claystones, greenish streaks and sharply defined spots of varying shapes (mostly oval) and diameters ranging from about 0.5 cm to a maximum of more than 10 cm, occur. In some horizons where the spots are concentrated, they appear as round forms on the bedding planes and, in cross section, as elongated streaks forming structures of branching channels filled with coarser material. They can be interpreted as the traces of plant root systems and their greenish colour as due to the reduction of Fe³⁺ to Fe²⁺ connected with humus compounds.

Apart from these spots, continuous layers of grey-olive-yellowish mudstones and clays which, as a rule, accompany sandstone packets that interbed and underlie them, occur within the series. Often grey-yellowish horizons gradually transit into brown and red.

In mudstones, sandstones may occur as concentrations of coarser material without sharply marked boundaries, but mostly as distinct layers of various thicknesses. In some sections of the profile, they form packages (< 2.5-3 m thick) of sandstones interbedded by mudstones; individual sandstone beds may exceed 1m in thickness. These beds are as a rule light- to dark-grey, massive, and firmly lithified. Different types of bedding can be seen – in some cases, horizontal, but mostly various types of cross-bedding. The presence of rich

sets of hieroglyphs, both bioglyphs (mainly ichnofossils) and mechanoglyphs, and petrified plant stalks (casts and internal moulds), is very characteristic.



Fig. 2 Cross-sections showing the situation of "Pałęgi", "Gościniec" and "Kozów" deposits within the profile of Lower Triassic (series according to Detailed Geological Map of Poland sheet Radoszyce 1:50000 - J. Jurkiewiczowa, 1965).



Fig. 2a. Explanations to Fig. 1 & 2.

As noted above, the clayey sediments in "Pałęgi" (and in "Kozów" and "Gościniec") comprise a full sequence from clays and claystones to sandy mudstones. Grain size analyses show that generally there is practically no fraction >1000 μ m (1.0mm) and very small (< a few %) contents of fraction >63 μ m; however, in some of the samples examined by the sedimentary method (mostly *Sedigraph* analyses), these fractions were represented (to even more than 20%) by undispersed clay-mineral aggregates. Predominant are fractions <20 μ m (75-90%). Contents of the finest fractions in "Pałęgi" are, in some cases, quite variable – <10 μ m ranging from 45-84% (mostly 60-70%) and <2 μ m from 15-55%. Clayey sediments in "Pałęgi" are, in general, coarser than in "Gościniec" and "Kozów".



Fig. 3. Selected diffractogram of clays from "Gościniec"

The chemical and mineralogical composition of the clays is rather constant. SiO_2 oscillates from about 60-70% (mostly 62-64%), and Al_2O_3 from about 14-19% (mostly 16-17%). The content of Fe₂O₃ is high (6-8.5%, mostly 7.2-7.5%, in grey-yellowish layers 3.5-4%). Higher than in other Triassic clay deposits is the content of MnO (from 0.03 even to 0.23% (average 0.07-0.09%). The contents of MgO (about 2-2.5%) and K₂O (2.5-3.5%) are also quite high. The low CaO (0.2-0.5%) is significant.

In most samples, clay minerals (with muscovite and chlorite) constitute 45-60% (average about 55%) and quartz 25-45% (mostly 32-35%) of the rock. Hematite (mainly 5-6%) is also significant. Feldspars, calcite and dolomite occur as traces.

Among clay minerals, illite is dominant (20-37%, average about 30%). Kaolinite constitutes 6-15%, average about 10%. Mixed complexes – illite/chlorite/smectite (10-15%, rising in some samples to 30%) are also significant. In sum, three-packet (2:1 type) minerals constitute about 50% of the rock (Table. 1).

Detailed examination of 7 samples (6 from "Pałęgi" and 1 from and "Gościniec"), including microscope, X-ray and differential thermal analyses, were carried out by a team led by Prof. P. Wyszomirski at AGH (Academy of Mining and Metallurgy) in Cracow. Under the miroscope, the basic mass of the rocks is seen to be a mixture of clay substances (mainly illitic with smectite, chlorite, kaolinite) and red-brown pigment of iron compounds (hematite) dispersed or forming aggregates and microveins, lamellae of micas (muscovite, rarely biotite) and their illitic pseudomorphs, relics of alkaline feldspars in some cases and heavy minerals (tourmaline, zircon, rutile, leucoxene, opaque ore minerals).

