STRUCTURAL DECOMPOSITION OF AN ORTHOCHLORITE DURING ITS ACID DISSOLUTION[1]

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ABSTRACT

The Mg, Fe and Al of a clinochlore were dissolved at the same rate in Si-saturated 2 *N* HCl at 60°C indicating a nonpreferential removal of "octahedral" and "tetrahedral" cations and suggesting a dissolution process in which the hydroxide sheet and the 2:1 sheet in the chlorite layer were equally attacked. The chemical data also suggested that the acid attack on the chlorite particles proceeded from the edges inwards along a well-defined reaction boundary leaving a reacted layer which formed a diffusion barrier. The combined evidence from *x*-ray diffraction and thermal analyses confirmed the equal attack on the two component sheets in the chlorite layer and the progress of the reaction along a well-defined reaction boundary but did not support unequivocally the diffusion-controlled reaction rate suggested by the chemical data.

INTRODUCTION

In a previous study on the acid dissolution of a chlorite the release of Mg, Fe and Al at several temperatures was determined and the activation energy of the reaction calculated (Ross 1967). The dissolution data appeared to follow a model in which the acid attack on a disk-shaped particle proceeded from the edges inwards and in which the reacted layer acted as a diffusion barrier. This model is represented by the equation

$$[1 - (1 - \alpha)^{\frac{1}{2}}]^2 = \frac{2kt}{r^2} = Kt$$

(Jander, 1927; Searle & Grimshaw, 1959). In this equation α is the fraction of the initial amount of cations dissolved at time t, k is the rate constant, and r is the initial particle radius.

This contracting disk model implied a nonpreferential attack on the hydroxide sheet and the 2:1 sheet in the chlorite layer and a direct relationship between the proportion of the total Mg, Fe and Al extracted and the amount of acid-extracted product accumulated. Therefore, the purpose of this study was to examine these implications regarding the structural decomposition by means of *x*-ray diffraction and thermal analyses so as to understand better the changes occurring in the chlorite during progressive acid attack.

[1] Contribution No. 249.

EXPERIMENTAL

The Na-saturated $<2\mu$ fraction of a clinochlore from Brewster, New York was used. This chlorite was obtained from Ward's Natural Science Establishment, Inc. Its chemical composition was determined by *x*-ray spectrochemical analysis (Kodama, *et al.* 1967) except FeO which was determined chemically (Reichen & Fahey, 1962). The total chemical analysis and the calculated structural formula are shown in Table 1.

TABLE 1. CLINOCHLORE: CHEMICAL ANALYSIS AND STRUCTURAL FORMULA

	Per cent based on ignited weight
SiO_2	36.30
TiO_2	0.07
Al_2O_3	21.38
Fe_2O_3	3.48
FeO	3.92
MnO	0.00
SrO	0.00
CaO	0.04
MgO	35.44
K_2O	0.00
Total	100.63

$[(Al_{1.05}Fe^{+3}_{0.22}Fe^{+2}_{0.27}Mg_{4.34})(Si_{2.98}Al_{1.02})O_{10}(OH)_8]$

*The content of SiO_2 based on air dry weight is 30.9 per cent. This value is used in calculations shown in the text.

The acid dissolution techniques used here were described in detail by Ross (1967). The clinochlore was treated with Si-saturated 2 *N* HCl at 60°C for different lengths of time, the ratio of weight of clinochlore to volume of acid solution being kept constant at 2:1. The mineral was kept in suspension by a trickle of air and then centrifuged immediately at the end of the reaction time. Mg, Fe and Al in the supernatant solutions were determined by atomic absorption spectrophotometry.

RESULTS

Dissolution rate

As shown in Fig. 1, the Mg, Fe, Al were dissolved at the same rate and followed a straight line when plotted according to the Jander equation as discussed in the introduction and in the previous paper (Ross 1967). The data gave no evidence for a preferential attack of the hydroxide sheet over the 2:1 sheet in the chlorite structure nor was there any evidence of a faster dissolution of octahedral over tetrahedral cations.

