

STABILITY OF HECTORITE IN WEAKLY ACIDIC SOLUTIONS

III. ADSORPTION OF HEAVY METAL CATIONS AND HECTORITE SOLUBILITY

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ABSTRACT: The heavy metal cations studied were adsorbed by hectorite suspended in 0.05 M calcium chloride as a pH-dependent reaction in the order, $\text{Cu} > \text{Zn} > (\text{Co}, \text{Mn}) > \text{Ni}$. The adsorption of heavy metal cations was accompanied by the removal from solution of silicic acid released by clay dissolution. It is proposed that the reaction takes place on edge surfaces such that the clay lattice is effectively extended. This result complements other work in which it has been shown that the adsorption of silicic acid by other silicate clays results in an increased adsorption of zinc, cobalt and nickel. The present study did not provide evidence of the exchange of zinc and other cations for lattice magnesium.

The solubility of hectorite was decreased in the presence of heavy metal cations in the same order that favoured their adsorption. It is proposed that they limit the dissolution of hectorite in weakly acidic solutions by adsorption on or near the sites most prone to proton attack, that is, the magnesium ions of the octahedral layer exposed at edges and defects.

Many of the factors which affect the solubility of minerals, such as particle size, degree of crystallinity and chemical composition have been reviewed by Grim (1953). The work of Garrels (1960) and others on mineral equilibria in aqueous solutions has brought attention to the usefulness of thermodynamics in the study of the solubility of some minerals. In two recent studies, Tiller (1968*a, b*) has considered the dissolution of hectorite in weakly acidic solutions from the point of view of the mechanism of the reaction and conditions for quasi-equilibrium. The derived equilibrium constant provided a basis for describing the equilibrium solubility for a range of concentrations of magnesium and hydrogen ions and silicic acid. Observations during earlier studies (Tiller & Hodgson, 1962) suggested

that the solubility of hectorite might also be reduced when cobalt or zinc were added in small amounts.

The main aim of these studies is to investigate the mechanism of adsorption of heavy metal cations by hectorite in the presence of 0.05 M calcium chloride. This will be achieved in two ways. Firstly, general aspects of the reaction, such as the effect of pH, concentration in solution, and differences between heavy metal cations, will be considered. Secondly, recent studies of hectorite dissolution will be used as a basis for investigating the roles of silicic acid and lattice magnesium in the adsorption of zinc, cobalt and other metal ions by hectorite since Elgabaly (1950) has already suggested that zinc fixation by magnesium clays is due to the substitution of zinc for magnesium in lattice positions. The latter experiments have been carried out under conditions for which—in the absence of heavy metal cations—the stoichiometry has been established and the products of dissolution of hectorite are known to remain in solution. Hectorite was used as a model clay for this reaction because these conditions cannot be attained for aluminous clays.

The second aim is to study the effect of heavy metal cations on hectorite solubility, especially in relation to their adsorption by hectorite.

EXPERIMENTAL

Materials

The preparation of the hectorite suspensions was given in detail previously (Tiller, 1968a). The hectorite used was separated ($<2\ \mu$) from sample A.P.I. No. 34 supplied by Ward's Natural Science Establishment, Rochester, N.Y. and treated with hot ammonium chloride solution to remove calcium carbonate. Calcium chloride solutions were prepared from A.R. reagent and extracted with dithizone to remove traces of heavy metal impurities.

Analytical methods

Silicon was measured spectrophotometrically using the reduced form of a silicomolybdate complex. Magnesium, copper, zinc, nickel, cobalt and manganese were determined by atomic absorption. The pH of the clear supernatant solution after centrifugation was determined by glass electrode.

General procedure

The clay samples, usually 50 mg (105° C oven-dry basis), were pipetted from a bulk suspension and washed twice in 0.05 M calcium chloride before being used in experiments. The reactions were carried out by shaking 25 ml of suspensions in 0.05 M calcium chloride solution in polypropylene tubes at $20 \pm 1^\circ\text{C}$. After shaking, the suspensions were centrifuged at about 1200 g for 20 minutes before taking aliquots for analysis. Details of the experiments are given in the appropriate sections of 'Results'.

