

# THE SPECIFIC SORPTION OF COBALT AND ZINC BY LAYER SILICATES

*by*

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## ABSTRACT

The sorption of Co and Zn by layer silicates was studied in dilute mineral suspensions containing, in most cases, about  $10^{-6}$  M Co or Zn. Electrostatic adsorption was eliminated by the presence of 0.1 N  $\text{CaCl}_2$ . Co and Zn were determined by a radioisotopic technique.

Detailed studies on montmorillonite and to a lesser extent vermiculite, muscovite and biotite revealed the presence of at least two forms of specifically sorbed Co, one of which was exchangeable by certain ions such as Cu, Ni, Zn, Fe, Mn or more Co and the other, occurring in much smaller amounts, was not exchangeable by these cations. The latter form is considered to result from lattice penetration; the former is associated with surface groups. These forms may be separated quantitatively by several desorption procedures including successive extractions with dilute acetic acid.

The total amount and relative proportion of these forms of sorbed Co and Zn depend on the pH of the system, time of reaction, mineral species used, and amount of Co or Zn added. Equilibrium is not readily attained but tends to approach a slow steady state after several days. Isotherms indicate a variation in bonding energy with surface coverage. The sorption of Co and Zn from dilute solutions by any mineral is related to its stability.

These studies, considered in conjunction with published data, suggest that a common mechanism may be involved in the specific sorption of many heavy metal cations by many minerals.

## INTRODUCTION

Many workers have studied the nonspecific adsorption of cations by pure minerals and soils; they have noted that certain of the heavy metal cations are not completely exchanged by common salts. This more firmly bound fraction has been found to be more significant at low concentration levels.

The work of Jones, Gall and Barnett (1936), Hibbard (1940) and Brown (1950) showed that part of the zinc added to soils could not be extracted by solutions of neutral salts. The last two authors gave evidence that this strongly bound zinc was associated with the mineral part of the soil rather than with the organic matter. Brown (1950) found that increasing amounts

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of the strongly bound zinc could be removed by using extracting salt solutions of increasing acidity. Gibbs and Marshall (1952) found that Putnam clay sorbed considerable Cu which was not extractable by ammonium acetate. Elgabaly and Jenny (1943) showed that part of the Zn sorbed by montmorillonite could not be exchanged by ammonium acetate. This strongly bound zinc was considered to have entered the crystal lattice and, in contrast to the work of Brown (1950), they concluded that the sorption of this strongly bound zinc had reduced the exchange capacity. In later work Elgabaly (1950) felt that the "fixation" of Zn by many minerals was entirely due to lattice penetration. Banerjee, Bray and Melstead (1953) studied the reaction of Co with certain soil and clay materials and found that part of the Co combined in a form that was extractable by acid but not ammonium acetate. This acid-extractable form increased with pH and time. Nelson and Melstead (1955) using a similar approach found similar results for Zn and furthermore concluded that the sorption of acid-soluble Zn had no effect on the cation exchange capacity of the clay. The results of Spencer and Gieseking (1954) suggested the presence of a much more strongly bound form of Co at low concentrations. DeMumbrum and Jackson (1956) also have demonstrated the sorption of Cu and Zn by montmorillonite from dilute solutions of Cu and Zn containing 0.5 N calcium acetate.

Recent studies by Hodgson (1960) on the reactions of Co with montmorillonite in the presence of excess  $\text{CaCl}_2$  showed the bound Co to consist of at least two main forms, one of which could be specifically exchanged with ions such as Cu, Zn, Ni, Fe, or Mn, or more Co. The second form, occurring in much smaller amounts, was not exchangeable by these ions. These forms could be separated quantitatively by several procedures including extraction with 2.5 percent acetic acid. These two forms were termed "exchangeable" and "nonexchangeable"; the former was considered to be bound chemically, lattice penetration being suggested for the latter.

