

analysis of this structure should be undertaken. I am also indebted to the Department of Scientific and Industrial Research for a maintenance grant during the tenure of which this work was carried out.

### References

- BEEVERS, C. A. & COCHRAN, W. (1947). *Proc. Roy. Soc. A*, **190**, 257.  
 BROWN, C. J. (1951). *Acta Cryst.* **4**, 100.  
 COCHRAN, W. (1951). *Acta Cryst.* **4**, 81.

- DUNITZ, J. D. & ROBERTSON, J. M. (1947). *J. Chem. Soc.* p. 142.  
 DYER, H. B. (1951). *Acta Cryst.* **4**, 42.  
 FURBERG, S. (1950). *Acta Cryst.* **3**, 325.  
 HUGHES, E. W. & MOORE, W. J. (1949). *J. Amer. Chem. Soc.* **71**, 2618.  
 JERSLEV, B. (1948). *Acta Cryst.* **1**, 21.  
 LLEWELLYN, F. J., COX, E. G. & GOODWIN, T. H. (1937). *J. Chem. Soc.* p. 883.  
 LONSDALE, K. (1947). *Miner. Mag.* **28**, 14.  
 ZUSSMAN, J. (1951). *Acta Cryst.* **4**, 72.

*Acta Cryst.* (1951). **4**, 495

## A Chemical Determination of 'Tetrahedral' and 'Octahedral' Aluminium Ions in a Silicate

BY G. W. BRINDLEY AND R. F. YUELL

*Physics Laboratories, University of Leeds, England*

(Received 20 March 1951)

Chemical analysis of the material extracted from a magnesian chlorite (penninite) by acid attack at constant temperatures after various time intervals shows that the percentage extractions of Mg, Fe and H<sub>2</sub>O follow the same curve when plotted against time; in the case of Al the extraction is closely similar up to about 47%, but thereafter proceeds very much more slowly. If the limit of the first stage of the reaction is taken to represent the octahedral Al, then the ratio of tetrahedral to octahedral Al in the structure is 53/47 = 1.13, which agrees closely with that given by the structural formula, namely, 1.16. X-ray examination shows that the mineral becomes effectively amorphous when the octahedral Al is removed. The retention of the tetrahedral Al suggests that the Si(Al)-O networks are still intact, and this is further confirmed by the fact that they can be reconstituted into a mica-type structure.

### 1. Determination of Al<sup>IV</sup> and Al<sup>VI</sup> in a chlorite\*

When the chemical analysis of a silicate mineral, expressed as percentages of oxides, is converted to a structural formula, the accepted procedure is to equate the number of oxygen atoms in the formula to the number in the unit cell and then to derive the corresponding numbers of the other atoms present. When the number of Si atoms is insufficient to fill the tetrahedral positions in the structure, Al atoms or occasionally Fe atoms are assumed to fill the gaps. The remaining Al atoms then go into octahedral positions. The correctness of this procedure is now unquestioned, but (so far as we are aware) no direct measurement of 'tetrahedral' and 'octahedral' Al, i.e. Al<sup>IV</sup> and Al<sup>VI</sup>, has been made.

In experiments on the chemical dissolution of chlorites, in which we were attempting to remove the crinitic layer without attacking the mica-type layer, data were obtained giving directly the ratio Al<sup>IV</sup>/Al<sup>VI</sup>; the result confirmed almost exactly the ratio deduced from the bulk analysis of the mineral.

\* The notation Al<sup>IV</sup> and Al<sup>VI</sup> is convenient for indicating aluminium atoms in fourfold and sixfold co-ordination, i.e. in tetrahedral and octahedral positions (cf. MacEwan, 1951).

The experiments were carried out as follows: about 1 g. of a chlorite, a penninite (or pennine) from Binental, Switzerland, kindly supplied by Dr F. A. Bannister from the British Museum (specimen No. B.M. 26647), crushed to pass a 100-mesh sieve, was treated with a considerable excess of 1:10 HCl, at thermostatically controlled temperatures, 60, 80 and 100° C., for varying periods of time. After each treatment, the solid residue, dried at 300° C., was weighed, and the products in solution were quantitatively analysed for Al, Mg and Fe, the principal cations other than Si, which is not removed by this treatment. The treatment was then continued with a fresh supply of acid. In later experiments separate samples of 0.2–0.3 g. were used for each acid treatment to avoid any accumulation of experimental errors.

