

ORDER-DISORDER PHENOMENA ACCOMPANYING THE DEHYDROXYLATION OF DIOCTAHEDRAL PHYLLOSILICATES

Key Words—Andalusite, Dehydroxylation, Iron, Montmorillonite, Mössbauer spectroscopy, Order-disorder, Smectite.

Fe ions occupying M(1) and M(2) positions in dioctahedral phyllosilicates become 6- and 5-coordinated, respectively, on dehydroxylation of the minerals (Heller-Kallai and Rozenson, 1980). No migration of cations was observed in the course of the dehydroxylation, which involved heating the specimens for 1 hr at temperatures up to 700°C. One specimen of phengite was heated for 3 hr at 700°C and for longer periods at lower temperatures. In this study the effect of more prolonged heating on the cation distribution of some of the specimens was investigated.

EXPERIMENTAL

Samples of montmorillonite and beidellitic montmorillonite, described by Heller-Kallai and Rozenson (1980), were heated in open crucibles at 600° or 700°C for various periods of time. Their Mössbauer and IR spectra were recorded and interpreted, and the wavelength of the $AlK\alpha$ emission was measured as previously described. The Mössbauer spectra were also determined on a magnetic scale and at 77°K to detect magnetic phases that may have formed in the course of the relatively protracted periods of heating.

Andalusite from Hondo Canyon, New Mexico, was identified by X-ray powder diffraction and infrared spectrographic methods. Microprobe analysis showed that Fe is the only cation other than Si and Al present in greater than trace amounts. The Fe content, calculated as Fe_2O_3 , is 2.09%.

RESULTS

Table 1 shows the Mössbauer parameters of montmorillonite and beidellitic montmorillonite heated at 600° and 700°C for various periods of time. The assignments were discussed by Heller-Kallai and Rozenson (1980). It is evident that prolonged heating did not change the parameters of the doublets of montmorillonite dehydroxylate, but affected their relative intensity. The ratio of Fe in M(2) to that in M(1) sites decreased from 2.33 to 1.05 after heating at 600°C for 21 days and to 0.95 after heating at 700°C for 28 days.

In the beidellitic montmorillonite examined almost all the iron occurred in M(2) sites. Only a single doublet was observed in the dehydroxylates obtained by heating for 1 hr at 600° or 700°C. After heating at 600°C for 28 days a second doublet appeared, with parameters similar to those established for Fe^{3+} in 6-coordinated sites of phyllosilicate dehydroxylates.

The wavelength of the $AlK\alpha$ emission of montmorillonite dehydroxylate was not noticeably affected by prolonged heating of the samples. It is uncertain whether this indicates that there was no migration of Al ions or whether minor changes occurred, but the sensitivity of the method was insufficient to detect them.

No effects on the IR patterns of the dehydroxylates were observed after heating the samples for prolonged periods.

DISCUSSION

It is generally accepted that in dioctahedral layer silicates octahedral (M1) sites are vacant (Bailey, 1975), although a detailed structure determination of a $2M_1$ phengite and a $2M_1$ muscovite (Güven, 1971) showed some excess electron density in the "vacant" sites. Güven suggested that this may be due to occupation by Mg or Fe ions. Mössbauer spectra of about 115 dioctahedral phyllosilicates studied in this labora-

tory and several others reported in the literature show that Fe does, indeed, occupy M(1) sites in some of these minerals. The distribution of iron ranges from complete preference for M(2) sites to none at all. Thus, in phengite sample 77L27 (Heller-Kallai and Rozenson, 1980), iron occurs only in M(2) sites, whereas in nontronite it occupies the M(1) and M(2) sites in equal proportions (Goodman *et al.*, 1976; Rozenson and Heller-Kallai, 1976). In other minerals intermediate states were observed. Comparison of the distribution of iron in nontronite with that in glauconite, in which iron shows strong preference for M(2) sites (Rozenson and Heller-Kallai, 1978) proves that the site occupancy is not dictated by the amount of iron present.

On dehydroxylation, effected by heating at 600° or 700°C for 1 hr, ions that occupied M(1) and M(2) positions became 6- and 5-coordinated, respectively, with no noticeable change in site populations. The present results show that on continued heating of dehydroxylated montmorillonite or beidellitic montmorillonite Fe ions migrate from sites with 5-coordination to those with 6-coordination (Table 1). The possibility that Al also migrates cannot be entirely excluded, but there is no evidence for it under the conditions of the experiments. With Fe, however, the effect is very considerable after only three weeks of heating at 600°C. It appears that Al ions in dioctahedral phyllosilicates and their dehydroxylates are much more rigidly confined to M(2) sites than Fe ions.