The work described in this paper was designed to study the nature and extent of these sorption reactions for Co and Zn with emphasis on several layer silicate minerals, but reference will be made to other minerals.

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## MATERIALS

The minerals used in this study together with the source of each are listed briefly below.

The samples of montmorillonite (H 25), nontronite (H 33b), halloysite (H 12), hectorite (H 34) and pyrophyllite (H 49) correspond to the minerals originally collected for the American Petroleum Institute Project No. 49. Phlogopite, muscovite, biotite, talc and vermiculite were obtained from Ward's Natural Science Establishment, Rochester, N.Y. The kaolinite is from Cornwall, England. Only hectorite, which was heated in ammonium chloride solution to remove calcium carbonate, was chemically treated prior to dispersion. Phlogopite, muscovite, biotite, talc, pyrophyllite and vermiculite were ground, in a mechanical pestle and mortar, to pass a 100 mesh screen. Care was taken to sieve the powder every 15 min to reduce excessive abrasion of the fine particles. All minerals were sodium saturated by washing with 1 N NaCl and dispersed in water. The 2–20  $\mu$  fraction was separated from the ground minerals by sedimentation and centrifugation; the less than 2  $\mu$  fraction was separated by centrifugation from the naturally occurring clay minerals. Both fractions were separated from the ground vermiculite. The two separates were flocculated and washed several times with 0.1 N CaCl<sub>2</sub> and adjusted to the required suspension concentration.

## METHODS

Most experiments were carried out at very low solution concentrations, of the order of  $10^{-6}$  M, in an endeavor to approach the levels occurring in soil solution, and using dilute mineral suspensions of one-sixth percent for the 2:1 layer silicates and one-third percent for 1:1 layer silicates. Larger amounts of Co and Zn, up to the equivalent of two symmetries, were used in isotherm experiments. In all experiments a large excess of CaCl<sub>2</sub> was used to provide constant ionic strength, to allow flocculation when not shaken, and virtually to eliminate the sorption of Co and Zn by nonspecific electrostatic bonding.

By the use of the technique described by Hodgson (1960) successive extraction of vermiculite, biotite and muscovite with 2.5 percent acetic acid showed that the specifically bound Co of these minerals could also be separated into two forms.

All reactions were carried out in 15-ml Pyrex centrifuge tubes using polyethylene stoppers. All tubes were agitated continuously at constant temperature of 25 °C. The detailed manipulations of the procedure are similar to those described by Hodgson (1960).

After the initial sorption reaction using cobalt labeled with Co<sup>58</sup>, the suspensions were centrifuged and aliquots of the supernatant solution were taken and evaporated on stainless steel planchets in which a piece of lens paper previously had been glued. The samples were extracted twice with dilute acetic acid, and following centrifugation the supernatant was sampled as before. These planchets were counted with a Geiger–Mueller tube. After

the second acetic acid extraction the mineral residue was washed with neutral 0.1 N  $\text{CaCl}_2$  solution and  $\text{Co}^{58}$  was counted in the residue by a scintillation counter in conjunction with a radiation analyzer.

The sorption of Zn was studied by using identical procedures with  $\text{Zn}^{65}$ .

## RESULTS AND DISCUSSION

### *Sorption of Co as a Function of Time*

The data plotted in Fig. 1 show that, except for vermiculite, no equilibrium is reached in 31 days, but that after several days the curve decreases

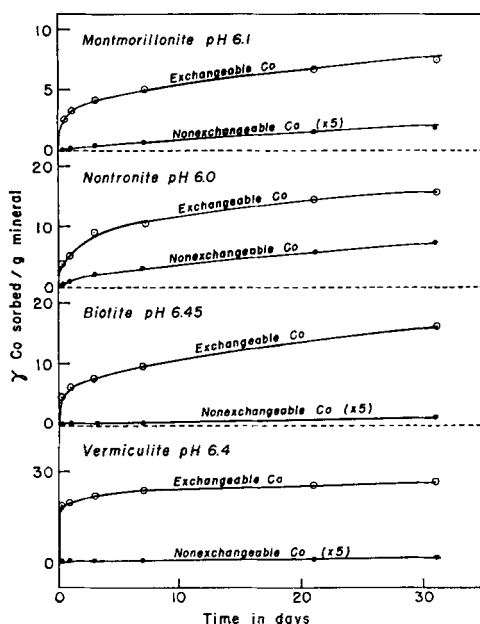


FIGURE 1.—Specific sorption of Co as a function of time.

