gibbsite and deter the formation of bayerite. However, at the same concentration of citric acid, the corresponding hydroxides precipitated from 10^{-4} M Al give only poorly defined patterns (Fig. 1D). This is evidently due to the increase of the citric acid:aluminum ratio. Moreover, the X-ray diffraction data show that the hydrolytic products of aluminum can be completely amorphous to X-rays if the citric acid concentration is sufficiently high (Fig. 1C). The crystallization of aluminum hydroxides is hindered or delayed by citric acid apparently because coordination of carboxylate groups with aluminum hampers the hydrolysis of the terminal groups of aluminum ions. Though the chemistry of Fe and that of Al are not the same, it is interesting to note that Schwertmann *et al.* (1968) observed a delay in the crystallization of iron oxides and a shift in the nature of the products formed in the presence of citric acid.

The inhibition or delay in the formation of crystalline aluminum hydroxides caused by the citric acid is further reflected in the electron micrographs of the hydrolytic reaction products of aluminum. In Fig. 2, for instance, the surface features of the reaction products aged 40 days in the absence and in the presence of 10^{-6} M citric acid are significantly different. In the absence of citric acid, the crystals formed are well-defined (Fig. 2A). The product in the presence of citric acid possesses a rather fluffy, rough surface (Fig. 2B).

The results of this investigation provide direct evidence to the effect that the hydrolytic reaction of aluminum and the surface features of the reaction products in the aqueous system are greatly influenced by the presence of citric acid. This is of basic importance in understanding the solution and colloid chemistry of Al, as well as the behaviour of aluminum in soil solutions and natural waters.

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Saskatchewan Institute of Pedology, K. F. NG KEE KWONG
University of Saskatchewan, P. M. HUANG
Saskatoon, Saskatchewan, Canada

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INTERLAYER BONDING IN TALC AND PYROPHYLLITE

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The bonding between the silicate layers of micas such as muscovite consists of ionic, van der Waals, and repulsion components (Bailey and Daniels, 1973). The origin of the ionic bonding has been supposed to originate in the partial substitution of aluminum for silicon in the tetrahedra which gives the silicate layers a negative electrostatic charge and attracts the positively charged potassium ions situated between the layers. Related layer silicates which do not have a net charge on the layer and no interlayer cation are of two types: the 1:1 phyllosilicates such as the kaolin and serpentine minerals, and the 2:1 phyllosilicates such as talc and pyrophyllite. The interlayer bonding of the 1:1 structures is known to involve long hydrogen bonds between the hydroxyls which form one of the surfaces of the 1:1 layer and the oxygens which form the adjacent surface of the next layer (Giese, 1973; Cruz *et al.*, 1972). The interlayer bonding in talc and pyrophyllite, which lack surface hydroxyls, has been assumed to be purely van der Waals (Ward and Phillips, 1971).

Ward and Phillips (1971) have calculated the specific surface energy of talc and pyrophyllite using the Lennard-Jones potential function to describe the van der Waals bonding between the oxygens on either side of the cleavage plane, (001). The force constants in the potential function were determined from the bulk modulus value of pyrophyllite (Bridgeman, 1924) and the calculated specific surface energies are 490 mJ/m^2 for both minerals or 17·1 kcal/mole for talc and 16·7 kcal/mole for pyrophyllite.

The assumption that there is no ionic contribution to the interlayer bonding and therefore there are only van der Waals interactions can be examined by a technique described elsewhere (Giese, 1974). In brief, the specific electrostatic surface energy of a layer structure can be determined by calculating the electrostatic energy for the normal structure and for a series of related, hypothetical structures which contain the same rigid silicate layers but have increasing distances between the layers. The plot of electrostatic energy vs the increase in interlayer distance is a simple curve which rapidly approaches a constant value for large separations. The numerical difference between the energy of the expanded structures and that of the normal mineral is the surface energy.

Such calculations have been done for talc and pyrophyllite using the most recent crystal structure refinements of

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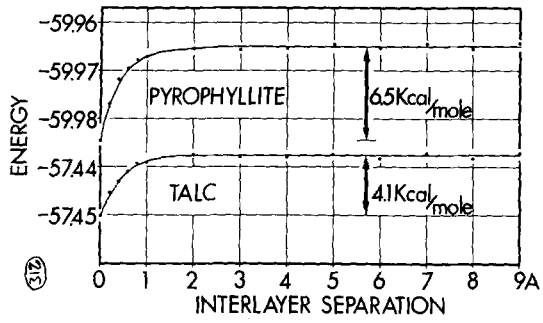


Fig. 1. A plot of the electrostatic energy (in e^2/Å) of pyrophyllite and talc vs the increase in the interlayer distance. The 0. Å separation corresponds to the normal crystal structure and the energy difference between this and the expanded structures (> 3 Å) is an estimate of the energy of the ionic interlayer bonding.

Raynor and Brown (1973) for talc and Wardle and Brindley (1972) for a one-layer pyrophyllite. For the purposes of the calculation, all atoms were assumed to be fully ionized (Giese *et al.*, 1971). The electrostatic energy vs increase in the interlayer distance for these minerals is shown in Fig. 1. The units along the vertical scale are e^2/Å (e = charge on the electron). Both curves rapidly approach a constant value and the energies for separations greater than 3Å are constant except for random fluctuations due to numerical round-off errors which originate in the process of generating the expanded structures. It is of some interest to note that similar calculations on muscovite approach the asymptotic value much more slowly and separations of more than 7Å are needed to accurately determine the energy of the isolated silicate layer. This probably is due to direct electrostatic attraction between the interlayer cation and the coordinating surface oxygens in the mica.

The curves demonstrate that the lack of a net electrostatic charge on the silicate layer does not preclude the existence of an electrostatic attraction between the atoms in one layer and those in another. In fact, in the case of talc and pyrophyllite, an imbalance in charge on the layer would result in a strong electrostatic repulsion between layers. The specific electrostatic surface energies of 6·5 kcal/mole for pyrophyllite and 4·1 kcal/mole for talc are less than the value calculated for muscovite $2M_1$ (32 kcal/mole) (Giese, 1974) which is in agreement with their different physical properties. It should be noted that the electrostatic surface energies reported here should be considered as upper limits since they are based on rigid layers. In a real experiment one would expect small rearrangements of the atomic positions in the surface layers which would tend to lower the electrostatic energy of the expanded structure and thus decrease the values of the surface energy. The talc and pyrophyllite electrostatic surface energies are not negligible compared to the calculated van der Waals surface energies (Ward and Phillips, 1971) and one must conclude that the latter value is probably in error since it is based on an incorrect assumption. A more accurate assessment of the interlayer bonding in talc and pyrophyllite must take into account both the ionic and van der Waals contributions.

State University of New York at Buffalo,
Department of Geological Sciences,
P.O. Box U, Station B,
Buffalo, New York, U.S.A.

R. F. GIESE, JR.

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