	Pałęgi	Kozów	Gościniec
Stratigraphy:	MB	UB	MB
Particle size ^{1} (%):			
<63µm (0.063 mm)	85.2 - 95.8 (92.3)	80.9 - 97.4 (89.1)	72.0 - 100 (99)
<20µm (0.02 mm)	72.6 - 92.4 (79.5)	63.4 - 86.1 (77.0)	92.8 - 95.2
<10µm (0.01 mm)	44.9 - 83.7 (61.8)	55.2 - 76.5 (68.3)	73.4 - 78.0
<2µm (0.002 mm)	21.9 - 43.0 (31.5)	33.5 - 51.8 (43.2)	30.6 - 46.8
Mineral composition (%):			
IIIlite	26 - 37	19 - 36 (22 - 25)	$44 - 56^2$
d-layer (I/S. Ch/S) kaolinite	10 - 19 6 - 12	10 - 32 (11 - 17) 5 - 19 (14 - 17)	11 - 15
chlorite	2-5	0 - S	11 15
quartz	30 - 45	22 - 53 (35 - 40)	27 – 33
feldspar	S - 3	0 - S	2-3
hematite	3 - 6	5 - 7	3
Chemical composition (%):			
SiO ₂	59.58 - 69.80 (62 - 67)	58.79 - 76.26 (63 - 67)	60.73 - 64.12
Al_2O_3	13.70 - 18.13 (16 - 17)	10.81 – 19.23 (15 - 17)	17.76 - 18.24
Fe ₂ O ₃	$3.35^{\circ} - 8.42 (6.5 - 7.5)$	5.24 - 8.11 (7.0 - 7.5)	6.91 - 7.77
110 ₂	0.84 - 0.99	0.64 - 0.97 (0.85 - 0.9)	0.90 - 1.03
MnO MgO	0.00 - 0.11 1 78 2 82	0.02 - 0.23 (0.03 - 0.05) 0.93 - 2.40	0.04 - 0.17 1.82 2.90
CaO	1.76 - 2.62 0.22 - 0.51	0.93 = 2.40 0.21 = 0.50	0.35 = 0.54
K ₂ O	2.19 - 3.08	1.85 - 3.68	2.55 - 3.01
loss through	6.31 – 7.03		5.12 - 7.10
annealing			
(105 - 1 000°C)			
Technological			
parameters:	17.56 24.41 (01.42)	14.97 27.04 (21.20)	14.04.26.75 (20.97)
drying shrinkage	17.30 - 34.41 (21.43) 5.1 - 8.9 (6.92)	14.07 - 27.04 (21.20) 49_94 (68)	14.94-20.75 (20.87) 5 10 - 9 20 (6.90%)
sintering temperature	$1140 - 1160^{\circ}C$	-1.7 = 7.4 (0.0) ca 1100°C	1110°C
compression strength	9 3 – 40 39 MPa	12.3 - 78.4 MPa	21.8 - 77.9 MPa
(1050°C)	0^4	0^4	0^4
content/activity of	no	no	no
marl			
predisposition to			
efflorescences			

Table 1. Properties of clay raw materials from portrayed deposits (in brackets average or most frequent values)

¹Results representing joined horizons with thin insertions of sandstones; ²2:1 type clay minerals altogether; ³Grey-yellowish layers; ⁴no traces of activity; MB-Middle Buntsandstein; UB-Upper Buntsandstein

Detrital material is represented mainly by aleuritic, in some cases, psammitic grains of quartz, micas, heavy minerals and small rock fragments (mainly hornstones or quartz-mica schists). Diffractograms and derivatograms clearly show the presence (apart from illite)

ofmixed-layer minerals – I/S, Ch/S, kaolinite and chlorite (clinochlore) – as well as quartz and hematite (Fig. 3). The absence of calcite and other carbonates is important.