in slope and indicates a possible steady state reaction, particularly for nonexchangeable Co. Equilibrium was approached for exchangeable Co with vermiculite (Fig. 1). Both solution concentration and amount sorbed remained fairly constant after 7 days but plotting the data on a larger scale showed that the nonexchangeable form still increased linearly with time. These curves show that the amount of Co sorbed and, in particular, the proportion of nonexchangeable Co present are determined arbitrarily by the duration of the reaction. Similar curves also were found for orthoclase, hematite, and muscovite. The data for the sorption of exchangeable Co by montmorillonite are in contrast with the earlier work of Hodgson (1960) in which this reaction came to equilibrium after three days. The variation

probably results from differences in pH and sources of montmorillonite. Whereas a high proportion of the Co sorbed by nontronite is nonexchangeable, only small amounts are associated with muscovite, biotite and vermiculite.

It is postulated that the formation of the nonexchangeable form involves an intermediate surface reaction followed by lattice penetration to the site of exchange with octahedral layer ions or filling of lattice vacancies.

On extraction for two 40-hr periods at 25 °C with 0.1 N HCl, all minerals lost about 80 percent of the nonexchangeable Co, regardless of the extent of dissolution of the mineral (Table 1).

The high proportion of nonexchangeable Co in nontronite, compared to montmorillonite, probably is related to the greater ease of penetration

TABLE 1.—DISSOLUTION OF MINERAL DURING EXTRACTION WITH 0.1 N HCl

Mineral	Percent Loss in Sample Wt.	Percent Nonexchangeable Co Extracted by HCl
Montmorillonite (< 2 $\mu$ )	3.5	80
Nontronite (< 2 $\mu$ )	15	88
Vermiculite (2–20 $\mu$ )	76	87
Muscovite (2–20 $\mu$ )	32	89
Biotite (2–20 $\mu$ )	49	81
Orthoclase (2–20 $\mu$ )	2	70
Hematite (2–20 $\mu$ )	21	78

of the more strained structure. Further evidence may be taken from a comparison of reactions carried out in Mg<sup>2+</sup> and Ca<sup>2+</sup> systems where the ionic radius of Mg<sup>2+</sup> is close to that of Co<sup>2+</sup>. Although the total amount of Co sorbed by nontronite is depressed in the Mg<sup>2+</sup> system, the amount of nonexchangeable Co is disproportionately reduced. This effect also is marked for phlogopite and vermiculite.

Although the electronic characteristics of an ion may be involved in the bonding of the exchangeable form, the ionic size may be more important to the nonexchangeable form, particularly if lattice diffusion is an essential part of the mechanism.

Most minerals have a much higher proportion of Zn than Co in the non-exchangeable form.

#### *Sorption of Co as a Function of pH*

The sorption of Co was found to be very pH sensitive and extreme care was used in the control of this factor. After the final pH adjustment of the system, a time interval of one week was always allowed before adding the Co or Zn. Isotherm experiments were limited in scope because at higher

concentrations of Co and Zn, with minerals of greater sorption capacity, there was a drop in pH during the reaction following the addition of Co and Zn.

