Journal of Thermal Analysis, Vol. 37 (1991) 969-981

THERMAL AND SPECTROSCOPIC ANALYSIS OF NATURAL TRIOCTAHEDRAL CHLORITES

A. C. Prieto[1]*, *J. M. Lobón*[1], *J. M. Alía*[2], *F. Rull*[1] *and F. Martin*[3]

[1]DEPARTAMENTO DE CRISTALOGRAFIA Y MINERALOGIA, FACULTAD DE CIENCIAS,
UNIVERSIDAD DE VALLADOLID, 47071 VALLADOLID, SPAIN
[2]LABORATORIO DE EDAFOLOGIA Y MINERALOGIA, UNIVERSIDAD DE CASTILLA-LA MANCHA, 13071 CIUDAD REAL, SPAIN
[3]DEPARTAMENTO DE INGENIERIA MECANICA E INGENIERIA DE MATERIALES,
ESCUELA UNIVERSITARIA POLITECNICA DE VALLADOLID, UNIVERSIDAD DE
VALLADOLID, 47071 VALLADOLID, SPAIN

(Received March 3, 1991)

A set of seven natural trioctahedral chlorites have been studied. Thermogravimetric techniques and infrared spectroscopy were used to determine the thermal dehydroxylation of the samples. Relationships between the compositions of the chlorites and their thermograms were established. A kinetic analysis was also undertaken.

Trioctahedral chlorites are phyllosilicates with structures of the 2:1:1 type. They are formed by a 2:1 layer (talc-like) alternating regularly with an interlayer sheet.

In this work, we analyze the dehydroxylation of seven natural trioctahedral chlorites, using dynamic thermogravimetry and IR spectroscopy. This yields information on the modified chlorite structures at the different stages of dehydroxylation. The kinetic behaviour is also investigated.

As far as we know, this type of chlorites has never been studied thermogravimetrically. The vibrational interpretation has been studied previously by some authors [1–7].

Chlorites are characterized by important variations in chemical composition as a function of the physical-chemical conditions of crystallization [8].

---

*Author to whom correspondence should be addressed.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Thus, it is expected that these chlorites will exhibit different thermal behaviour, depending on the particular composition.

Experimental

The samples were provided by the Museums of Natural History in Paris and Bern. This set of chlorites covers a wide range of different solid solutions (Table 1). Three of them are magnesians with the ratio Fe/(Fe+Mg) approximately constant and an increasing substitution of Si/Al: P137510, P12644 and P108902 (Fig. 1). Another two are ferromagnesians with up to 50% of Fe/Mg substitution: B2976 and P107749. The last two chlorites are ferrous, being very rich in Fe: B5204 and P12466. Their general formula [5] is

$$(Si_{4-x}R_x^{3+})(R^{3+},R^{2+})_3O_{10}(OH)_2(R^{2+}_{1-x/3},R^{3+}_{x/3})_3(OH)_6$$

All the Si was assigned to the tetrahedral sheet and the number of tetrahedral atoms per formula was then completed up to 4 with Al. The remaining Al was assigned to the octahedral sites, as was Mg and Fe. Iron was assumed to be divalent, since there was no constraint on its valence. The excellent correlation between the Fe and Mg contents at constant Fe+Mg

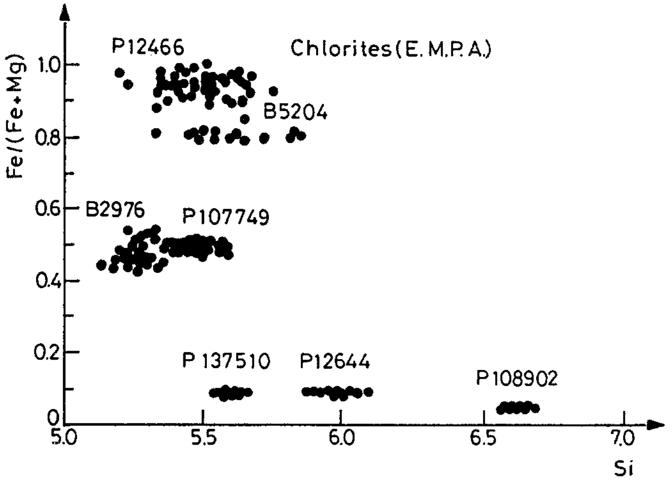

Fig 1 Projection of the composition of chlorites in the Fe /(Fe + Mg)–Si plane

Table 1 Mineralogic formula of chlorites calculated from electron microprobe analysis (E.M.P.A.) [7] M = Molecular weight