Due to their grain size, the chemical and mineralogical composition are key technological properties of the clays as ceramic raw material. In general, the raw material can be described as of illitic type, kaolinite-illitic variety according to classification of K. and R.Wyrwicki), of medium plasticity (drying shrinkage mostly 6.5 -7%) and low drying sensitivity, as free of carbonates and sulphates and with high contents of Fe and Mn. The result is a raw material susceptible to strong sintering at about 1100°C. After burning in temperatures from 1050°C to about 1200°C, the end product displays an intense red-dark-brown colouration, high compression strength and complete frost resistance.

ithin the last 6-7 years, clays from "Pałęgi" and "Kozów" have become one of the best known and most appreciated raw materials for roof tiles and, especially, for ceramic clinker (bricks, tiles) production. Clays from "Pałęgi" (with addition from "Gościniec") are also used to produce high quality ceramic masses – both plastic and casting.

STOP 2: Gagaty Sołtykowskie – protected area

The protected area of Gagaty Sołtykowskie, located near Odrowąż town, covers 13.33 ha and belongs to the Stąporków commune. The reason for the protection of the area of Gagaty Sołtykowskie lies in the didactic and scientific value of the Lower Jurassic rocks outcrops where interesting mineralogical and paleontological specimens may be found.

It is the place where ceramic clays of Lower Jurassic age (Hettangian, ca 200 Ma) were exploited and dinosaurs traces have been found. The traces have been protected against the weather and access for tourists is allowed. The most important paleontological discoveries are:

- the largest (more than 60 cm) trace of a predatory dinosaur found in Poland, a representative of the theropods (*Ichnogenus Kayentapus*), cousins of the Upper Jurassic allosaurus;
- the oldest record of sauropods in herds (Ichnogenus Parabrontopodus);
- the oldest indication of probable caring for progeny;
- traces of full dinosaurs pat; it is hardly ever noticed that digitigrade dinosaurs left this kind of trace during special behaviors such as hunting a potential meal or while staying at and eating the caught animal or during display behavior.

The most important mineralogical findings are various forms of siderite and the rare gemstone – gagate. The flora and fauna is also protected, e.g., sundews (*Drosera rotundifolia*), orchids and the imposing bulrush (*Typha*). In the outer part of the Gagaty Sołtykowskie area, within mixed forest consisting of pine, aspen and birch, common species of frogs and reptiles can be found.

STOP 3: Samsonów old ironworks

Samsonów village is located at the Bobrza river near Kielce. Its history is connected with iron processing. According to legend Marek Topór, the knight of Bolesław Krzywousty, could produce iron from the ore located in the neighbourhood. In 1594, a forge was working there which was leased by Łukasz Samson in 1594. Cracov's bishops, the owners of the land at the Bobrza river, brought some metallurgists from Bergamo in Italy in XVII century as they wanted to modernize military factories. Three iron blast furnaces were built: the first in Bobrza village, the second in Cedzyna village and the third

in Samsonów in 1641. In these furnaces, liquid iron was produced enabling the casting of cannon, mortars, grenades and shot.



Fig. 4. The Samsonów ironworks - present view. Photo: Józef Lewandowski.

In 1818-1822, the Samsonów ironworks (Fig. 4) was rebuilt (thanks to Stanisław Staszic), and a modern factory "Josef Ironwork" was built by Bogusław Szmidt in which 800 tons of the pig iron was produced every year. The ironworks was wood coal fired, and water was the propelling force for all machinery. Additionally, a storehouse for iron, ore and carbon were built and houses for workers. The ore sources were the following mines: Miedzianogóra, Świniagóra, Dziadek and Lubianka. From 1847, the Samsonów factory was owned by the Polish Government. When the January Insurrection broke out, this was the place where the guns for the Polish rebels were produced. This is why Russian soldiers set it on fire and the iron blast furnace, seriously damaged, was closed in 1866

In 1976, the provincial conservator of monuments in Kielce bought the ruins from Modesta Czmuchowska, the daughter of Józef Fert. Consevation work was carried out on the ruins; defects in the walls were repaired, the water canal was patented, the discharge stack was rebuilt and the floor was paved.

