THE INFLUENCE OF COMPOSITION AND FINE STRUCTURE ON A THERMOGRAPHICAL CHARACTERISTICS OF MICAS

I. L. Lapides

The Hebrew University of Jerusalem, Department of Inorganic and Analytical Chemistry, 91904 Jerusalem, Israel

Abstract

Several isomorphic groups of micas: Muscovite - Phengite-Muscovite - Li-Muscovite; Biotite - Zinnwaldite - Lepidolite and Biotite - Phlogopite were investigated by DTA, TG and DTG. Octahedral vacancies and the sites of octahedral cationic occupancy were determined from the IR-spectra of the hydroxyls. The influence of a composition and fine structure of the micas on the shape of the thermal curves was discussed. A one to one correspondence between the isomorphic series members and individual thermal curves makes it possible to determine the chemical composition of a mica sample. The combination of thermal and IR-spectra of hydroxyl analyses permits to link the Order-Disorder data with thermal properties of mica.

Keywords: biotite, IR spectra, lepidolite, mica, muscovite, octahedral vacancy, octahedral cation occupation, phlogopite, thermal analysis

Introduction

The history of thermal investigations of layer silicates is a long one, and different aspects of it were summarized in several reviews [1–5]. A new trend of these investigations is analysis of volatile products of the clay mineral pyrolysis [6–8].

DTA/TG curves for the different mica minerals were reported. But they were not studied systematically, and no correlation has been made between DTA/TG curves, exact chemical composition of the mineral, and its fine structure.

It is known that thermal transformation of layer silicates consists of dehydroxylation, oxidation of octahedral Fe^{2+}, destruction of the network, formation of new phases, etc. The resulting heating curves reflect the superposition of these processes. In this paper the influence of composition, structural vacancies and cation site population on the shape of thermal curves is discussed.

In the structure of layer silicates such as micas there is a possibility of iso-morphic substitution in octahedral position by several cations, mainly Mg, Fe^{2+}, Al^{3+}, Fe^{3+}, Li and F, O^{2-} in hydroxyl positions. One of the three octahe-dral positions of mica may also be vacant, therefore there is a complicated sys-tem of solid solution, although not necessarily a continuous one.

Experimental

Materials

Samples of natural mica minerals from alkaline granites and pegmatites of different genesis were used in the present study. They were previously de-scribed [5]. Octahedral composition of the samples is shown on Fig. 1. The mica structural formula were calculated by the Stevens method [9] from chemi-cal analysis data. In this series there are several isomorphic groups: Muscovite (Mu) - Phengite-Muscovite (Ph-Mu) - Li-Muscovite (Li-Mu); Biotite (Bt) - Zinnwaldite (Zin) - Lepidolite (Lep); Bt - Phlogopite (Phl). Discontinuity is ob-served between Mu and Lep as well as between Mu and Bt. The samples of phlogopite have no octahedral vacancies (in fact, IR-OH-spectra of these sam-ples have no I and V- peaks, and the corresponding structural formula were cal-culated on the basis of 7 cations). It is possible, that a discontinuity exists within the solid solution Bt - Phl between samples with and without vacancies.

Methods

The samples were investigated by means of the combined thermography (Derivatograph 'Paulik, Paulik and Erdey', Hungary - simultaneous DTA-TG-DTG [10]) and IR-spectroscopy (IR-spectrophotometer 'Specord 75 IR', Karl-Zeiss, Jena). The number of vacancies in octahedral positions was determined from the IR-bands of hydroxyls [11]. A cation site occupancy was analyzed by a computer fitting of OH-stretching bands [12]. The end products of the mica thermal destruction were identified by X-ray [13].