RESULTS

Adsorption

The hectorite suspensions were shaken with variable amounts of acid for five weeks to achieve quasi-equilibrium over the desired range of final pH before adding 5 μ -mole of the required cation. The reaction was allowed to proceed for a further two weeks. After centrifugation and analysis the amount of cation adsorbed was calculated by the difference from that initially added. The results for the adsorption of copper, zinc, cobalt, and nickel ions by hectorite as a function of pH are as shown in Fig. 1. Other unpublished data showed that the adsorption of manganese ions by hectorite was similar to that of cobalt ions. The adsorption of the heavy metal cation by non-specific electrostatic adsorption was minimized by the presence of excess calcium chloride. Cation concentrations were chosen so that precipitation of the hydroxide would not take place. Nevertheless, copper may have precipitated in some experiments in the samples of higher pH.

The extent of the adsorption of these cations was strongly dependent on pH and, for a final concentration in solution of about 10^{-4} M, varied in the following order, $\text{Cu} > \text{Zn} > (\text{Co}, \text{Mn}) > \text{Ni}$. The weak adsorption of nickel by clays, when compared with similar cations, will be considered in later work. Tiller & Hodgson (1962) have shown previously that cobalt and zinc were bound more strongly by

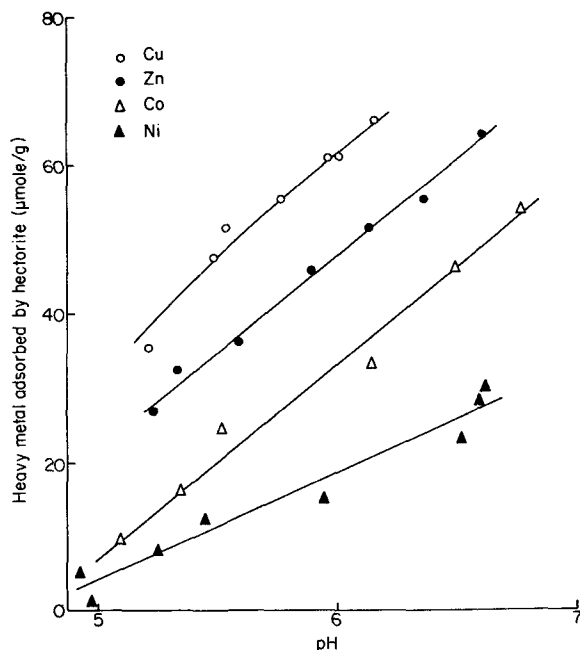


FIG. 1. The adsorption of copper, zinc, cobalt and nickel ions by hectorite in 0.05 M calcium chloride as a function of pH.

hectorite than by other silicate clays and that their adsorption by hectorite was accompanied by the release of hydrogen ions.

Some data were also obtained on the effect of concentration on the adsorption of cobalt and zinc by hectorite in 0.05 M calcium chloride at pH 6.5–7.0. The experimental conditions differed in the following respects from other adsorption experiments discussed above. After equilibrium of the pH of the suspensions for two weeks, radioactive cobalt and zinc were added and allowed to react for seven days at 25° C. Portions of the supernatant solution and the clay, after washing once with 0.05 M calcium chloride, were analysed for cobalt and zinc by radio-isotopic methods. The results are shown in Fig. 2. The small amount of divalent cobalt and zinc adsorbed by non-specific adsorption, calculated as 2 μ -moles/g of clay at 2×10^{-4} M assuming that

$$\frac{\text{Ca}^{2+}(\text{clay})}{\text{Co}^{2+} \text{ or } \text{Zn}^{2+}(\text{clay})} = \frac{\text{Ca}^{2+}(\text{solution})}{\text{Co}^{2+} \text{ or } \text{Zn}^{2+}(\text{solution})},$$