Migration of cations into vacant octahedral sites in the dehydroxylated structures perturbs the local balance of charges and is therefore expected to render the structure unstable. In fact, dehydroxylates of iron-rich layer silicates are less stable than those of the iron-poor analogues and decompose at relatively low temperatures (e.g., celadonite, Heller-Kallai and Rozenson, 1980).

Dehydroxylates of dioctahedral 2:1 phyllosilicates are readily obtained in the laboratory and show characteristic X-ray patterns. Yet, naturally occurring dehydroxylates have not been reported. It is possible that such materials may have escaped detection due to their poor crystallinity, but it seems more probable that they are unstable and decompose rapidly into other minerals. The results obtained in this study suggest that if the dehydroxylates are maintained at relatively low temperatures, migration of cations constitutes the first stage of the decomposition process.

Phyllosilicate dehydroxylates display one very unusual feature: they contain trivalent cations in 5-coordination. Of the commonly occurring minerals, only andalusite shows this feature. Halenius (1978) resolved the Mössbauer spectrum of andalusite into two Fe^{3+} doublets, with Q.S. 1.8 and 1.2 mm/sec. Fe^{3+} exhibited strong preference for the sites associated with the outer doublet. Halenius assigned this to Fe^{3+} in 6-coordination and the small inner doublet to Fe^{3+} in 5-coordination. In view of the low I.S. (0.12 mm/sec), the small inner doublet could also be associated with Fe^{3+} in tetrahedral coordination. The sample of andalusite investigated in the present study showed only a single doublet assigned to Fe^{3+} in 6-coordinated sites (the Mössbauer parameters are included in Table 1).

The similarity between the Mössbauer parameters of Fe^{3+} in 6-coordinated sites in andalusite and in phyllosilicate dehydroxylates should be noted. The similarity is remarkable because the Q.S. of the doublets is unusually large. No change

Table 1. Mössbauer parameters.

Sample	Treatment	6-coordinated site			5-coordinated site			P1/P2	χ^2
		I.S.	Q.S.	Γ	I.S.	Q.S.	Γ		
Montmorillonite	600°C 1 hr	0.38 (1)	1.80 (10)	0.74 (4)	0.33 (1)	1.31 (5)	0.67 (2)	2.33 (40)	238
Montmorillonite	600°C 21 days	0.38 (1)	1.78 (2)	0.51 (2)	0.37 (1)	1.16 (2)	0.51 (2)	1.05 (10)	205
Montmorillonite	700°C 28 days	0.38 (1)	1.80 (2)	0.53 (3)	0.38 (1)	1.23 (2)	0.53 (3)	0.95 (8)	205
Beidellite	600°C 1 hr	—	—	—	0.38 (1)	1.29 (2)	0.65 (2)	∞	212
Beidellite	600°C 28 days	0.37 (1)	1.73 (1)	0.65 (3)	0.39 (1)	1.18 (2)	0.65 (3)	1.45 (8)	220
Andalusite ¹	—	0.35	1.73	—	0.12 ²	1.17 ²	—	0.07 ²	—
Andalusite ¹	—	0.36	1.81	—	—	—	—	0.00	—
Andalusite 12900	—	0.38 (1)	1.78 (1)	0.47 (2)	—	—	—	0.00	260
Andalusite 12900	600°C 21 days	0.37 (1)	1.79 (1)	0.45 (2)	—	—	—	0.00	255

Abbreviations: I.S. = isomer shift relative to Fe; Q.S. = quadrupole splitting; Γ = half width; all in mm/sec.

P1/P2 Ratio of Fe in 5-coordinated sites to that in 6-coordinated sites.

¹ Halenius (1978).

² See text.

occurs in the Mössbauer spectrum of andalusite on heating for up to 21 days at 600°C. This might have been expected, because there are no vacant sites in the andalusite structure, and migration of Fe ions would necessitate a countermovement of Al ions.

Andalusite in nature is commonly derived from pyrophyllite under metamorphic conditions at low vapor pressure. It may be speculated that pyrophyllite dehydroxylate acts as a "transition complex" in the transformation to andalusite at relatively low temperatures. Dehydroxylation may be followed by a migration of cations leading to unstable combinations of the type $M^{3+}-M^{3+}-M^{3+}$ in three adjacent sites, and thereby cause partial breakdown of the structure. Some of the relics, comprising 5- and 6-coordinated Al and Fe^{3+} in distorted 6-coordination are incorporated into newly formed andalusite. On heating phyllosilicates rapidly to higher temperatures, or at higher vapor pressure, the reaction follows a different course, giving rise to other decomposition products, such as spinel, as generally described in the literature (e.g., Grim, 1968).

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