Results and discussion

DTA, TG and DTG

The Mu - Ph-Mu - Li-Mu group has 2 or 3 endothermic effects (Fig. 2a) but only the second and third are associated with structural thermal transforma-tions. The first and the second peaks are associated with weight loss, the first one corresponds to the evolution of the adsorbed water (they are not distinct) and will not be further discussed. The second peak (T_{DH}), describes the process
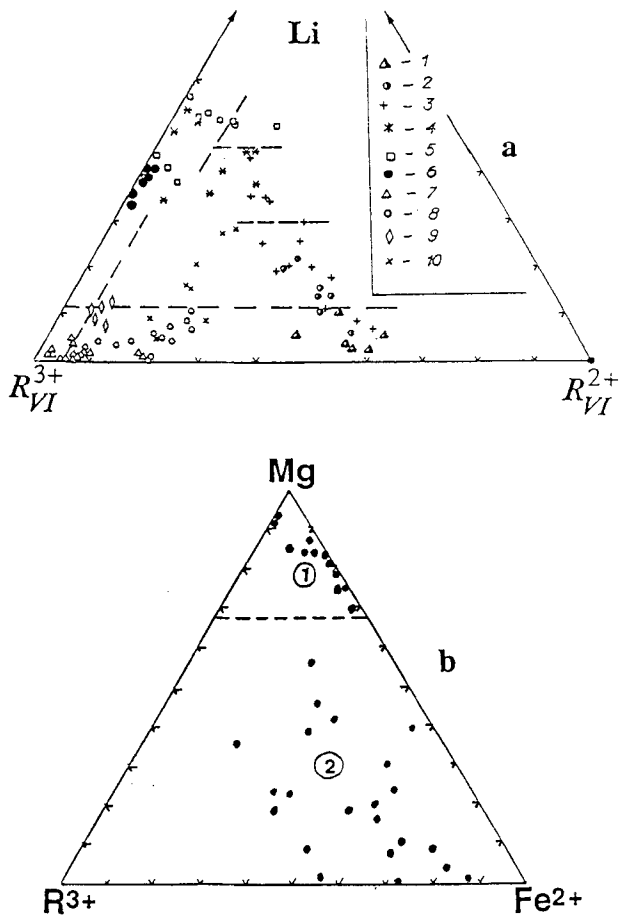
Fig. 1 Diagrams of mica's composition: a) $Li + R^{3+} + R^{2+} = 100\%$; 1- Biotite; 2- Li-Biotite; 3- Zinnwaldite; 4- Fe-Lepidolite; 5,6- Al-Lepidolite; 7- Muscovite; 8- Phengite-Muscovite; 9- Li-Muscovite; 10- Li-Phengite-Muscovite; b).$Mg + R^{3+} + Fe^{2+} = 100\%$; 1- Phlogopite; 2- Biotite

of dehydroxylation. The third peak (T_{LD}) is an endothermic effect of a lattice destruction. The values of ΔT ($\Delta T = T_{LD} - T_{DH}$, in fact, is the temperature range of dehydroxylated mica stability) decrease very quickly in this isomorphic series from Mu to Li-Mu (Fig. 3).