was removed by the washing with calcium chloride. The amounts of cobalt and zinc adsorbed under these conditions increased sharply with increasing solution concentration up to values of about 50 μ -moles/g of clay, when the concentration in the final solution was about 10^{-5} M. At higher concentrations of cobalt and zinc in solution the slope of the isotherms were markedly lower, with the amount of metal ion adsorbed increasing by about 0.3 μ -moles/g for each further increment of 10^{-5} M in solution concentration.

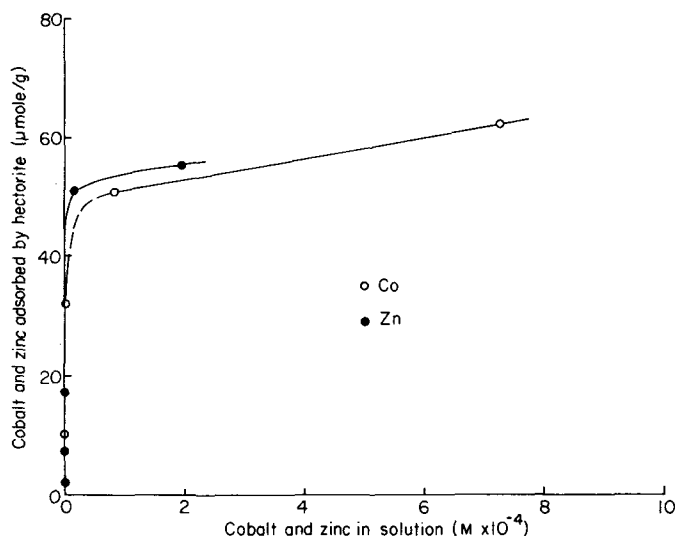


FIG. 2. The adsorption of cobalt and zinc by hectorite in 0.05 M calcium chloride as a function of final concentration of cobalt and zinc in solution.

Hence the adsorption of cobalt and zinc by hectorite at pH 6.5–7.0 in the presence of calcium chloride approaches a limit of about 60–80 μ -moles/g which is much less than the capacity for non-specific electrostatic adsorption (500 μ -moles/g for divalent cations). This limiting value for specific adsorption which is lower at lower pH values, is of the same order of magnitude as the number of magnesium atoms exposed at edges of clay particles (Tiller, 1968a).

Effect of adsorption on the release of silicon and magnesium

These and previous studies (Tiller, 1968a) showed that the addition of acid to hectorite in the presence or absence of heavy metal cations, always resulted in the equimolar release of silicon and magnesium when compared with samples to which acid was not added. This applied even for quite small amounts of acid equivalent to the hydrogen ions released by cation adsorption in these studies. It is assumed, therefore, that hydrogen ions released during the adsorption of heavy metal cations will also release silicon and magnesium in equimolar amounts. If the *only* result of the adsorption of these heavy metal cations was the production of hydrogen ions, then the difference between the amounts of silicic acid and magnesium released (Mg–Si) would be independent of the amount of heavy metal adsorbed even though the actual amounts of each of magnesium and silicic acid would have increased. These increases would both be proportional to the amount of hydrogen ions released.

Any variation in the value of (Mg–Si) can only result from an inequality in the net amounts of magnesium and silicic acid released due to other more specific effects associated with the adsorption of heavy metal cations. A quantitative assessment of these specific effects was made in the following way. The heavy metal cations were added to clay suspensions to which acid was not added so that the dissolution of hectorite was minimized. By this means, the amount of hydrogen ions produced during adsorption contributed significantly to the total amount of hectorite decomposed.