Chlorites			Mineralogic formula				(E.M.P.A.)		M
P108902	$Si_{3.313}$	$Al_{0.640}$	O_{10}	$Mg_{5.123}$	$Al_{0.687}$	$\square_{0.012}$	$Fe_{0.250}$	$(OH)_8$	563.41
P137510	$Si_{2.798}$	$Al_{1.204}$	O_{10}	$Mg_{4.346}$	$Al_{1.203}$	$\square_{0.022}$	$Fe_{0.429}$	$(OH)_8$	569.50
P12644	$Si_{2.999}$	$Al_{0.985}$	O_{10}	$Mg_{4.564}$	$Al_{1.001}$	$\square_{0.010}$	$Fe_{0.442}$	$(OH)_8$	569.19
B2976	$Si_{2.631}$	$Al_{1.464}$	O_{10}	$Mg_{2.385}$	$Al_{1.370}$	$\square_{0.072}$	$Fe_{2.081}$	$(OH)_8$	620.61
P107749	$Si_{2.749}$	$Al_{1.274}$	O_{10}	$Mg_{2.379}$	$Al_{1.252}$	$\square_{0.062}$	$Fe_{2.286}$	$(OH)_8$	626.91
B5204	$Si_{2.788}$	$Al_{1.512}$	O_{10}	$Mg_{0.834}$	$Al_{1.213}$	$\square_{0.188}$	$Fe_{3.477}$	$(OH)_8$	685.66
P12466	$Si_{2.751}$	$Al_{1.396}$	O_{10}	$Mg_{0.255}$	$Al_{1.250}$	$\square_{0.159}$	$Fe_{4.191}$	$(OH)_8$	684.96

indicates clearly that iron and magnesium undergo mutual substitution at the R^{2+} site.

Table 2 Structural parameters, molecular weight, total content of Fe, experimental and theoretical loss of mass and kinetic parameters of chlorites

Chlorites			Weight, %					
d_{001}| = |Å	M	Fe, total	Exp.	Theor.	n	E,	$Z\times10^{-10}$	T
b_0| = |Å						kJ/mol	s^{-1}	°C
P108902			9.37	9.59	2.7	84.2	1.42	589
14.33	563.41	0.250						
9.240			2.58	3.20				810
P137510			9.37	9.49	2.3	84.9	1.13	590
14.15	569.50	0.429						
9.240			2.80	3.16				838
P12644			9.30	9.49	2.7	98.8	3.38	597
14.17	569.19	0.442						
9.240			2.87	3.17				836
B2976					2.2	75.7	0.81	533
14.10	620.61	2.081	8.50	8.70				
9.288					2.0	79.3	1.89	604
P107749					1.5	93.1	2.48	500
14.15	626.91	2.286	8.46	8.60				
9.300					2.0	82.9	1.19	611
B5204					1.4	67.8	0.69	469
14.12	685.65	3.477	7.56	7.88				
9.328			75%Q		1.2	72.1	0.69	550

Therefore, the Fe^{3+} content is probably lower than a few percent of the total Fe content and supports the assumption concerning the iron valence. The chemical analysis of the Fe/(Fe+Mg) and Si contents shows that the studied chlorites are characterized by important variations in Fe, Mg, Si and Al.

A Perkin-Elmer TG apparatus, model 3600, was used for the thermogravimetric analysis. The experiments were carried out under a nitrogen stream and at a fixed heating rate of 20 deg·min^{-1}. An open crucible and no more than 10 mg of crystal sample, carefully ground with a pestle and mortar, were used (Table 2). The IR spectrometer was an FTIR Mattson Cygnus 100.