STOP 4: The Oak Bartek

The most famous tree in Poland is the oak (*Quercus robur*) called Bartek (Fig. 5), located in Zagnańsk. It is exceptional because of its structure and age.

At present, the Bartek oak is 30 m high, the circumference of the trunk is 9.85 m at the height of 1.30 m and 13.4 m at the base. The crown of a tree is 20 m x 40 m, the crown hood is 720 m², and the breast height diameter is 314 cm. The volume of the tree is ca 72 m³, and the trunk volume is ca 46 m³.

The age of this, the biggest known tree in Poland, is estimated to be 645-670 years (a Pressler drill was used). In the 1930s, it was believed that the Bartek oak was as old as 1200 years. As the core of the tree is touch wooded, its precise age cannot be detected. Since 1952, it is protected as a natural monument.

In 1829, there were 14 main and 16 lateral branches. It now consists of 8 main branches. In 1906, the oak was damaged when neighbouring dwellings went on fire. In the 1920s, the core of the tree was filled by concrete seals. On the 3th of June 1991, lightening damaged one of its branches and a part of the trunk.

The recent problem with the Bartek oak is the progressing touchwooding. The thickness of the healthy tissue is up to 20 cm, usually ca 5 cm. What is more, one of its branches tilts the oak dangerously.



Fig. 5. The oak Bartek. Photo: Józef Lewandowski.

References:

- PISKORZ S., NIEDŹWIEDZKI G, SZAJN J., 2006: Nowe złoża dolnotriasowych surowców ilastych w zachodniej części Świętokrzyskiego (New deposits of Lower Triassic clay raw materials in the western part of Holy Cross Region). LXXVII Scientific Congress of Polish Geological Society. Conference materials, 139-140.
- SZAMAŁEK K., 1989: Właściwości surowcowe na tle litologii skał ilastych triasu dolnego w północno-zachodnim obrzeżeniu Gór Świętokrzyskich (Raw material properties in connection with lithology of clay rocks in the nort-western margin of Holy Cross Mountains). Bull. of State Geol. Inst. (PIG) 361.
- WYSZOMIRSKI P., 2003: Czerwone iły triasowe i ich aktualne znaczenie w polskim przemyśle ceramicznym (Red Triassic clays and their current importance in Polish ceramic industry). Ceramika/Ceramics 81, 66-77.
- WYSZOMIRSKI P., 2006: Triassic red clays in Poland and their importance for ceramic industry. 3rd Mid-European Clay Conference, Opatija (Croatia), 18-22.09.2006. Abstracts Book; 123.
- WYSZOMIRSKI P., GALOS K., SZAJN J., PISKORZ S., 2006: Gościniec nowe złoże iłów dla przemysłu ceramicznego (Gościniec – new clay deposit for ceramic industry). Ceramika/ Ceramics 96, 617-625.
- WYSZOMIRSKI P. STOBIERSKA E., POMADOWSKI H., WIŚKOWSKA A., 2004: Surowiec ilasty ze złoża Pałęgi do produkcji płytek ceramicznych (Clay raw mateial from Pałegi deposit forceramic tiles production). Ceramika/Ceramics 84, 559-566.

http://www.ciekawe-miejsca.net/wydania/artykuly/2009/Marzec/ CM_03.2009_gagatysoltykowskie.pdf http://www.wiadomosci24.pl/artykul/ gagaty_soltykowskie_najstarsze_na_swiecie_slady_dinozaurow_54432.html http://www.e-tour.pl/przewodnik/_rezerwaty/gagaty_soltykowskie/ gagaty_soltykowskie.html http://www.gory-swietokrzyskie.pl/dab-bartek http://skps.m-b-z.net/old/skps/samsonow.htm http://www.e-tour.pl/przewodnik/samsonow/samsonow.htm

AUTHOR'S INDEX

Czesław AUGUST 67

Radu BAILAU 68 Kamila BANASIK 68 Wojciech BARTZ 69 Arjan BEQRAJ 71 Grażyna BZOWSKA 104