A. Heavy metals added initially

In several experiments, various concentrations of copper, cobalt and zinc were added to hectorite samples immediately after washing with calcium chloride and allowed to react for four or five weeks. The final amounts of magnesium ions and silicic acid in solution and of metal ions adsorbed were determined. The variation in the difference (Mg–Si) as a function of metal adsorbed in each experiment is shown in Fig. 3 for three representative experiments. The results are interpreted as indicating that there is either a relative increase in magnesium released or relative decrease in silicon released corresponding to 0.6–0.7 moles for each mole of metal ion adsorbed. Furthermore, examination of the actual concentrations of each of silicic acid and magnesium in the final solutions of each experiment showed that silicic acid always decreased but magnesium did not increase appreciably as the amount of metal adsorbed increased. When higher amounts of copper were removed from solution, presumably by precipitation, the difference (Mg–Si) was not appreciably

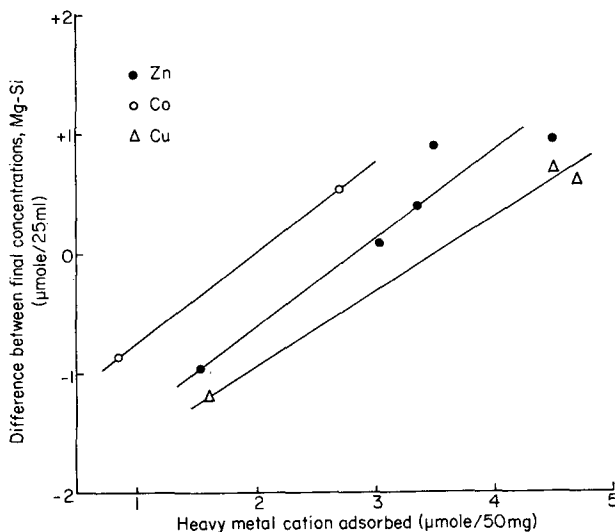


FIG. 3. The effect of the adsorption of heavy metal cations on the difference between the amounts of magnesium and silicon released. Heavy metal cations were added initially.

increased further. This suggests that only adsorbed heavy metal cations are involved in the relationship of Fig. 3.

B. Heavy metals added after equilibration of suspensions

In order to check that these results were not partly due to an effect of heavy metal cations on the kinetics of silicon or magnesium release, the suspensions of hectorite were equilibrated for nearly seven weeks before their reaction with up to 5 μ -moles of cobalt, zinc and other cations for a further two weeks. Reference suspensions to which no heavy metal cations were added were also included in each experiment. At the end of the experiments, silicon and magnesium were determined in the supernatant solutions of the suspensions to which metal ions were added as well as of the reference suspensions shaken for the same period. The inclusion of reference suspensions permitted the results to be presented as one curve. The data were assessed as above except that the values of (Mg-Si) for the appropriate reference suspensions were subtracted from the final value of (Mg-Si) corresponding to each level of each cation added. These corrected values of (Mg-Si) are shown in Fig. 4 in relation to the amounts of cobalt, zinc, nickel and manganese adsorbed. As before, the adsorption of heavy metal cations has resulted in an inequality in the amounts of silicon and magnesium released which, when expressed as the difference (Mg-Si), is equivalent to 0.6–0.7 moles per mole of cation adsorbed.

Examination of the actual amounts of magnesium and silicon in solution at the end of these experiments, in contrast to the consideration of their difference (Mg-Si), showed that the final amounts of silicon in solution decreased as the

