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THE ROLE OF THERMAL ANALYSIS IN MINERALOGICAL STUDIES

PART II

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A b s t r a c t. A quantitative mineralogical analysis of an impure pyrophyllite was possible only when thermogravimetry reinforced chemical and XRD analyses. Vein material from a basalt was shown by thermal analysis to consist of pectolite with a trace of natrolite. Diatomite from Almeria contained smectite and calcite; the diatomaceous silica holds much water loosely in both large and small pores and a small amount firmly in silanol groups.

INTRODUCTION

In the three studies reported here, on pyrophyllite, pectolite and diatomite, identification and quantitative analysis of mineral phases were required to solve industrial problems. In two cases thermal analysis provided information which could not have been obtained by other means. Part I /Robertson, 1980/ dealt with clay minerals.

PYROPHYLLITE FROM SOUTH AFRICA

X-ray diffraction analysis had established that the massive form of pyrophyllite, known as South African "Wonderstone" /S 3984/, contained "about 12 per cent kaolinite", "about 10 per cent diaspore", "about 5 per cent quartz" and albite judging by a line at 4.04 \AA . One could not from these figures arrive at a reliable estimate of the pyrophyllite content.

A chemical analysis /by W. H. Herdsman/ is given in Table 1, column 1. Interpretation of the analysis mineralogically could be little bet-

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The final corrections can now be made by combining the evidence of thermal /TG/ and chemical analyses /CA/ in Table 1. TiO_2 , Fe_2O_3 , Na_2O + CaO , MgO + FeO , and K_2O are ascribed to rutile, goethite, albite, chlorite and muscovite, respectively, the chlorite being calculated by Brough and Robertson's convention /1958/. TG losses were used for estimating gibbsite, diaspore and kaolinite. Pyrophyllite was calculated from the residue of the alumina - that is, the alumina not already accounted for by other minerals; and free quartz was taken as the remaining silica. Some moisture and water lost at high temperature remained after the mineralogical calculation, which is given in Table 2. This analysis was not arrived at without testing other assumptions, such as potash in orthoclase or illite, but these other calculations led to too great a departure from the sum of 100 per cent, to too little quartz or to difficulties in allocating the $\text{H}_2\text{O}+$. In Table 1 the oxide which forms the basis of the calculation is shown in heavy type.

PECTOLITE - VEIN MATERIAL IN BASALT FROM FIFE, SCOTLAND /S 4334/

A sample of zeolite was extracted from a specimen of white vein material collected by G. G. Pearson from the basalt of Orrock Quarry, Fife. Zeolitic material had on several occasions formed a heat-reflecting white layer on the surface of molten basalt in a glass furnace.

The specimen consisted of white, silky, radiating crystals and appeared to be monomineralic. By visual inspection one could not tell whether this was natrolite, $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$, or pectolite, $\text{NaCa}_2\text{Si}_3\text{O}_8/\text{OH}/$, since these zeolites have a similar crystal habit.

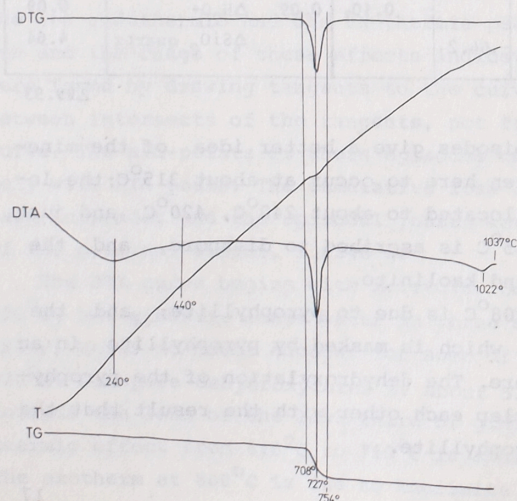


Fig. 1. Thermal analysis of pectolite /S 4334/

DTA /Fig. 1/ shows a shallow endothermic trough centred on 240°C , a very small endotherm at 440°C and a sharp endothermic reaction between 708° and 754°C , with a peak at 727°C . There is also a high temperature exotherm at 1037°C .

DTG shows only the sharp thermal effect with a peak at 727°C .