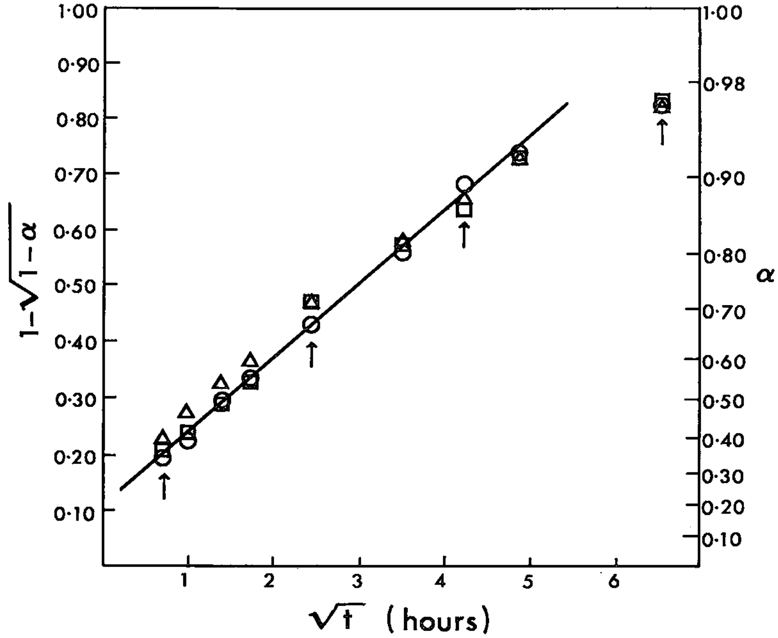

FIG. 1. Plot of $(1 - \sqrt{1-\alpha})$ versus $\sqrt{t}$ for Mg(○), Fe(△) and Al(□) extracted from clinochlore dissolving in 2.0 N HCl at 60°C. Scale of α, fraction dissolved, is shown on the right. Arrows indicate the samples from which the residues were examined by x-ray diffraction and thermal analyses.

Extrapolation of the straight line shows that the fraction of cations dissolved (α) was greater than zero at zero time. This is usually explained by the initial rapid dissolution of cations on edges and fresh surfaces (Gastuche & Fripiat 1961; Osthaus 1956; Ross 1967). Since the 1.5–1.0 micron fraction dissolved at the same rate as the <2 micron fraction and gave the same intercept at zero time, the effect of the fine particles (6% less than 0.2 micron) was considered to be small (Ross 1967).

X-ray diffraction analysis

The x-ray diffraction patterns for the untreated and acid-extracted samples, denoted by arrows in Fig. 1, showed a gradual decrease in intensity with time of acid treatment (Fig. 2). However, a distinct and characteristic chlorite pattern persisted even after 97% of the Mg, Fe and Al had been extracted. Some of the decrease in intensity could be caused by poorer preferred orientation of the acid-treated specimens, as is evident from the appearance of the 020 reflections at 4.6 Å ($2\theta = 22.4°$), but most of the decrease was attributed to the dilution of the unattacked