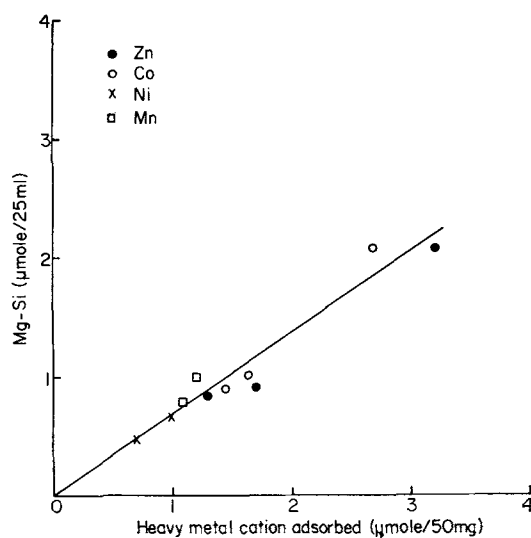


FIG. 4. The effect of the adsorption of heavy metal cations on the difference between the amounts of magnesium and silicon released. Heavy metal cations were added after shaking hectorite suspensions for 47 days.

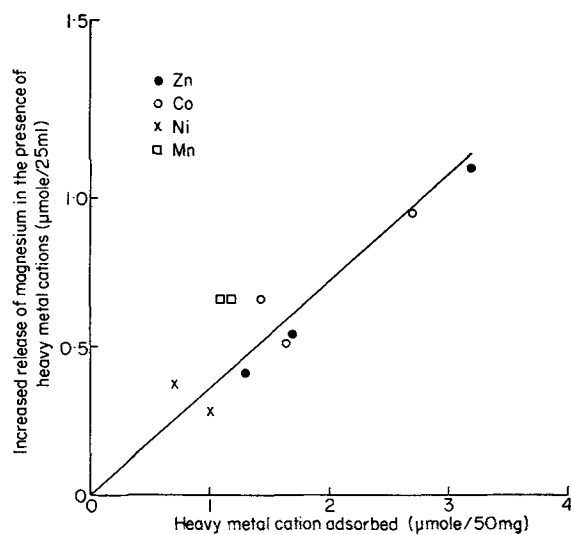


FIG. 5. The relation between the amounts of heavy metal cations adsorbed and magnesium released.

amount of heavy metal cation increased whereas the amount of magnesium increased. Fig. 5 shows that the final amount of magnesium increased about 0.3–0.4 moles per mole of cation adsorbed.

Solubility of hectorite

In this paper the final concentrations of magnesium and silicon in solution are used as a measure of hectorite solubility at a defined pH except under conditions where magnesium and silicon precipitate. The effect of heavy metal cations on the equilibrium solubility of hectorite in 0.05 M calcium chloride was assessed in the following experiment. Five μ -moles of each heavy metal cation studied was added to suspensions containing variable amounts of hydrochloric acid. The suspensions were shaken for 45 days, centrifuged and the supernatant solution sampled for the measurement of pH and magnesium and silicon concentration. The final concentrations of silicon and magnesium are shown as a function of pH in Fig. 6. The deficit in the amount of silicon released associated with the adsorption of heavy metals, discussed above, is small in relation to the amount released by the acid added. It would not affect significantly the final concentration of silicon in solution except at the lowest points of each curve where acid was not added. The essentially identical trends in solubility shown in both figures (apart from the points of lowest pH in Fig. 6(a) which are due to the presence of amorphous silica) suggest that the solubility data reflect properties of the hectorite only and not experimental artefacts. Conditions were chosen to ensure that precipitation of metal hydroxides, with the possible exception of that of copper at the point of highest pH, did not occur.