In another isomorphic series (Li-Bt - Zin) there are also two endothermic effects, but the thermal curves are more complicated as compared with those of muscovite because, in addition to the dehydroxylation and lattice destruction, the oxidation of Fe^{2+} and the fluorine loss also occur (Fig. 2b). In Mu-series as well as in Bt-series most of the hydroxyl are lost before the fluorine is lost. The
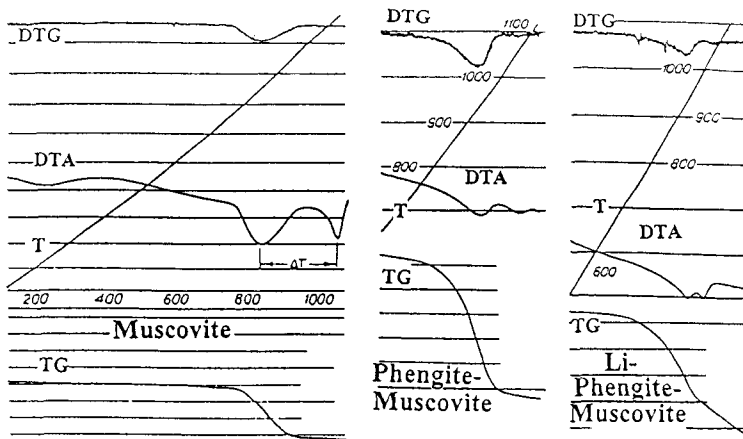
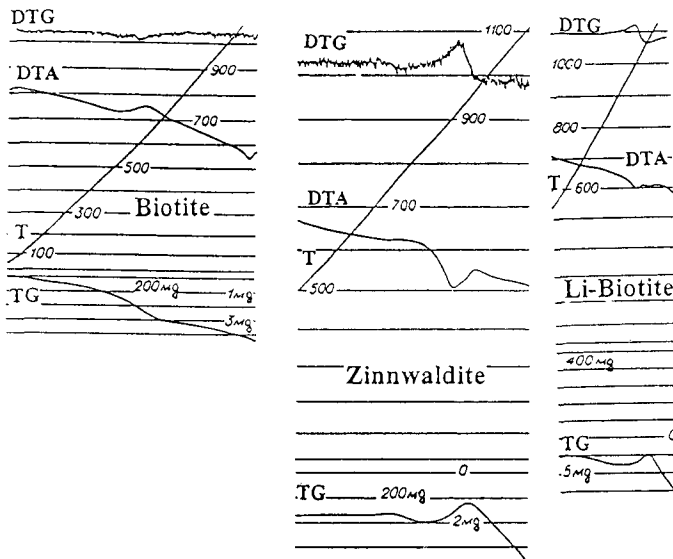**Fig. 2a** The DTA/TG/DTG curves of mica minerals

Fig. 2b The DTA/TG/DTG curves of mica minerals

main fluorine loss occurs from the amorphous phase. The thermal curves of this series reflect the dependency of the thermal transformation processes in micas upon the overall composition (mainly upon the Fe^{2+} and Li content, and the OH/F ratio). With the increase in Li-content (which is correlated with F-content) the dehydroxylation effect tends to coincide with the reaction of mica lat-
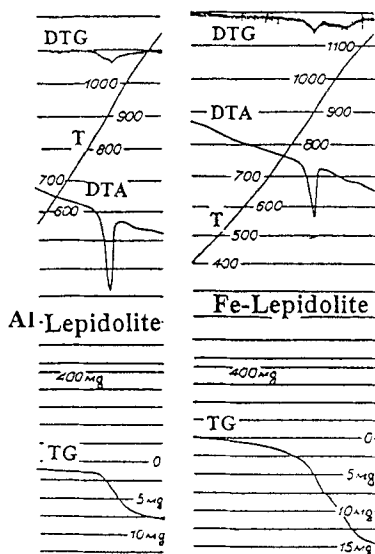
Fig. 2c The DTA/TG/DTG curves of mica minerals

tice destruction. It may be connected with the oxidation of small part of the Fe^{2+}.

The thermal curves of lepidolites are different from those of Mu- and Bt-series (Fig. 2c). They show one sharp endothermic peak at about 880°C. This peak indicates several processes – dehydroxylation, mica lattice destruction, partial melting of the material, and partial loss of fluorine. Fe-lepidolite and Al-Lep (Fe-free) are characterized by different stages of fluorine loss during the heating. The increase in fluorine content caused a new step of a gradual weight loss which continues above 1000°C (Fig. 2c). Several of the lepidolites showed a little broad peak above ~1040°C which may be attributed to lattice destruction (T_{LD}). The influence of the chemical composition of the samples on the temperature of the lattice destruction is shown in Figs 4 and 5. Figure 4 shows that the temperature depends on fluorine content and decreases with increasing fluorine. In the micas with fluorine content smaller than ~0.2 formula units (Mu-series, Li-Bt) the effect is not clear, and the shape of the thermal curves may be dependent on other components and/or the fine structure of the mica and not necessarily on fluorine.