Fig. 1 shows the progress of extraction of Al, Mg, Fe and H<sub>2</sub>O, expressed as percentages of their total content in the mineral, when acted on by 1:10 HCl at 100° C. The percentage of water extracted from the mineral was obtained by difference and therefore is less accurate than the other data. Within the limits of experimental error, Mg, Fe and H<sub>2</sub>O are extracted at the same rate, and a single curve has been drawn through the observed

values; their extraction is complete after about 2 hr. Al, on the other hand, is removed rapidly at first up to about 40–50% of the total and then very gradually. The results suggest that part of the Al, presumably the  $Al^{VI}$ , is extracted in the same way as Mg and Fe, and that the remaining Al, the  $Al^{IV}$ , is more firmly held. The mean curve for Mg, Fe and  $H_2O$  extraction, if plotted with suitably reduced ordinates, coincides closely with the initial part of the Al curve; this is shown in Fig. 1 by the broken curve which we interpret as representing the extraction of  $Al^{VI}$ .

The limiting value of the broken curve in Fig. 1 is at 47%. The ratio  $Al^{IV}/Al^{VI}$  is therefore  $53/47 = 1.13$ . This ratio can now be compared with the structural formula based on the chemical analysis of the mineral.

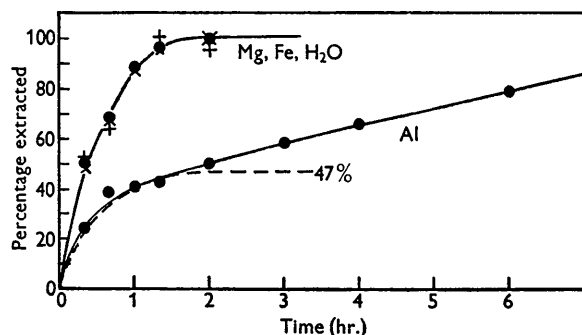
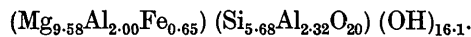


Fig. 1. Percentage extraction of Mg (●), Fe (×),  $H_2O$  (+) and Al (○) from a magnesian chlorite (penninite) by 1:10 HCl at 100°C., as a function of the time of extraction.

Chemical analysis of penninite (BM. 26647) gave

$SiO_2$	29.85	FeO	4.05
$Al_2O_3$	19.25	$H_2O$	12.70
MgO	33.85	Total	99.70

Careful examination showed that there was no more than a trace of ferric iron; the iron content was therefore determined wholly as FeO. On the basis of 20 oxygen atoms per unit cell, the structural formula is



The ratio  $Al^{IV}/Al^{VI}$  is therefore  $2.32/2.00 = 1.16$ .

The agreement between the two values for the ratio  $Al^{IV}/Al^{VI}$  is very close and suggests that the curve for the extraction of Al from the mineral has been correctly interpreted. It would, of course, be easy to adjust the broken curve of Fig. 1 to give a ratio agreeing exactly with that obtained from the chemical analysis, but we

prefer to leave the diagram as it was originally drawn before the bulk chemical analysis was evaluated.

We do not suggest that this method should or, indeed, could be generally applied, but we think it worth while to place on record this direct determination of a ratio which hitherto has been obtained only by inference, and to note that  $Al^{IV}$  and  $Al^{VI}$  are in some circumstances chemically distinguishable.

## 2. Existence of Si(Al)-O amorphous networks

The experiments described above included X-ray examination of the chlorite at stages during its dissolution. No evidence was obtained of any preferential attack on the brucitic layer of the structure and, in fact, the data in Fig. 1 for the extraction of Mg and Fe suggest that both octahedral layers in the chlorite are equally attacked. By the time the octahedral ions are fully extracted, the mineral has become effectively amorphous to X-rays. Nevertheless, the Si(Al)-O networks must still persist, for otherwise we cannot explain the fact that only some 47% of Al has been extracted. The mineral still retains its flaky appearance and micaceous sheen, although the flakes are now white instead of their original green colour. These results recall similar observations by Méring (1949), who studied the activation of montmorillonite by treatment with hot concentrated acids. He found that when the octahedral ions had been largely removed and an amorphous product formed, it was possible, by treating the residue with a solution containing the appropriate ions, to reconstitute a montmorillonite-type product. He deduced that the Si-O network was not fully destroyed when the octahedral ions had been extracted. We have likewise found that it is possible to reconstitute the Si(Al)-O networks from a chlorite into a mica-like product with a characteristic 10A. spacing.

We wish to thank Dr F. A. Bannister for the specimen of penninite used in these experiments, and the Department of Scientific and Industrial Research for a grant to one of us (G. W. B.) to employ a research assistant.

## References

- BRINDLEY, G. W. & ALI, S. Z. (1950). *Acta Cryst.* **3**, 25.  
 MAC EWAN, D. M. C. (1951). See Chap. 4 of *X-ray Identification and Crystal Structures of Clay Minerals*. Edited by G. W. Brindley. London: The Mineralogical Society.  
 MÉRING, J. (1949). *Bull. Soc. chim. Fr.* p. D218.