The solubility of hectorite is decreased by the addition of these heavy metal

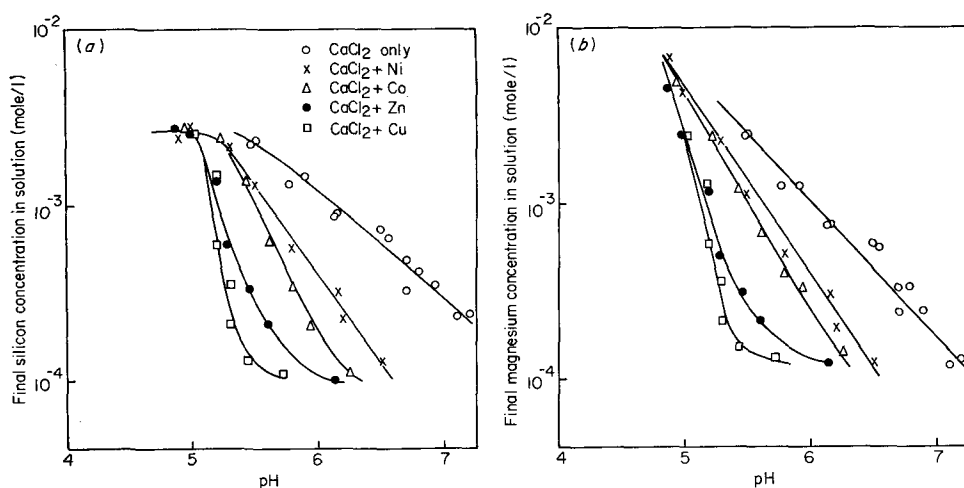


FIG. 6. The effect of heavy metal cations on hectorite solubility—(a) the final concentration of silicon and (b) magnesium in solution as a function of pH. Note that the ordinate scales are logarithmic.

cations in the weakly acidic range, pH 5–7 for the batch of clay used but not at lower pH values. The effectiveness of these cations in decreasing hectorite solubility is in the same order as their reactivity with hectorite, that is, $\text{Cu} > \text{Zn} > \text{Co} > \text{Ni}$. The amounts of heavy metal cations adsorbed by hectorite for the points of lowest solubility ($< 4 \times 10^{-4}$ M Mg in Fig. 6(b)) ranged in μ -moles/g from 46–54 for cobalt, 55–63 for copper, 56–61 for zinc and 15–30 for nickel. The importance of the amount of heavy metal cation adsorbed was also studied by adding varying concentrations of zinc to hectorite suspensions in calcium chloride. The solubility of hectorite decreased with increasing amounts of zinc absorbed. This work was extended to study the effect of zinc on the solubility of montmorillonite (A.P.I. No. 25) but zinc has no effect for pH values from 4 to 6.

GENERAL DISCUSSION AND CONCLUSIONS

Adsorption of heavy metal cations

It has been shown (Fig. 5) that the adsorption of these cations increases the final concentrations of magnesium in solution when compared to reference samples without heavy metal cations present. Magnesium released during the reaction with heavy metals could result from (i) the normal dissolution of clay due to the hydrogen ions present at the start of the reaction, (ii) the exchange of magnesium ions of the octahedral layer by heavy metal cations, and (iii) the dissolution of the clay by hydrogen ions released during the adsorption reaction. Contributions from (i) were largely allowed for by sampling all suspensions at the same time. Negligible quantities of hydrogen ions were introduced with the heavy metal cations. If the specific adsorption of zinc and other cations occurred only as described under (ii), a line of slope equal to unity would have resulted in Fig. 5. However the data of the figure could be consistent with about 0.4 of the total amount of heavy metal cations having been adsorbed by direct exchange with magnesium ions of the lattice, provided that the remaining 0.6 did not cause the release of hydrogen ions and thence magnesium ions. Nevertheless, it has been shown that hydrogen ions are released during the adsorption of heavy metal cations by hectorite. Unpublished studies in this laboratory have also established that the adsorption of zinc by montmorillonite from very dilute zinc solutions in the presence of excess calcium or sodium salts involves only hydrolysed zinc ions. The evidence of Hodgson *et al.* (1964) also favoured the adsorption of cobalt by clays in the presence of excess salt as the hydrolysed ion. If this mechanism also applies to other heavy metal cations, then the adsorption of each mole of hydrolysed ions will cause 1 mole of hydrogen ions to appear in solution due to simultaneous hydrolysis. These hydrogen ions will, in turn, yield 0.47 moles of magnesium on reaction with hectorite (Tiller, 1968*a*). In the absence of any specific effects of the heavy metal cations, it is assumed that an approximately equal amount of silicon would also be released. Hence all the additional magnesium released during adsorption can be explained by alternative (iii) without the need to postulate the specific exchange of zinc and other cations for magnesium in octahedral lattice positions which was suggested by