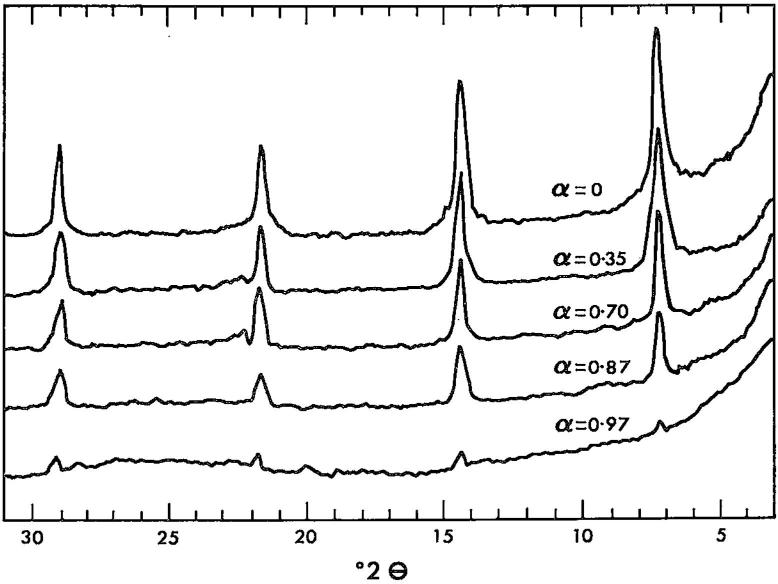

FIG. 2. X-ray diffraction patterns of oriented specimens of clinochlore after progressive acid attack. The degree of acid attack is expressed by α which is the fraction of the initial amounts of Mg, Fe and Al dissolved. Oriented specimens were prepared by suspending 20 mg dry sample in 1 ml of water and placing the suspension on 37.5 mm × 25.0 mm microscope slides. The air-dry specimens were scanned with GE-XRD-5 diffractometer using Fe-filtered Co-radiation (Co $K\alpha$; λ = 1.7902 Å).

chlorite with the amorphous residue persisting after acid attack (Brindley & Youell 1951; Ross 1967). This amorphous residue gave an x-ray pattern with a broad peak at about 4 Å which is characteristic of amorphous silica. Solvating the acid-treated samples with glycerol or heating to 700°C had no effect on peak positions indicating that there was no formation of an expanding-layer phase which presumably would result from a preferential removal of the hydroxide sheet (Bayliss 1964; Droste *et al.* 1960; Johnson 1964).

The x-ray data (and the thermal data shown below) were further analyzed to obtain additional evidence for the correctness of applying the Jander model to the dissolution data. This model required that the reacted layer, forming the diffusion barrier and consisting of amorphous silica in this case, should remain intact and not dissolve. The proportions of amorphous residue and unattacked chlorite in a treated sample should be related to the extent of acid attack measured by the amounts of Mg, Fe and Al extracted. These proportions were estimated from the standardized x-ray intensities since these intensities should be proportional to the amount of unattacked chlorite in a sample. According to the TGA data (shown below) the loss in weight of the amorphous residue was approximately 10%. This corresponds to the upper limit of the H_2O content in opal (Deer, Howie & Zussman 1963) and thus for the purpose of the calculations the amorphous residue was considered an opaline silica with a composition of 90% SiO_2 and 10% H_2O. Designating the proportion of dissolved Mg, Fe and Al as α, the per cent unattacked chlorite in a treated sample is

$$\frac{(1-\alpha)100}{(1-\alpha)+\alpha(1.11A)}$$

where A is the proportion of silica (0.31) of the initial untreated sample. This proportion is multiplied by 1.11 to account for the 10% H_2O associated with the silica. As seen in Fig. 2 and Table 2, the decrease in x-ray intensity corresponded to the expected decrease.

TABLE 2. CLINOCHLORE: INTEGRAL X-RAY DIFFRACTION INTENSITIES AFTER PROGRESSIVE ACID ATTACK

Proportion of initial amount of Mg, Fe, Al extracted α	Total areas under first, second, third and fourth order peaks (inches^2 × 100)	X-ray intensity based on peak areas of untreated sample %	Unattacked chlorite in sample %
0	889	100	100
0.35	662	75	84
0.70	437	49	55
0.87	269	30	30
0.97	58	8	8

Thermal analyses

The endotherms in the DTA patterns at 600°C and at 820°C and the corresponding weight losses in the TGA patterns at 580°C and 840°C for the untreated and acid-extracted chlorite (Fig. 3) were assigned to the decomposition of the hydroxide sheet and the 2:1 sheet of the chlorite, respectively (MacKenzie 1957). Like the x-ray patterns, the thermal patterns of the treated material remained similar to the patterns of the untreated chlorite and distinct endotherms and weight-loss steps were present at the original positions even after 97% of the total Mg, Fe and Al had been dissolved. To estimate the proportions of unattacked chlorite and amorphous residue in the treated samples from the thermal data, the thermal intensities were measured in the same manner as the x-ray intensities. Hence the approximate areas of the two endotherms were measured with a planimeter, and the corresponding weight losses in the TGA curves were estimated from the lengths of the lines from a to b and c to d according to the procedure described by Neumann (1963). In

