SHORT COMMUNICATIONS

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Lattice parameters and composition limits of mixed Mg, Al hydroxy structures

THESE and similar structures have compositions of the form $[R^{2+}_{1-x}R^{3+}_{x}(OH)_2]^{+x}R^{-n}_{x/n}(H_2O)_y$ where R^{-n} is commonly CO_3^{2-} as in hydrotalcite and rarely OH^- as in meixnerite. The variation of the hexagonal lattice parameters a and c with x and the limiting values of x have been discussed in detail by Brindley and Kikkawa (1979) for hydroxy carbonates of Mg, Al and Ni, Al and by Mascolo and Marino (1980) for wholly hydroxide structures of Mg, Al. The lattice-parameter data obtained in these independent studies, which were in process of publication at about the same time, are compared in fig. 1.

The parameter $c' = c/3$ is the layer spacing of these hydroxide layer structures. Fig. 1 shows that the plots of c' versus $x = Al/(Al+R^{2+})$ lie on parallel lines and that c' values for the Mg, Al compositions with interlayer OH^- ions are slightly less than those for Mg, Al compositions with interlayer carbonate ions. The results suggest that interlayer OH^- ions pack more closely than the more bulky CO_3^{2-} ions. The variation of c' with x reflects principally the variation of the electrostatic attraction between positively charged layers and the interlayer anions.

Fig. 1 shows that the a parameter values as given by Mascolo and Marino for interlayer OH^- ions lie on a line remarkably different from those given by Brindley and Kikkawa for the Mg, Al and Ni, Al hydroxy carbonate systems. The difference is indeed remarkable because the a parameter depends mainly, or even wholly, on the composition of the hydroxide layer as shown by the fact that the values of a extrapolated to $x = 0$ agree with those for the simple hydroxide structures. For the Mg, Al system the extrapolated a value is 3.144 Å as compared with 3.147 Å for brucite; for the Ni, Al system the corresponding values are 3.110 and 3.126 Å. It is hard to find any explanation for the differences in the a parameter values for the Mg, Al systems in the two studies.

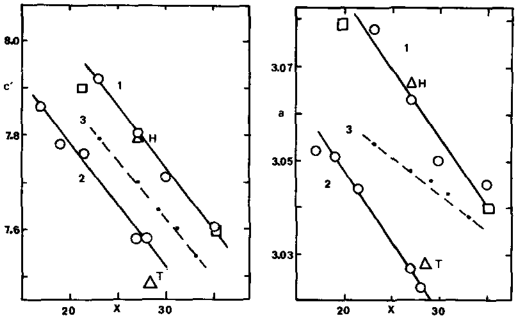

FIG. 1. Lattice parameters, c' and a in Å, plotted against $x = [Al/(Al+R^{2+})] \times 100$. Lines 1, 2, and 3 correspond respectively to data of Brindley and Kikkawa for Mg, Al and Ni, Al hydroxy-carbonate systems, and of Mascolo and Marino for Mg, Al wholly hydroxide system. Circles show experimental data of Brindley and Kikkawa; squares, data of Gastuche, Brown, and Mortland (1967); triangles marked H, data for hydrotalcite and marked T for the nickel mineral takovite.

The composition limits of these hydrotalcite-like phases were discussed in detail by Brindley and Kikkawa. The maximum substitution is clearly near $x = 0.33$ which corresponds to the composition Mg_2Al. Mascolo and Marino quote Allmann (pers. comm.) as suggesting that $x = 0.33$ 'is only possible if Mg and Al are ordered'. An additional important feature is that a 2:1 ratio of Mg and Al represents the highest proportion of Al compatible with Al not occupying adjacent octahedral sites in the layer structure. Since replacement of Mg by Al gives rise to a local excess of positive charge, it is reasonable from Pauling's rules that such excess charges are not adjacent. The lower limit of x is less clearly indicated by considerations of simple models. However, with $x = 0.25$, corresponding to the ratio Mg_3Al which is commonly found in hydrotalcite, an ordered system is possible with Mg-occupied octahedra placed between pairs of Al-occupied octahedra. With higher proportions of Mg to Al, small regions of Mg-occupied octahedra must come together and these may act as nuclei for the development of brucite.

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