The low temperature effects are not reflected in the TG curve, which shows a loss of 13 mg = 2.65 per cent. The total loss of 18 mg = 3.69 per cent appears to take place over the whole temperature range evenly except for the main drop around 727°C . Since pectolite contains 2.71 per cent $\text{H}_2\text{O}+$ and natrolite 9.48 per cent $\text{H}_2\text{O}+$, we are not dealing with the latter.

The DTA curve is very like that of pectolite from Bergen Hill, New Jersey, except that the American zeolite has its sharp peak at 780°C and ranges from 744° to 845°C /Mackenzie, 1957/.

Peng /1955/ in his study of the thermal analysis of the zeolite group shows that they all have a small peak in the neighbourhood of 455°C . The small weight loss around 440°C in the Orrock Quarry zeolite could be about 2 mg = 0.41 per cent. This means that the sample might contain 4.3 per cent of natrolite and 95.7 per cent of pectolite.

DIATOMITE FROM ALMERÍA, SPAIN

Four diatomite samples from Almería, Spain, were examined. A thermogravimetric curve for the diatomaceous silica was constructed by subtracting the losses estimated for smectite and calcite in one of the samples /S 4590/. Weight loss occurred at different rates in the temperature ranges $20-288^\circ$, $288-738^\circ$, and $738-1000^\circ\text{C}$. Comparison is made with the three rates of weight loss found by Hannay /1877/ in opal. Segnit et al. /1965/ showed that diatomaceous silica lost free water at two different rates and bound water from silanol groups at a high temperature.

A sample of diatomite, from Almería, Spain, /S 4574/ appeared to have been lightly calcined. It had the astonishingly low bulk density of 109 kg/m^3 . The diatoms are mainly disc-forms and elongated species. The slender, slightly curved diatoms, up to $170-200 \mu\text{m}$ in length, look like *Thalassiothrix* of the textbooks / $175 \mu\text{m}$ in Kainer, 1956/. These "sea-fibres" are the cause of the low bulk density.

In the belief that this remarkable diatomite should be used for highly specialised markets, I asked for four samples to be sent to me to illustrate variation in quality over a wide area. Preliminary observations are tabulated in Table 3.

Table 3

Characteristics of four diatomite samples from Almería, Spain

Sample number Name of quarry	S 4589 Cantera N° 3	S 4590 Ramblo de guerero	S 4591 Inesperada	S 4592 Guitarra
Bulk density /brushed through 0.7 mm sieve/, kg/m ³	134	167	125	162
Grit, > 0.7 mm	Up to small stones	Nil	Nil	Nil
Colour /air dried/, Munsell	N 8.5 very light grey	10 YR 8.5/2 v.v. pale orange	N 8.5 very light grey	10 YR 8/2 very pale orange
- " - /after calcining/	N 9.25	Redder than 5 YR 6/4, brownier than 10 R 7/6	10 YR 8/2 v. pale orange	5 YR 8/4 moderate to orange pink
Dispersion in water	Easy	Easy	Easy	Poor, smectitic
Moisture adsorption, at RH 56%, % on dried sample	4.2	2.4	1.5	1.7
Loss on ignition, % on dried sample	21.84	15.28	17.89	17.40
Methylene blue adsorption, meq./100 g dry sample	5.8	7.9	6.3	6.8
ditto., after pre-swelling	ND	ND	ND	14.3
Calcium carbonate, %, from CO ₂ released by acid	5.76	4.63	7.54	11.12

Since the moisture adsorption of montmorillonite has been found to be about $5.36_2 \times MA_{56}$ /moisture adsorption at Relative Humidity 56/, and the MA_{56} of diatoms is much smaller, we can make an estimate of the upper limit of the smectite content, /1/ in Table 4. The H_2O^+ and H_2O^- contents may then be calculated. Since we know the calcite contents we can calculate the content of diatomaceous silica /2/, assuming that there are no other phases present. By subtracting the losses due to CO_2 in calcite and H_2O^+ in smectite /4/, we can estimate the H_2O^+ content of the diatomaceous silica /5/. If, on the other hand, the $8H_2O$ associated with Si_8 in the smectite were part of the loss on ignition, we should have less H_2O^+ in the diatomaceous silica /6/.

The question posed by these simple calculations is whether the diatomaceous silica can have a water content of more than 15% /5/ or whether the lower values of /6/ are the more probable. Thermal analysis was then brought to bear on the problem.