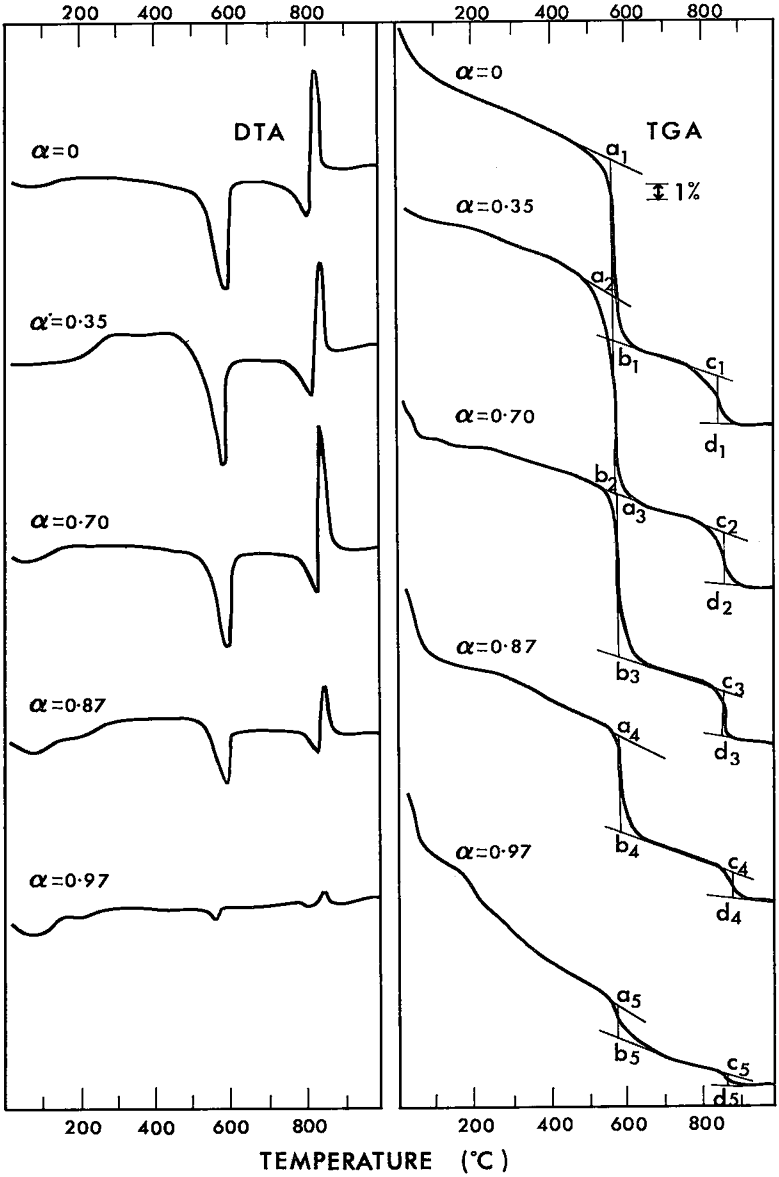

FIG. 3. DTA and TGA patterns of clinochlore after progressive acid attack. The symbol α is explained under Fig. 2. The subscripts for *ab* and *cd* indicate the appropriate curve. DTA patterns were recorded at a heating rate of 10°C/min on 50 mg of sample mixed with 50 mg of calcined Al_2O_3. TGA patterns were obtained on 150 mg of sample at a heating rate of 5°C/min with an analytical balance and a Fisher Balance Assembly mounted over a cylindrical furnace containing a suspended Pt dish.