Kinetic method

The analytical method employed has been reported previously [4]. This method is based on solving the kinetic equation of a dynamic process, where

$$f(\alpha) = (1-\alpha)^4$$

where α is the fraction of solid reactant decomposed at time t, and n is the "reaction order". This factor tends to be higher than one: as it approaches closer to one, the nucleation stage predominates over the growing stage of the new phase. As concerns $f(\alpha)$, it is relevant to remember that what it is happening at a certain time depends on what has happened before.

Consequently, the kinetic equation is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{Z}{\beta}\exp(E/RT)\,(1-\alpha)^n \qquad (1)$$

where T is the temperature, Z and E are the kinetic parameters representing the pre-exponential factor and the activation energy, respectively, and β is the heating rate.

Solution of this equation via least square fitting gives the optimum values of Z, E and n.

Results and discussion

The aim of this work was a comparative study of the dehydroxylation of the seven natural chlorites already described.

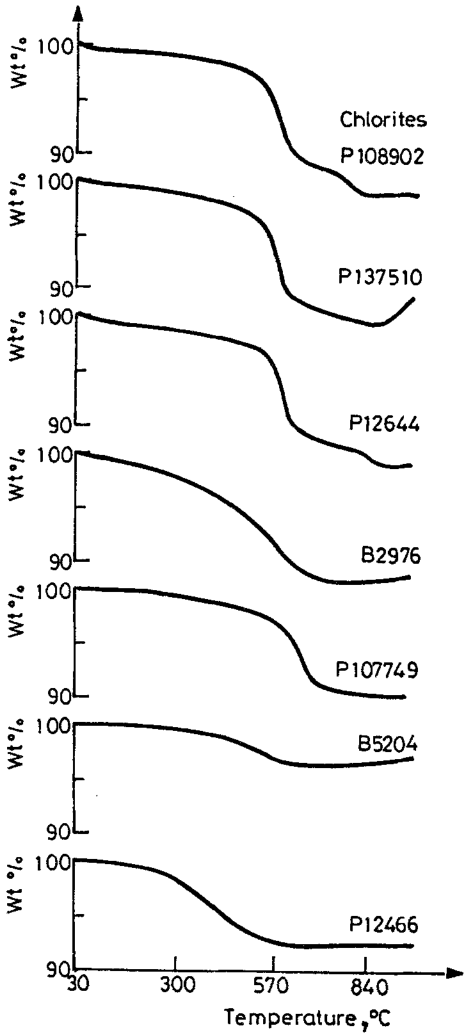

Fig. 2 TG curves of chlorites at 20 deg/min heating rate

Thermogravimetric study

The TG and DTG curves are given in Figs 2 and 3, respectively. The TG curves reveal that the dehydroxylation process occurs in several stages. As shown in Table 2, the total mass loss indicates that three molecules of warer are evacuated. This corresponds to the six hydroxyl groups of the interlayer sheet.

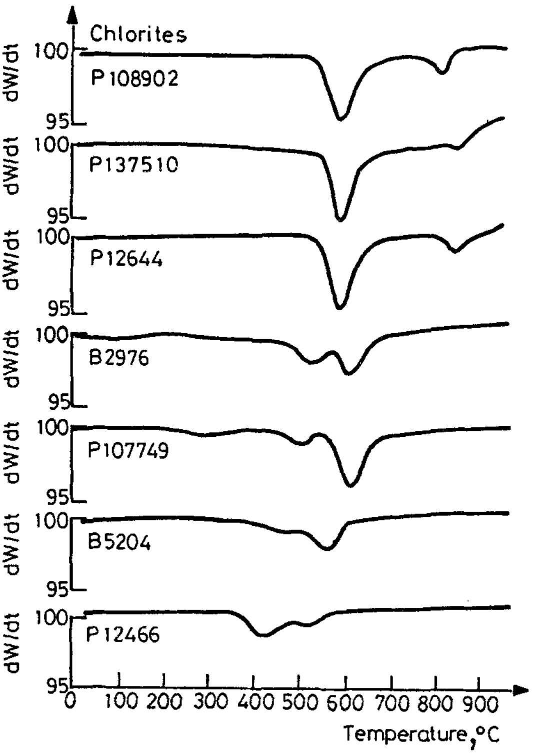

Fig. 3 DTG curves of chlorites at 20 deg/min heating rate

A detailed analysis of the TG curves (Fig. 2) shows a first stage in the range 100 to 150°, which is assigned to the desorption of absorbed water. For the second stage, from approximately 200° to 700°, the mass loss can be assigned to the dehydroxylation of the interlayer sheet. This was confirmed by the IR results.