Figure 5 shows the influence of the number of octahedral cations per formula (Y) on the temperature of peak T_{LD}. According to Fripiat et al. [14], for the dioctahedral Li-free micas the thermal stability decreases with increasing Y. This is in agreement with our observations shown in Fig. 5. But for trioctahe-
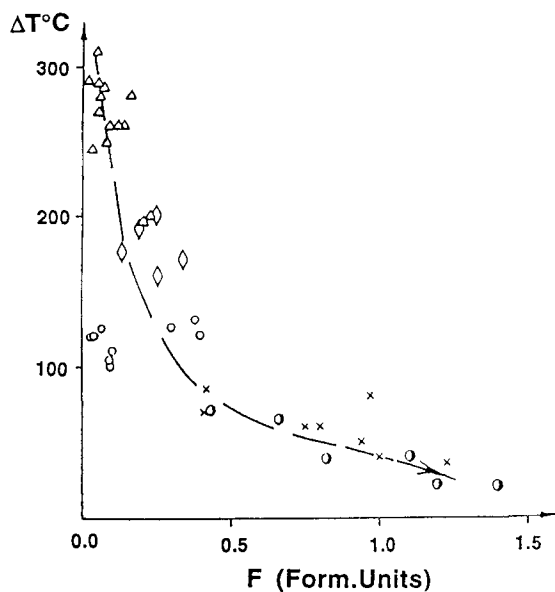
Fig. 3 The value ΔT vs. fluorine content in micas (For symbols of the different series see Fig. 1a)
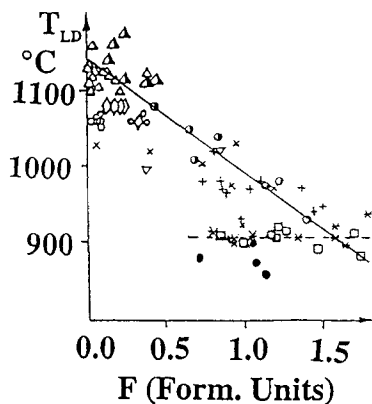

Fig. 4 The influence of fluorine content on the temperature of lattice destruction of micas (For symbols of the different series see Fig. 1a)

dral micas the thermal stability in the series Li-Bt - Zin is not dependent on the composition of the octahedral sheet. This peak appears in the temperature range 900–1200°C, whereas the magnitude of Y is approximately constant. Also, lepidolites do not show this regularity. Although T_{LD} always appears at about 900°C, the value of Y changes from 2.4 to 3.0.
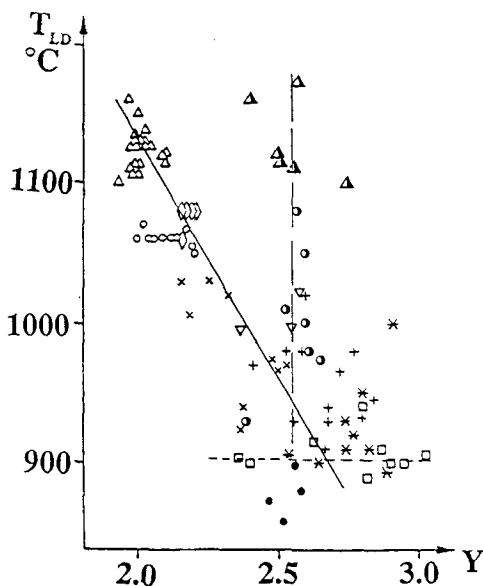
Fig. 5 The influence of octahedral cation content in micas on the temperature of their lattice destruction (For symbols of the different series see Fig. 1a)

The DTA peak temperature of the lattice destruction of Li-free micas decreases with the increasing of octahedral vacant positions (Fig. 5).

IR spectra

It is difficult to determine the number of vacancies because in nature the number of octahedral population is between 2 and 3. The natural micas with integer number 2 or 3 are rare. Usually, the number of vacancies is calculated on the basis of chemical analysis and by balancing the formula according to the charges of the ions. There is a possibility to determine this number in OH-bearing micas from their IR-spectra. The calculation is based on the fact that the O–H bond is a good indicator of the electric field gradient in brucite-like structures. The models of Vedder [15], Raussel-Colom, *et al.* [16] were developed and the coefficient of 'V-band' was defined to determine the vacancies number in biotites [11]. On the basis of a new model of quantitative analysis of OH-bands in phlogopites, the site population of Fe^{2+} and Mg in the octahedral position was determined [12]. Figure 6 illustrates the typical computer fitting of mica's OH-spectra used for this purpose. The IR-spectra of micas from Bt-Phl series (Fig. 1b) were investigated up to the temperature of the OH loss.