Table 4

Calculation of water associated with four Spanish diatomites

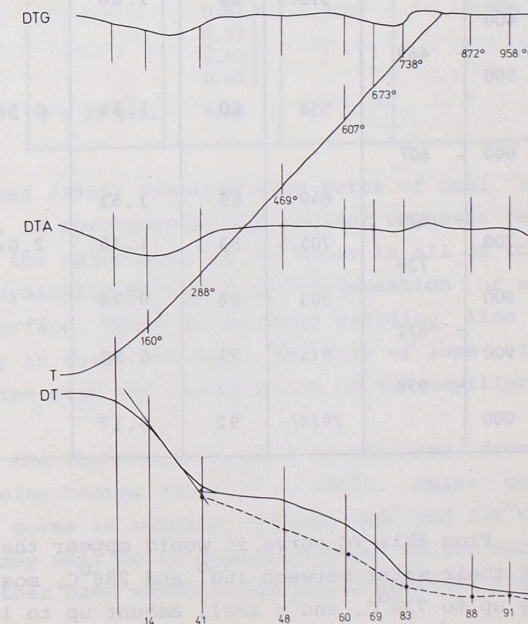
	S 4589 %	S 4590 %	S 4591 %	S 4592 %
1 Smectite from MA_{56}	22.52	12.87	8.04	9.12
1a - " - x 0.0411 $\rightarrow H_2O^+$	0.93	0.53	0.33	0.37 ₅
1b - " - x 0.1644 $\rightarrow H_2O^-$	3.70	2.12	1.32	1.50
2 Diatoms /100-smectite-calcite/	71.73	83.50	84.42	79.76
3 CO_2 from calcite	2.53	2.04	3.31	4.89
4 Loss on ignition - $CO_2 - H_2O^+$	18.38	12.41	14.25	12.14
5 H_2O^+ /diatoms, %	25.62	15.41	16.88	15.21
6 Water/diatoms, %	20.47	12.84	15.32	13.34

DTA of sample S 4590 /Fig. 2/ shows a large endotherm between 20° and 320°C; TG shows no loss under 50°C, but 1.21 per cent loss up to 105°C, the conventional temperature for drying clays. In fact the TG curve shows an inflection at 80°C with a loss of 0.55 per cent H_2O . This may be a measure of the true moisture content.

Before examining the TG curve in detail, I shall comment on the other curves. The DTA curve shows the same large initial loss, a very

Fig. 2. Thermal analysis of diatomite /S 4590/

Dotted line with points - calculated loss due to diatomaceous silica only /total less smectite and calcite/



small loss at about 500°C and another large loss with a peak at 738°C. The last may reasonably be ascribed to calcite; the effect is also seen in the DTA curve.

The DTA curve shows no evidence of the dehydroxylation of a smectite, but I suspect that a small amount of organic matter may have neutralised this effect and contributed to the exothermic peak at 790°C. However, the TG curve promises to give far more information about the mineralogy of this sample /Table 5/.

Table 5

Thermal analysis of diatomite from Almería, Spain /S 4590/

T °C	TG		TG	LOSS	LOSS ascribed to smectite and calcite %	ΔLOSS due to diatom- aceous silica %
	Episode limits °C	Mid- points °C	Cumul- ative mg	Episodal %		
100	50	65	3.3	0.55	2.12 montmorillonite's 8 H ₂ O	0.23
	80					
200	160	120	14	1.80	2.12 montmorillonite's 8 H ₂ O	4.53
	288	224	41	4.53		
400	469	378.5	48	1.66	0.53 montmorillonite's 4 OH	2.66
	500					
700	607	538	60	1.53	2.04 calcite	0.82
	673	640	69	1.51		
800	738	705.5	83	1.35	2.04 calcite	0.74
	872	805	88	0.74		
900	958	915	91	0.50		0.50
	1000	/978/	92	0.17		

Σ 9.65

From this TG curve it would appear that the diatoms lose about half of their water between 160° and 288°C, most of the rest rather gradually up to 738°C, and a small amount up to 1000°C. There are thus three ranges of loss.

As long ago as 1877, Hannay examined the "hydrous content of opal" by a very sensitive method of thermal analysis, his so-called "time method". This method consisted of placing a known weight of substance in a drying tube, immersed in a water-bath and heated to boiling; passing a current of air first through several vessels of strong sulphuric acid /and occasionally through P₂O₅ as well/ and then over the substance in the tube. The evolved moisture was collected in two U-tubes containing pumice-stone saturated with sulphuric acid, one being attached to the instrument while the other was being weighed. By these means the dehydration was kept going constantly. Weighings were made every 5 minutes or longer when the rate became slower /Table 6/.