This second stage is the area of our interest, since the data are very clear, so that the comparison of the chlorites is more reliable.

In the TG curves of the magnesian chlorites (Figs 2 and 3), a third stage of lower magnitude is observed at around 800°. The mass loss corresponds to the removal of one molecule of water. The only possible assignment is that of the two hydroxyl groups of the octahedral sheet. For the ferromagnesian and ferrous samples, this third stage must appear at higher temperature and is therefore out of the experimental temperature range available.

It must be noted that these chlorites are natural substances extracted from different deposits, and it is very rare to find such materials in a pure state. Talc is always present in samples of this kind. The initial steps of the second stage are faster for the more impure chlorites.

The quartz in sample B5084 accounts for up to 75% of the total mass. This makes the corresponding TG curves in Fig. 2 very abnormal.

Dehydroxylation of the interlayer sheet

The aim of this section is to give a satisfactory interpretation of the different processes taking place in the second stage observed in the thermoanalytical curves. To do so, we shall use the information provided by the DTG curves (Fig. 3) and Table 1, which gives the chemical compositions of the natural chlorites studied.

The magnesian samples show a single peak at around 580–600°, while the ferromagnesians give two peaks, one at around 500–530° and the other at around 600–610°. The ferrous chlorites are also characterized by two peaks, at 450–470° and 520–550° (Table 2). Before an interpretation of these experimental facts, it should be remembered that the second peak is always dependent on the first peak, since what is happening at a given instant of time depends on what has happened before.

Our interpretation is as follows. The first peak for the ferric and ferromagnesian chlorites is due to the presence of Fe in the interlayer. The second peak, at around 520–550° and 600–610° for the ferric and feromagnesians, respectively, is due to the presence of Mg, also in the interlayer. The only peak for the magnesians is, of course, due to the presence of Mg in the interlayer sheet.

Fe has the effect of lowering the reaction temperature, since it is known that, for equal charge, the bonding energy of the cation-oxygen bond decreases as the cation radius increases (Fe^{2+} = 0.76 Å, Mg^{2+} = 0.65 Å). Therefore, it is evident that the Fe-OH bond weakens the structure and the reaction temperature will be the lower, the higher the content of Fe.

The peak at around 580–610°, assigned to the Mg–OH bond, should not change in any thermogram, but for the ferrous samples this peaks shifts to lower temperature (520–550°) since the content of Mg is very low and the content of Fe is very high (Table 1). Consequently, in this last case, Fe must dominate the full dehydroxylation reaction.

Furthermore, the influence of the contents of Fe and Mg in the reaction is consistent, as we will see, with the behaviour of every family of samples considered separately.

Firstly, it is clear that in the magnesian chlorites there is very little Fe present and, therefore, its influence is rather insignificant. Secondly, for the ferrous chlorites it is observed that sample P12466 contains 69% less Mg than sample B5204, and for the latter sample the second peak dominates over the first one (Fig. 3). And thirdly, the ferromagnesian samples have the same content of Mg. Sample B2976 has a lower Fe content than sample P107709 (Table 1). This results in the reaction temperature of the first peak being 33 deg lower for sample P107709 than that for sample B2976, which is consistent with the general behaviour of the presence of Fe in the chlorites.

Kinetic analysis

The kinetic analysis and, more particularly, the comparative study of the kinetic parameters and reaction orders for the different samples may shed light on their general behaviour.

Table 2 lists the kinetic parameters and the reaction orders, together with the mass losses for the samples studied.