Only those minerals with sorption data for Co and Zn are shown in Fig. 2. The reactions with Co and Zn are compared on the basis of sorption as a percentage of that added. The amount of kaolinite used in these comparisons was twice that of the other minerals, and hence its relative reactivity on a weight basis is even less than that suggested by Fig. 2. Even though the

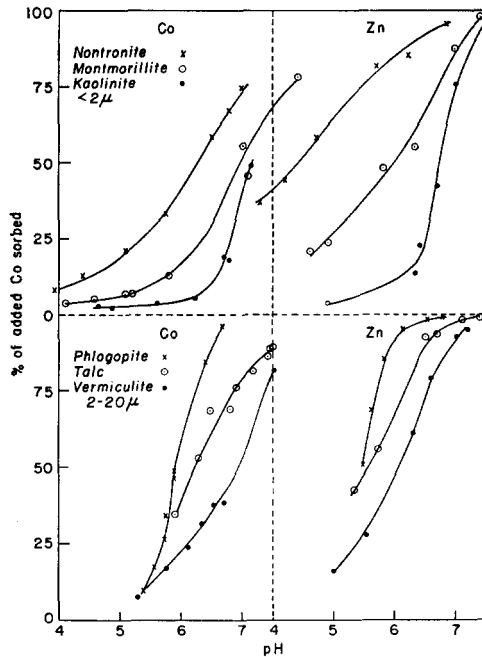


FIGURE 2.—Specific sorption of Co and Zn as a function of pH.

data are plotted on the basis of sorption as a proportion of that added, the data for Co and Zn cannot be compared in the same reference axes, as the amount of Zn added ( $1.11 \mu\text{g}$ ) was a little greater than the Co added ( $0.6 \mu\text{g}$ ). The general shape of the curves and the relation between minerals is the same for Co and Zn. There is also a fairly constant ratio of Co to Zn sorbed for all minerals where solution concentration is less limiting at lower pH. These observations also apply to some minerals not reported here and strongly indicate that a similar mechanism operates for each ion. The main difference is that Zn is bound more strongly than Co at the low concentration used in these experiments.

The pH-sorption curves may be used to compare the reactivity of various minerals with respect to the specific sorption of Co and Zn. Minerals were compared on the basis of same amount of Co added, particle size range, reaction time, and age of suspension. All experiments were conducted (as usual) in 0.1 N CaCl<sub>2</sub> with a reaction time of 7 days at 25 °C.

Comparison of these pH sorption curves for the 2–20 μ fraction of some ground minerals suggests the following decreasing order of reactivity:

muscovite > phlogopite > talc > biotite = vermiculite > pyrophyllite.

The < 2 μ fraction of some expanding 2:1 layer silicates and 1:1 layer silicates also are compared and have the following order of reactivity:

hectorite > vermiculite > nontronite > montmorillonite > halloysite > kaolinite.

Note that with the exception of vermiculite, these minerals are from natural clay deposits and were not ground.

#### *Effect of Grinding*

The possible influence of grinding must always be kept in mind in comparisons between minerals. Many studies have shown great changes in the properties of minerals during grinding, particularly if continued for long periods. Two of the most commonly considered effects of grinding are lattice distortion and formation of a secondary phase. Some information has been obtained (Tiller, 1961) on the latter by studying the effect of pretreatment of the minerals with dilute sodium hydroxide using conditions similar to those used by Hashimoto and Jackson (1960) for the removal of allophane. The < 2 μ fraction of some ground minerals became markedly less reactive after this treatment even though the sample weight decreased only slightly. An attempt has been made to assess the possibility of lattice distortion by comparing the sorption of Co by ground minerals using the same suspensions but aged for different periods.

The results of these experiments are shown in Fig. 3. The curves marked "fresh" describe the reactions carried out using suspensions that had been prepared 2–3 weeks earlier. The curves marked "aged" were carried out under exactly the same conditions, but using the same suspensions 7 months later. In each case 30 μg of Co sorbed per g of mineral corresponds to complete sorption of added Co.