All the peaks assigned by Vedder [15] as N, I and V decrease and the relative intensity of V(V/N + I + V ratio) also decreases. There are no V-peaks after
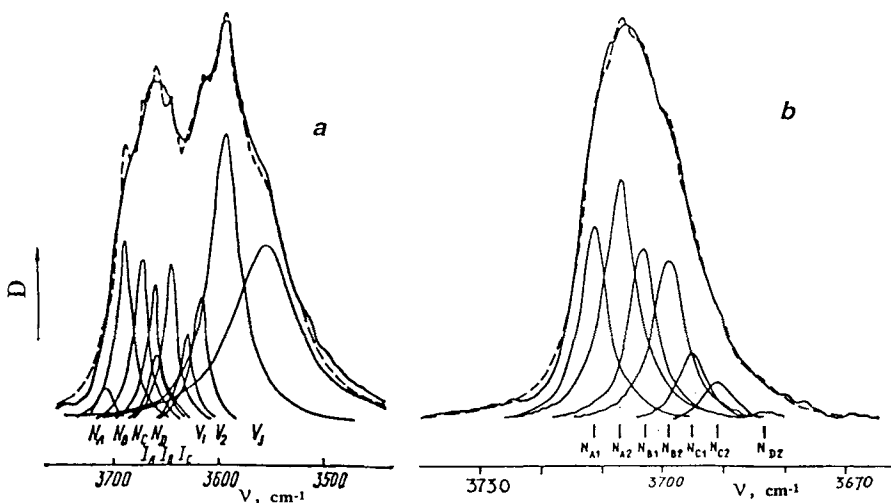
Fig. 6 The computer fitting of mica IR-OH-spectra: a) biotite, the individual OH-peaks con-
nected with octahedral cation triads: N - $R^{2+}R^{2+}R^{2+}$; I - $R^{2+}R^{2+}R^{3+}$; V - $R^{2+}R^{3+}$V,
$R^{3+}+R^{3+}$V(V - vacancy); b) phlogopite, A_i, B_i, C_i, D_i - the individual OH-peaks con-
nected with $R^{2+}R^{2+}R^{2+}$ octahedral cations and different tetrahedron hexagonal rings,
which coordinate the hydroxyl

the exothermal effect (~650°C). According to Vedder and Willkins [17] after
static heating at 500–600°C the units with vacancies disappear. The relative in-
tensity of N and I peaks decreased upon heating approximately with correspon-
dence to the sum of the electronegativity of the octahedral cation. It seems that
the sequence of unit cell dehydroxylation is as follows: (1) units of the Fe^{3+}
only; (2) units of the Fe^{3+} and Fe^{2+} combinations; (3) units of the Fe^{2+} only;
(4) units of the Mg, Fe^{3+} and Fe^{2+} combinations; (5) units of the MgMg and
Fe^{2+} and Fe^{3+} combinations; (6) units of the Mg only. This model must be fur-
ther investigated. It seems that the dehydroxylation of different unit cells in one
sample of phlogopite (which has no vacancies) does not depend on the elec-
tronegativity of the cations.

X-ray

There is also a correlation between the mica composition and the end prod-
ucts of its thermal destruction [13]. An amorphous phase was present in the fi-
nal product of all the mica. The principal crystalline phases which were
identified at the end of the thermal analysis (~1200°C) are as follows: Mu, γ-
Al_2O_3 + Quartz; Al-Lep, Leucite + β-eucriptite; Fe-Lep, Leucite; Zin,
Leucite + Hematite + Spinel; Bt and Li-Bt, hematite + Spinel; Bt-Phl,
Spinel; Phl, Olivine + Spinel.

The Spinels, which as a rule are the common end phases, are defective. Their crystallographic parameter a depends on the total Al-content in the initial mica. Only the phlogopite's final phase is a normal Al-Mg-spinel.