Justyna CIESIELCZUK 72, 95, 155 Jerzy CZERNY 97

Janusz DAŃKO 114 Sabina DOŁĘGOWSKA 119 Justyna DOMAŃSKA-SIUDA 74 Andrzej DOMONIK 108 Agata DUCZMAL– CZERNIKIEWICZ 75 Krzysztof DUDEK 76

Said EL NISR 77 Andreas ERTL 78

Małgorzata FRANUS 79 Wojciech FRANUS 79

Irina GALUSKINA 68 Agnieszka GAŁUSZKA 31, 44, 119, 122 Renata GASEK 114 Adam GAWEŁ 76 Aleksandra GAWĘDA 81, 82, 83 Viktor GAZEEV 68 David G. GEE 97 Maciej GÓRA 111 Agnieszka GURDZIEL 84

Stanisław HAŁAS 108 Peter HAUGHTON 39 Katarzyna HELIOS 90 Dušan HOVORKA 40

Sławomir ILNICKI 119

Artur JAKUBIAK 85 Aleksandra JAŹWA 86 Irena JERZYKOWSKA 187

Bartłomiej KAJDAS 88, 92 Paulina KAPTUROWSKA 75 Łukasz KARWOWSKI 89, 90, 125, 133, 155 Jörn KASBOHM 75 Monika KASINA 88, 92 Pádhraig KENNAN 43 Angelika KEDZIERSKA 115 Jakub KIERCZAK 93 Joanna KOSTYLEW 94 Ryszard KOTLIŃSKI 95 Paweł KRÓL 99 Sebastian KRUPCZYŃSKI 76 Ryszard KRYZA 13, 14, 90 Nikolay KUZNETSOV 98 Barbara KWIECIŃSKA 20

Anna LADENBERGER 98

Alicja ŁACIŃSKA 96 Eliza ŁOZOWSKA 93 Ewelina ŁYCZEWSKA 85

Jarosław MAJKA 96, 97 Kamilla MALEK 111 Hervé MARTIN 108 Leszek MARYNOWSKI 111, 149 Jolanta MESJASZ-PRZYBYŁOWICZ 87 Artur MICHALIK 122 Marek MICHALIK 14, 87, 88, 92, 114 Zdzisław M. MIGASZEWSKI 31, 44, 119, 122 Piotr MIGOŃ 67 Moghazi A. MOGHAZI 77 Andrzej MUSZYŃSKI 90, 110 Marek NARKIEWICZ 51 Jerzy NAWROCKI 60 Krzysztof NEJBERT 99 Monika NOWAK 101, 102

Anna PIETRANIK 85, 86

Maria RACKA 104, 149 Tadeusz RATAJCZAK 76 Anna ROGÓŻ 105 Mariusz ROSPONDEK 110, 111 Maria RUDY 69

Sylwester SALWA 106, 107, 142 Mohamed M. EL SAYED 77 Zbigniew SAWŁOWICZ 105 Minella SHALLO 71 Marek SIKORA 76 Magdalena SIKORSKA 72, 82 Ewa SŁABY 108 Wojciech STAWIKOWSKI 102 Mike STYLES 96 Józef SZAJN 155 Jacek SZCZEPAŃSKI 109 Marek SZCZERBA 110, 111 Piotr SZNAJDER 93 Eligiusz SZEŁĘG 112 Krzysztof SZOPA 83, 113, 125, 133, 155 Adam SZUSZKIEWICZ 74

Michał ŚMIGIELSKI 108

Ekkehart TILLMANNS 78 Wiesław TRELA 133

Krzysztof TURNIAK 74

Conçalo VIEIRA 67

Magdalena WDOWIN 79 Rafał WIECZOREK 99 Wanda WILCZYŃSKA-MICHALIK 114 Roman WŁODYKA 125, 133 Sebastian WOJTYCZKA 95 Piotr WYSZOMIRSKI 14

Beata ZYCH-HABEL 115

Jerzy ŻABA 95