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NOTES

Surface charge density dependency on Al_2O_3 content in imogolite*

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AN ANALYSIS of the available literature data indicates that the cation exchange capacity and surface charge density of imogolite decrease systematically as the mole % of Al_2O_3 (i.e. $100Al_2O_3/SiO_2 + Al_2O_3$) increases. This behavior is analogous to that of synthetic aluminosilicates. In contrast, no relation is apparent between the cation exchange capacity and mole % Al_2O_3 for allophane. This difference is rather striking and although both are amorphic, i.e. show minimal specific X-ray diffraction effects, imogolite is somewhat more crystalline than allophane (Russell *et al.*, 1969).

The cation exchange capacity of amorphic aluminosilicates is largely dependent upon the coordination number of aluminum in such a structural arrangement that one negative charge results from each aluminum ion in four-fold coordination. Therefore, it is not surprising that the cation exchange capacity of synthetic amorphic alumino–silicates increases as the % Al_2O_3 (i.e. $100Al_2O/SiO_2 + Al_2O_3$) increases up to 20–30 mole % (30–40 wt %); however, at higher Al_2O_3 values the cation exchange capacity decreases (DeKimpe *et al.*, 1961, and references cited therein). The decrease in cation exchange capacity as the mole % Al_2C_3 is increased above 20–30 results when aluminum goes into octahedral coordination because fewer corners of silica-tetrahedra remain free to share corners with aluminum-tetrahedra. The mole % of Al_2O_3 at which aluminum ceases to go into tetrahedral coordination varies with the hydroxyl ion concentration and ionic strength of the solution. DeKimpe *et al.* (1961) found that the cation exchange capacity of synthetic alumino–silicate precipitates from both low and high ionic strength solutions increased linearly with increasing pH of the mother liquor (approximately 35 me/100g per pH unit). At pH 8 the precipitates from a high ionic strength solution such as saturated NaCl yielded an amorphic gel with a cation exchange capacity of 232 me/100g, which was 45 me/100g higher than the comparable precipitate from the dilute solution to which no NaCl was added.

The dependence of cation exchange capacity upon the mole % Al_2O_3 in laboratory alumino–silicate precipitates suggests the appropriateness of a similar explanation for the marked variations in cation exchange capacity values reported for allophanic and imogolitic clays. Therefore, data on soil clay separates and geological specimens from several sources were utilized in the plot of cation exchange capacity vs. mole % Al_2O_3. The results, shown in Fig. 1, show that a general decrease in cation exchange capacity occurs between about 37 and 49 mole % Al_2O_3 in the case of imogolite (round symbols). No relationship is apparent between cation exchange capacity and mole % Al_2O_3 for allophane (angular symbols). Most of the allophane values (angular symbols) lie above the imogolite values.

Not all of the surfaces in the interior of amorphic clay aggregates are physically accessible to aqueous solutions (Aomine and Otsuka, 1968), hence, not all of the potential exchange sites can be expected to be available for cation exchange. This could cause cation exchange capacity to be affected by particle size. Therefore, one would expect the mole % Al_2O_3 to be more closely correlated with surface charge density than with cation exchange capacity. The imogolite data of Aomine and Yoshinaga (1955) show a uniform decrease in surface charge density as the mole % Al_2O_3 increases from 37 to 49 (Fig. 2), which tends to confirm this idea. The scatter of the data of Aomine and Yoshinaga about the curve is much less in Fig. 2 than in the cation exchange capacity vs. mole % Al_2O_3 shown in Fig. 1. In contrast, the scatter of Besoain's (1969) data for imogolite is much greater when the surface charge density is plotted (Fig. 2) than when the cation exchange capacity is plotted (Fig. 1).

The imogolite surface charge density values calculated from the data of Besoain are about three times greater than those of Aomine and Yoshinaga; they are also higher than those of Aomine and Otsuka (1968) for allophanic clays, which range from 1·3 to 2·0 $\mu e/m^2$ (microequivalent per m^2). The higher surface charge density values of Besoain are in part due to his exchange capacity measurements being carried out at pH 8·2 (saturated with Na^+, displaced with NH_4^+) vs. pH 7·0 (saturated with NH_4^+, displaced with Na^+) in the case of Aomine and Yoshinaga (1955). (Aomine and Otsuka (1968) neither indicate pH or cations used nor give chemical analyses.) The importance of controlling or at least knowing the pH at which the exchange capacity is determined is indicated by the data of Lai and Swindale (1969) which show that delta cation exchange capacity values (i.e. the value at the high pH less the value at low pH) range from 54 to 165 me/100g as the pH of measurement increased from 4·0 to 8·5.