All minerals except talc had a lower reactivity after aging in suspension. In general, the minerals hardest to grind—muscovite and phlogopite—changed in reactivity the most on aging, and talc, the softest mineral, changed the least. The rest were intermediate in hardness and change in reactivity on aging. This is as might be expected, for the soft minerals would have been least distorted on grinding and would in any case probably re-establish an ordered structure more readily.

Similar experiments carried out using  $< 2 \mu$  fractions of montmorillonite, nontronite and vermiculite (separated from ground material) did not show any significant change in reactivity on aging of the suspension for seven months.

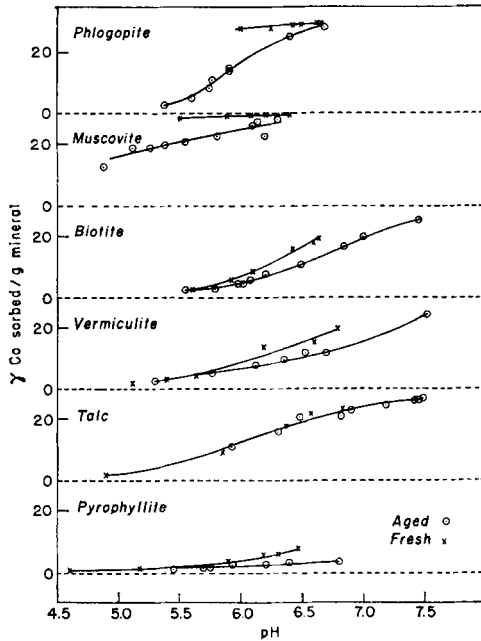


FIGURE 3.—Effect of aging of suspensions of ground minerals on the specific sorption of Co.

### *Sorption as Related to Structure and Composition*

Earlier in the discussion it was shown that different minerals, under similar conditions, sorbed different amounts of Co and Zn from dilute solutions. The variation in reactivity between structurally different mineral groups and within any particular isomorphous series is, in general, similar to that known for the resistance of minerals to acid attack and to natural weathering processes. The most resistant mineral was the least reactive.

When ground minerals are considered, the 2:1 layer silicates are more reactive than those having a continuous framework of linked tetrahedra. Within the 2:1 layer silicates phlogopite and talc with only Mg in the octahedral positions are generally the most reactive. Vermiculite and biotite are intermediate whereas pyrophyllite, with Al only in octahedral positions, is least reactive. Muscovite is an exception to this order. This mineral is the most reactive of the group but its reactivity may be introduced



largely as a result of extensive grinding since it was more difficult to grind than the other minerals. Some work also was done on other silicate minerals and of these the feldspars, albite and orthoclase, were similar to pyrophyllite in reactivity. Gibbsite and quartz are less reactive still.

In considering the naturally occurring clay minerals the 2:1 layer minerals are more reactive than the 1:1 layer minerals. Within each group the reactivity is again related to stability to weathering and acid attack. For example, hectorite is both least stable and most reactive and montmorillonite is most stable and least reactive.

The variation in nonexchangeable Co with structure follows the same pattern but is more pronounced, being much higher in the strained structures containing only  $\text{Fe}^{3+}$  or  $\text{Mg}^{2+}$  in the octahedral positions. The proportion of the nonexchangeable form sorbed decreased in the order nontronite, phlogopite, hematite and talc for the minerals in which it was most significant. The separation of the two forms with hectorite is probably obscured by the partial dissolution of the mineral by acetic acid.