As the loss on ignition was 8.85 per cent, Hannay inferred that the difference of 0.61 per cent could be added to the more slowly-released water. What is important is that showed that nearly all of the water could be removed from opal by dry air at 100°C, whereas a thermogravimetric curve gives one the impression that temperatures above 100°C are necessary for releasing this water.

Nearly a century later the Australian research workers Segnit, Stevens and Jones /1965/ examined many sorts of opal as well as diatomite by DTA, TG, IR spectroscopy and nuclear magnetic resonance. They concluded that the major part of the water in all of these opaline silicas is held physically by capillary condensation or as multilayers on the silanol surface. There is no sharp dividing line between water held physically in these two ways. The rate of loss of this water is controlled by the size and distribution of the capillary pores.

In the Spanish diatomite the lightly held water is released from the diatomaceous silica on being heated from 20° to 288°C. Water coming from narrower or closed pores is released between 288° and 738°C. The remaining 1.41 per cent may well be in silanol groups on the surface of the silica; on the other hand magnetic resonance spectra sug-

Table 6

Evolved moisture analysis of opal
/Hannay, 1877/

Heating spells	Dehydr- ation %	Sub- totals %	Rate of dehydration °C/min.
5 minutes	1.31 1.28 1.20 1.22	5.01	0.25
20 minutes	0.18 0.72 0.58 0.61 0.52 0.60 0.02		
2 h 25 min.	8.24	3.23	0.026

gested that perhaps some 70 per cent of the water is chemically bound in opal /Segnit et al/. The Australian authors could give no explanation for this difference; but I am inclined to think that Hannay's very delicate "time method" showed rather strongly that there is only a small proportion of bound water, and that there are two populations of pore sizes. The Derivatograph appears to confirm Hannay's observations, but Hannay's technique, modernised - as it has been, should be used for studying diatomites and opal.

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ZNACZENIE ANALIZY TERMICZNEJ W BADANIACH MINERALOGICZNYCH

CZĘŚĆ I I

S t r e s z c z e n i e

Podano dalsze przykłady /p. część I/ ilustrujące możliwość stosowania analizy termicznej do rozwiązywania problemów mineralogicznych. /1/ Ilościowa analiza mineralogiczna zanieczyszczonego pirofyllitu z Południowej Afryki okazała się możliwa dzięki uzupełnieniu wyników badań chemicznych i rentgenowskich analizą termogravimetryczną. /2/ Ana-

liza termiczna materiału żyłowego z bazaltów w Fife w Szkocji wykazała, że jest to pektolit z domieszką natrolitu. /3/ Diatomit z Almería /Hiszpania/ zawiera smektyt i kalcyt; krzemionka diatomitowa wykazuje znaczną zawartość wody luźno związanej w dużych i małych porach oraz małą ilość wody silnie związanej w formie grup silanolowych.

OBJAŚNIENIA FIGUR

Fig. 1. Analiza termiczna pektolitu /S 4334/

Fig. 2. Analiza termiczna diatomitu /S 4590/

Роберт Г. С. РОБЕРТСОН

ЗНАЧЕНИЕ ТЕРМИЧЕСКОГО АНАЛИЗА В МИНЕРАЛОГИЧЕСКИХ ИССЛЕДОВАНИЯХ

ЧАСТЬ II

Р е з ю м е

Указываются дальнейшие примеры /см. часть I/ иллюстрирующие возможность применения термического анализа в решении минералогических проблем. /1/ Количественный минералогический анализ загрязненного пиррофиллита из Южной Африки оказался возможным благодаря дополнению результатов химического и рентгеновского исследования термогравиметрическим анализом. /2/ Термический анализ жильного материала из базальтов Файф в Шотландии показал, что этот материал представляет собой пектолит с примесью натролита. /3/ Диатомит из Альмерии /Испания/ содержит смектит и кальцит; диатомитовый кремнезем обнаруживает значительное содержание воды свободно заключенной в крупных и мелких порах, а также небольшое количество воды, сильно связанной в виде кремневодородных групп.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Термический анализ пектолита /S 4334/

Фиг. 2. Термический анализ диатомита /S 4590/