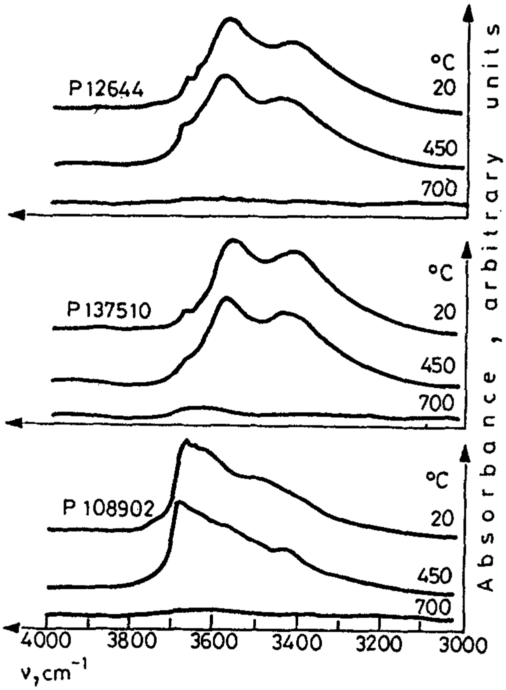

Fig. 4 Fourier Transform Infrared spectra of hydroxyl groups in the 3000–4000 cm^{-1} spectral range of magnesian chlorites at 20, 450 and 700°C

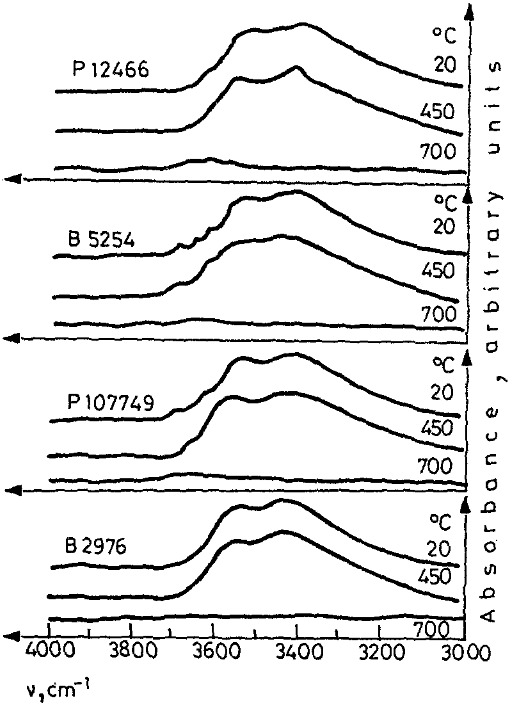

Fig. 5 Fourier Transform Infrared spectra of hydroxyl groups in the 3000–4000 cm^{-1} spectral range of ferromagnesian (B2976 and P107749) and ferrous (B5204 and P12466) chlorites at 20, 450 and 700°C

The reaction order of the Mg peak tends to decrease as the Mg content decreases; which means that the reaction is progressively faster (Eq. 1) and the nucleation stage therefore predominates over the growing stage. This is congruent with the fact that, as the number of defects and impurities increases, the sample is not so homogeneous and the propagation of the new phase is then more difficult, which implies the predominance of nucleation over growing.

As concerns the activation energies for the Mg peak, we observe that for similar reaction orders we have similar activation energies (Table 2). The values are lower for those samples in which nucleation is predominant.

For the Fe peak, it can only be stated that the reaction orders are between acceptable values of 1.4 and 2.2. The activation energies for samples P12466 and B5204 are lower than those for samples P107749 and B2976. That is, we observe the same behaviour as for the Mg peak.

Spectroscopic analysis

The chlorite structures were subjected to spectroscopic analysis at different steps of the dehydroxylation process. The ideal procedure would be to examine the vibrational data while the samples are being heated, but this is not possible at this time, and we therefore applied a different experimental procedure.

The samples were heated for a period of one hour at 450° and at 700°. Of course, this is not equivalent to the dynamic process in the thermogravimetric experiments, but it may shed light on the structural changes in the samples.