#### *Sorption of Co and Zn as a Function of Solution Concentration*

Isotherms at 25 °C are shown in Fig. 4 for total Co and Zn sorbed plotted against concentration of ion in solution. The data shown are for the  $< 2 \mu$  fraction except muscovite for which the 2–20  $\mu$  fraction was used. The

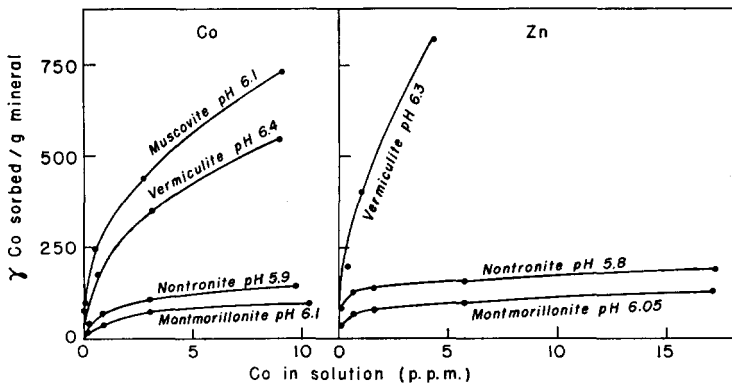


FIGURE 4.—Sorption isotherms for Co and Zn at 25 °C in the presence of 0.1 N  $\text{CaCl}_2$ .

reaction time was 7 days. At larger solution concentrations the amounts of Co and Zn attributed to the mineral by electrostatic forces and left in the entrapped solution after centrifugation introduce a significant error in the determination of the amount bound by specific forces of attraction. To ensure that contribution from these sources was negligible, the mineral suspensions were washed with fresh  $\text{CaCl}_2$  solution before assaying for Co

and Zn on the mineral. A separation of exchangeable and nonexchangeable forms was made, but generally the contribution of the nonexchangeable form was sufficiently low that the curves represent a good approximation of the exchangeable form.

Although these isotherms are difficult to treat theoretically owing to the lack of equilibrium conditions and the apparent heterogeneity of the surface involved, the lack of inflection in the curves at high concentration can be taken as evidence against multilayer formation. Great care was used in these experiments to avoid precipitation.

Analysis of the isotherms suggests a decrease in bonding energy with surface coverage. This makes it difficult to evaluate an adsorption maximum, since as bonding energy decreases it becomes increasingly difficult to distinguish from nonspecific electrostatic bonding. Odd points, not plotted, for higher solution concentration confirm that no sorption maximum is approached in the presence of  $\text{CaCl}_2$  even when amounts of Co and Zn equivalent to two symmetries are added.

## CONCLUSIONS

(1) Specific sorption reactions for Co and Zn take place in the presence of excess  $\text{CaCl}_2$  with a large range of minerals, including expanding and nonexpanding 2:1 layer silicates, 1:1 layer silicates, and also feldspars, hematite, goethite, gibbsite and quartz.

(2) The specifically bound cation exists in at least two main forms. The dominant form can be characterized by an exchange by certain other cations and acetic acid whereas the other can not. The nonexchangeable form is associated probably with lattice penetration, the exchangeable form with surface groups. The amount and proportion of these two main forms strongly depend on the mineral system used, the amount of Co or Zn added, and, in particular, the pH and time of reaction.

(3) These specific sorption reactions do not readily attain equilibrium but after an initial period of several days tend to approach a nearly steady state reaction.

(4) Analysis of the adsorption isotherm indicates a variation in bonding energy with surface coverage.

(5) Reactivity appears to be related to mineral stability. The amount of Co and Zn vary within a mineral group with the nature and proportion of cations in the octahedral layer. The implications of this are discussed in the succeeding paper (these Proceedings).

(6) There have been many observations in the literature which suggest a similarity in the reaction of the heavy metal cations, especially Co, Cu and Zn, with clay minerals. Detailed studies using montmorillonite (Hodgson, 1960) indicated that specific exchange reactions between various ions in

dilute solution were restricted to the heavy metal cations. In these experiments a close similarity was noted for the sorption of Co and Zn by many minerals under varying conditions of pH and solution concentration. All these data suggest that a common mechanism is involved in the bonding of at least Co and Zn, and probably other heavy metal cations. The difference in amount of Co and Zn sorbed from dilute solutions is due to the specificity of the reaction rather than to a different mechanism.

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