Elgabaly (1950) for the fixation of zinc by magnesium clays. It is concluded that direct exchange of zinc and other similar cations for magnesium in lattice positions, if it occurs at all, can play only a minor role in the process of fixation at room temperatures in an aqueous environment. The emphasis given in the literature to the latter mechanism involving the exchange of lattice ions may be partly a reflection of the property of some magnesium minerals, particularly when ground, of having relatively high pH values in aqueous suspensions. The pH values attained can often give rise to misleading results because of the possibility of precipitation of compounds of zinc, cobalt and similar ions.

Previous work (Tiller, 1968*a*) has shown that the silicon released during the dissolution of hectorite under the experimental conditions used here was not appreciably adsorbed by the clay. The adsorption of Mg was minimized by using suspensions in M/20 calcium chloride. It is against this background that the effect of the adsorption of heavy metal cations on the final relative concentrations of silicon and magnesium has been considered. The results of Figs 3 and 4 could have been interpreted either as a relative enrichment of magnesium or depletion of silicon, each with respect to the other, equivalent to about 0.6–0.7 moles per mole of heavy metal cation adsorbed. Most data have also shown an actual decrease in silicon concentration whereas some data showed smaller increases in the final concentrations of magnesium. The increased magnesium concentrations have been discussed and it is concluded that they are largely associated with normal dissolution by released hydrogen ions. Hence it is concluded that the disparity in the relative amounts of silicon and magnesium released in the presence of heavy metal cations is largely due to the reaction of released silicic acid with adsorbed heavy metal cations.

It is proposed that heavy metal cations are adsorbed as hydrolysed ions at edge sites adjacent to the octahedral layer cations and that this provides adsorption sites for silicic acid such that, on the average, two molecules of silicic acid are bound at sites adjacent to the tetrahedral layer for every three cations of zinc, cobalt etc. adsorbed. This is equivalent to a partial extension of the clay lattice. Such an extension would be imperfect with respect to hectorite because of the proportion of the constituents involved. In complementary studies, Tiller (1968*c*) has shown that the adsorption of silicic acid provides additional sites for the adsorption of some heavy metal cations on aluminous layer-silicate clays but not on alumina. This association with silicic acid may stabilize the adsorption of heavy metal cations by soil clays and thus make them less available to plants.

The effect of heavy metal cations on the solubility of hectorite

In the absence of added heavy metal cations, the solubility of hectorite is described by the equilibrium constant of the dissolution reaction (Tiller, 1968*b*). The results of Fig. 6 shows that the solubility at any particular pH value is decreased in the presence of heavy metal cations.

The association of silicic acid and heavy metal cations adsorbed on the edge surface of hectorite, as discussed above, could be considered as a rudimentary layer

of a separate metal silicate phase. Accordingly, the solubility of hectorite in the presence of heavy metal cations could be interpreted in terms of the stability of the corresponding metal silicate. This point of view may have only limited relevance to the problem of stability because the extent to which the cation studied favours hectorite stability is not related to its tendency to form silicates either synthetically (Caillère & Hénin, 1961) or in nature (Rankama & Sahama, 1950).

The preferred interpretation of the results is that heavy metals control hectorite solubility by an adsorption reaction. This arises from the observation that their effect on hectorite solubility follows the same order as that favouring their adsorption by hectorite.

It is proposed that the dissolution of hectorite continues until the concentration of hydrogen ions in solution decreases to such a value that heavy metal cations can compete successfully for adsorption sites associated with the exposed magnesium ions of the crystal lattice. The adsorbed cations are considered to prevent the displacement of magnesium ions from lattice positions by hydrogen ions. With the more strongly bound cations, hectorite can resist dissolution at lower pH values.

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