Since we are studying the dehydroxylation process, the vibrational modes of interest will be the OH stretching region, between 3000 and 4000 cm^{-1}. The vibrational modes of our samples were studied previously, and we refer

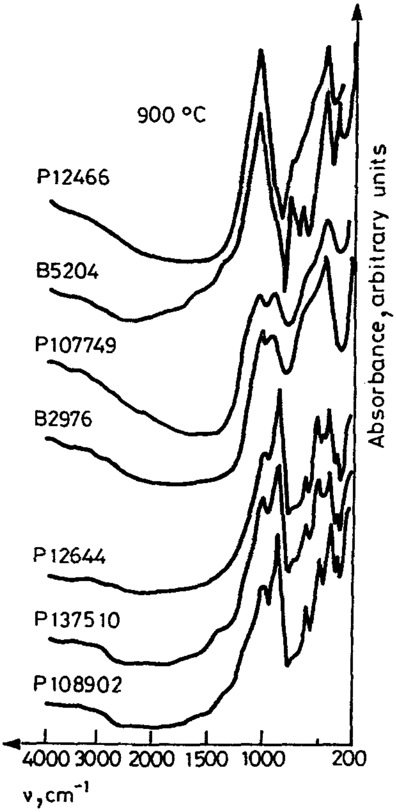

Fig. 6 Fourier Transform Infrared spectra of residual products after heating chlorites at 900°C

to the relevant publications for further information [5–7]. The vibrational modes at about 3680 cm^{-1} are assigned to the stretching vibrations of the OH in the octahedral sheet, and those at 3560 and 3450 cm^{-1} to the corresponding stretching vibrations of the OH in the interlayer sheet.

The vibrational spectra (FTIR) of the samples are depicted in Figs 4 and 5, at 20, 450 and 700°. At 700°, the OH stretching modes have largely disappear, which shows that the dehydroxylation has been completed. It is interesting to compare the spectra at 20° and 450°. The relative intensities of the modes at 3560 and 3450 cm^{-1} compared with that of the mode at 3680 cm^{-1} are higher for the samples at 450° that for those at 20°. In other words, the dehydroxylation starts with the loss of the OH groups of the interlayer sheet. Future, more careful vibrational studies, combined with dynamic thermal studies, may give extra information about the dehydroxylation of these samples.

Figure 6 shows the vibrational spectra of the samples after heating in an oven for one hour at 900°. After this time, the chlorites had been decomposed and the residues were a mixture of different oxides (SiO_2, Al_2O_3, Fe_2O_3 and MgO). The vibrational spectra are similar, but not identical, since the percentages of the oxides depend on the particular compositions of the chlorites. The spectra for each of the three groups of chlorites are very similar.

* * *

The authors thank the Museum of Natural History in Paris and the Museum of Natural Science in Bern for providing the samples studied.

References

1 V. C. Farmer, Miner. Soc. Monograph., 15 (1974) 331.
2 H. Hayashi and K. Oinuma, Am. Mineral., 50 (1965) 476; Am. Mineral., 52 (1967) 1206.
3 H. Shirozu and K. Ishida, Miner. J., 11 (1982) 161.
4 H. Shirozu, Clay Sci., 6 (1985) 167.
5 A. C. Prieto, J. Dubessy, M. Cathelineau and F. Rull, Boll. Soc. Esp. Miner., 13 (1990) 25.
6 A. C. Prieto, J. Dubessy and M. Cathelineau, Bull. Liaison Soc. Franç. Minér. Cristallogr., 2 (1990) 36.
7 A. C. Prieto, J. Dubessy and M. Cathelineau, Clay Minerals, (in press) 1991
8 M. Cathelineau, "Les interactions entre fluids et roches: thermométrie et modelisation", PhD sis, CREGU Nancy, France, 1987.
9 F. Martin, A. C. Prieto, F. Rull and J. A. De Saja, J. Thermal Anal., 32 (1987) 1539.
10 Reports of the Central Custons Laboratory, ed. K. Wada, Japan 1987, Chapt. 18.

Zusammenfassung — Es wurde eine Reihe von sieben natürlichen trioktaedrischen Chloriten untersucht. Mittels TG-Techniken und IR-Spektroskopie wurde die thermische Dehydroxylierung der Proben untersucht. Es konnten Zusammenhänge zwischen der Zusammensetzung der Chlorite und ihrer Thermogramme festgestellt werden. Weiterhin wurde eine kinetische Analyse vorgenommen.