The greater scatter of values for allophane than for imogolite in the plot of cation exchange capacity vs. mole % Al_2O_3 may be due to two factors. The greater abundance of data for allophane, which implies a wider sampling of the natural population, undoubtedly contributes to the variance. It is considered more likely that the scatter is

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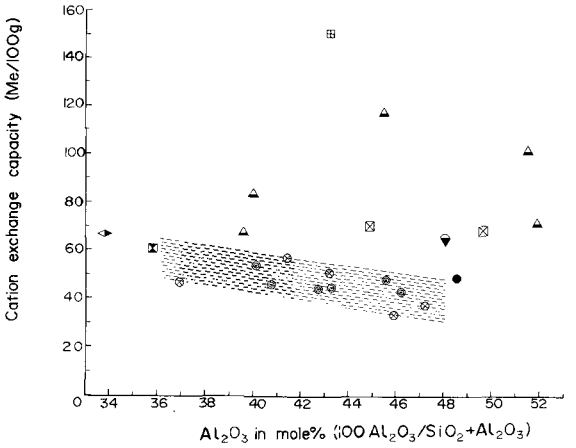


Fig. 1. Variation of cation exchange capacity with mole % Al_2O_3.

Allophane (Angular Symbols)

⊞ Yoshinaga and Aomine, 1962a,b (H_2O_2 treated, deferrated, pH 10–11 dispersed, $<2\mu$, CEC = pH 7).

▲ Lai and Swindale, 1969 (H_2O_2 treated, deferrated, boiled in 2% Na_2CO_3, $<0{\cdot}1\mu$, CEC = pH 7).

⧓ Park, 1969 (Deferrated, washed with 2% Na_2CO_3, $<0{\cdot}2\mu$, allophane separated by electrophoresis: The value plotted is $100(Al_2O_3+Fe_2O_3)/(SiO_2+Al_2O_3+Fe_2O_3)$; the $100Al_2O_3/SiO_2+Al_2O_3$ value is 31·1).

◆ Aomine and Wada, 1962 (Deferrated, boiled in 2% Na_2CO_3, $<2\mu$).

⊠ White, 1953 (Geologic specimen).

Imogolite (Round Symbols)

● Yoshinaga and Aomine, 1962b (H_2O_2 treated, deferrated, pH 3·5–4 dispersed, $<2\mu$, CEC = pH 7).

◎ Besoain, 1969 (H_2O_2 treated, deferrated, pH 3·5–4 dispersed, $<0{\cdot}2\mu$).

⊗ Aomine and Yoshinaga, 1955 (H_2O_2 treated, dispersed with 0·002 N HCl, $<2\mu$, CEC = pH 7).

Imogolite – Allophane undifferentiated

▼ Miyauchi and Aomine, 1966 (Gel from pumice bed, H_2O_2 treated, deferrated, ultrasonified but unsized).

chiefly due to the less crystalline nature of allophane, in comparison with that of imogolite (Yoshinaga *et al.*, 1968) and therefore, its greater susceptibility to sample treatment effects such as variable pH, etc. The cation exchange capacity of amorphic alumino-silicates is highly dependent upon pH, salt concentration, cations and anions used, volume of alcohol wash, and the water content of the alcohol wash used for removal of excess salts (Birrell and Fieldes, 1952; Harada, 1955; Birrell and Gradwell, 1956; Aomine and Jackson, 1959).

The scatter of Besoain's data on the surface charge density-mole % Al_2O_3 plot may be due to the effect of different pH values and ionic strength during formation as well as to crystalline mineral impurities and possible errors in surface area measurement. A further possibility is that in certain of Besoain's samples substitution of aluminum by iron may have occurred in the allophane to a significant degree. Thus, another plot of surface charge density vs. mole % $Al_2O_3+Fe_2O_3$ was made but

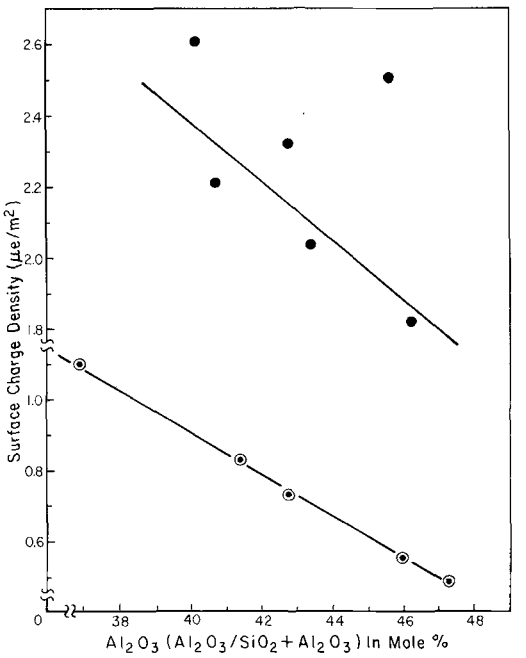


Fig. 2. Variation of surface charge density of imogolite with mole % Al_2O_3.