Conclusions

Each member of the isomorphic series of micas has a thermal curve with a characteristic shape. This makes it possible to determine the approximate chemical composition of the sample on the basis of its DTA and TG analyses. The combination of thermal and IR-spectra analyses makes it possible to link the Order-Disorder phenomena to the thermal characteristics of the silicates.

The influence of the fine structure of micas on their thermal behaviour can be the following. The structural unit cells with vacancies are the first (from the statistical point of view) to enter into conversion.

The sequence of events is strongly dependent on the sum of electronegativity of the octahedral cations in these cells. It seems that with unit cells without vacancies there is no correlation between electronegativity sum and the sequence of events.

<p align="center">* * *</p>

References

1 R. C. Mackenzie (Ed), 'Differential Thermal Analysis', Acad. Press, London 1970, 1972.
2 A. Langier-Kuzniarowa, 'Lecture Notes in Earth Sciences' (Ed. by S. Bhattacharji, G. M. Friedman, H. J. Neugebauer and A. Seilacher), Vol. 38, 'Thermal Analysis in the Geosciences'. Springer-Verlag, 1991, p. 314.
3 S. Guggenheim and A. F. Koster van Groos, J. Thermal Anal., 38 (1992) 1701.
4 S. Guggenheim and A. F. Koster van Groos, J. Thermal Anal., 38 (1992) 2529.
5 I. L. Lapides, V. I. Kovalenko and P. V. Koval, 'Sludy redkomatalnukh granitoidov', 'Nauka', Novosibirsk, 1977, p. 104. (The Micas from Raremetal Granitoids).
6 W. D. Keller, Amer. Miner., 71 (1986) 1420.
7 L. Heller-Kallai, I. Miloslavski and Z. Aizenshtat, Clay Miner., 22 (1987) 339.
8 L. Heller-Kallai, I. Miloslavski, L. Halicz and Z. Aizenshtat, Amer. Miner., 73 (1988) 376.
9 R. E. Stevens, U. S. Geol. Surv. Bull., 950 (1946) 101.
10 F. Paulik, J. Paulik and L. Erdey, Z. Anal. Chemie, 160 (1958) 241.
11 B. G. Ponomaryov and I. L. Lapides, USSR Mineralogical J., 12 (1990) 78.

12 I. L. Lapides and B. G. Ponomaryov, USSR Geol. and Geophys., 4 (1991) 8.

13 E. K. Vasilyev and I. L. Lapides, Kristall und Technik, 15 (1980) 231.

14 J. J. Fripiat, P. Rouxhet and H. Jacobs, Amer. Miner., 50 (1965) 1937.

15 W. Vedder, Amer. Miner., 49 (1964) 736.

16 J. A. Raussel-Colom, J. Sanz, M. Fernandez and J. M. Serratosa, Intern. Clay Conf., 1978, (Ed. M. M. Mortland, V. C. Farmer), Amsterdam 1979 p. 27.

17 W. Vedder and R. W. T. Wilkins, Amer. Miner., 54 (1969) 482.

Zusammenfassung — Mittels DTA, TG und DTG wurden einige isomorphe Glimmergruppen untersucht: Muskovit - Phengit-Muskovit - Li-Muskovit; Biotit - Zinnwaldit - Lepidolit und Biotit - Phlogopit. Anhand der IR-Spektren der Hydroxyle wurden oktaedrische Gitterlücken und die Stellen der Besetzung mit oktaedrischen Kationen bestimmt. Der Einfluß der Zusammensetzung und Feinstruktur der Glimmerarten auf den Verlauf der thermischen Kurven wurde diskutiert. Eine eindeutige Korrelation zwischen den Mitgliedern der isomorphen Serie und den einzelnen thermischen Kurven ermöglicht die Bestimmung der chemischen Zusammensetzung einer Glimmerprobe. Eine Kombination der thermischen Analyse und der Auswertung der IR-Spektra der Hydroxyle gestattet die Herstellung eines Zusammenhanges zwischen den Angaben über Gitterordnung/-störung und den thermischen Eigenschaften der Glimmerarten.