TABLE 3. CLINOCHLORE: THERMAL DECOMPOSITION AFTER PROGRESSIVE ACID ATTACK

Proportion of initial amount of Mg, Fe, Al extracted α	DTA: Peak areas (inches² × 100) Hydroxide sheet (B)	2:1 sheet (M)	Ratio B/M	B + M %*	Unattacked chlorite in sample %
0	172	44	3.91	100	100
0.35	171	43	3.97	99	84
0.70	147	38	3.87	86	55
0.87	66	17	3.88	38	30
0.97	9.4	2.5	3.76	6	8

Proportion of initial amount of Mg, Fe, Al extracted α	TGA: Weight losses (%) Hydroxide sheet (B)	2:1 sheet (M)	Ratio B/M	Total	B + M %*	Unattacked chlorite in sample %
0	6.33	1.74	3.63	14.80	100	100
0.35	7.00	1.97	3.55	13.80	111	84
0.70	5.93	1.68	3.53	12.73	94	55
0.87	3.46	1.00	3.46	11.60	55	30
0.97	0.94	0.27	3.48	11.60	15	8

*B + M endotherm areas and B + M weight losses set at 100 per cent when α = 0.

addition to the *ab* and *cd* steps in the TGA pattern of the untreated chlorite there was a gradual weight loss over nearly the complete temperature range. A similar continuous weight loss has been reported in the thermal decomposition of montmorillonite and has been attributed to the overlapping of a slow loss of adsorbed water and a slow loss of lattice hydroxyls (Brydon & Kodama 1966; Neumann 1963). In the procedure used it was assumed that the overall rate of weight loss would have been constant if it had not been interrupted by the reactions shown by *ab* and *cd*.

As shown in Table 3, the ratios of the endothermic peak areas were approximately the same as the ratios of the per cent weight losses in the TGA curves. More importantly, however, these ratios remained essentially constant with progressive acid attack indicating that the chlorite remaining in the acid-treated samples was like the original unattacked chlorite. Although the sizes of endotherms and *ab* and *cd* weight-loss steps decreased with increasing acid attack owing to the dilution of crystalline with amorphous material, this decrease was smaller than would be expected from the amounts of unattacked chlorite calculated to be present in the treated samples (Table 3).

DISCUSSION

Previous acid dissolution studies on phyllosilicates have shown that in most cases octahedral cations were dissolved at a faster rate than tetrahedral cations (Brindley & Youell 1951; Gastuche & Fripiat 1962; Osthaus 1954; Osthaus 1956). Based on this differential dissolution, acid dissolution methods have been used to determine directly the ratio of octahedral to tetrahedral cations present in phyllosilicates. The results of those studies were different from the results obtained in this experiment which showed equal rates of extraction of Mg, Fe and Al and hence of octahedral and tetrahedral cations. Gastuche (1963) also failed to obtain evidence for the differential removal of octahedral and tetrahedral cations in the acid dissolution of a biotite.

The observation that the *x*-ray and thermal patterns of the acid-treated samples decreased in intensity but remained distinct and characteristic of chlorite is evidence for a reaction proceeding along a well-defined reaction boundary between the unattacked chlorite and the amorphous residue. The foregoing interpretation is different from the interpretation of TGA data for acid-extracted montmorillonite by Neumann (1963) who favoured the hypothesis of uniform attack throughout the structure. This difference in acid attack may be related to the difference in specific surface areas. A uniform attack throughout the structure and the absence of a well-defined reaction boundary seems more probable in the case of montmorillonite than of chlorite, since montmorillonite would expose a much larger surface area to acid attack than would chlorite.

No evidence was obtained for the formation of an expanding layer phase resulting from a preferential dissolution of the hydroxide sheet. In their acid dissolution studies on chlorite Hossner (1965) and Brindley & Youell (1951) also failed to obtain evidence for the preferential removal of the hydroxide sheet.

From the results of this study it is concluded that the acid dissolution reaction of clinochlore under the experimental conditions applied proceeded along a well-defined reaction boundary dissolving Mg, Fe and Al and hence octahedral and tetrahedral cations at equal rates. Although the chemical data indicated a model in which the reaction rate was diffusion controlled, the combined evidence did not support this model unequivocally and further study is required to assess its validity.

The difference between the results obtained in this experiment and those reported in other acid dissolution studies points out that different phyllosilicates may react quite differently upon acid treatment. Consequently, acid dissolution studies to determine the rates of tetrahedral and octahedral Al and Fe dissolution as an aid in the calculation of structural formulae can not be uniformly applied to different phyllosilicates.

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