◉ Aomine and Yoshinaga, 1955 ($<2\mu$, Na-Saturated prior to chemical analyses, surface area by ethylene glycol, exchange capacity by NH^+ displaced with Na^+ at pH 7).

● Besoain, 1969 ($<0{\cdot}2\mu$, deferrated before chemical analysis, surface area by glycerol, exchange capacity by Na^+ displaced with NH_4^+ at pH 8·2).

the scatter of the data about a straight line was not noticeably reduced. However, it should be pointed out that the apparent fit of Park's (1969) value is considerably improved by plotting mole % $Al_2O_3+Fe_2O_3$* instead of Al_2O_3 (see Fig. 1 caption).

Thus, the cation exchange capacity of imogolite clays decreases over the interval between about 37 and 49 mole % Al_2O_3. As with synthetic materials, this relationship results from the fact that at higher aluminum contents, aluminum goes into sixfold rather than fourfold coordination. Using the data of Aomine and Yoshinaga (1955), it has been shown that this relationship can be seen more clearly when surface charge density is plotted against mole % Al_2O_3.

The allophanic clay cation exchange capacity values show no systematic variation with mole % Al_2O_3. If the three cation exchange capacity values greater than 100me/100g are disregarded, then the values scatter between 60 to 84 me/100g. It is probable that part of the cation exchange capacity variation of allophanic clays is real and is due to structural and particle size differences

*The value of Fe_2O_3 used was that remaining after deferration.

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but a significant part of the variation is probably a result of experimental technique. These data suggest that it may be necessary to use both cation exchange capacity and surface charge density vs. mole % Al_2O_3 to test for errors in cation exchange capacity and surface area determination or for the presence of other minerals which would effect these characterizations.

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Effects of repeated NaTPB-alteration and K-fixation upon a phlogopite

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THE PARTICLE size of a phlogopite "weathered" in the laboratory by repeated K-removal and K-fixation was observed to decrease solely as a result of the "weathering" process. Structural expansion of the mica by hydrated cations during exchange reactions may produce strain sufficient to induce particle break-up (Brown and Newman, 1970). As particle size decreased, the extent to which interlayer potassium became non-exchangeable increased. This process of particle size reduction and its resultant effect on K-exchange properties of the mineral can occur equally well in both the laboratory and in nature.

To accomplish the "weathering," a 15–20 μ (e.s.d.) fraction of phlogopite, $(K_{0\cdot92}[(Mg_{2\cdot32}Al_{0\cdot38}Fe^{2+}_{0\cdot13}Fe^{3+}_{0\cdot01}) \times (Si_{3\cdot01}Al_{0\cdot99})O_{10}Cl_{0\cdot02}F_{1\cdot10}(OH)_{0\cdot88}])$*, was repeatedly cycled through successive K-extractions using NaTPB (sodium tetraphenylboron) solutions (Scott *et al.*, 1959, 1960a, 1960b, 1962a, 1962b, 1966, 1968), followed by K-fixation using N KCl solutions. Five cycles were completed, one cycle being denoted as the combination of K-extraction and reintroduction of potassium into the mica (See Flow Chart, Fig. 1). In cycle 3, however, Mg-saturation followed K-removal, since more complete K-saturation was expected with Mg rather than Na as the complementary ion (Brown and Newman, 1970).

Equal amounts of mica and NaTPB mixed with 200 ml of N NaCl solution were agitated constantly with a magnetic stirrer. Alteration was continued until no more potassium could be removed. The rate of K-extraction was followed by analyzing for K and Na, representative mica samples taken periodically during the alteration period. The KTPB precipitate was removed from the samples using 4 washes with 70%(v/v)acetone-30%(v/v)N NaCl followed by 3 rinses with 70%(v/v)-acetone–30%(v/v)water.

Potassium was "fixed" into the altered micas (the basal spacing collapsed from 12·2 to 10·1 Å) by washing the samples 4 times with N KCl solution; the samples were shaken overnight after each KCl application. After K-saturation excess KCl was removed with 3

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