

THE LOCATION OF BOUND COBALT ON 2:1 LAYER SILICATES

by

J. F. HODGSON AND KEVIN G. TILLER¹

United States Plant, Soil and Nutrition Laboratory, Agricultural Research Service, U.S.D.A.,
and the Department of Agronomy, Cornell University, Ithaca, New York

ABSTRACT

Three techniques have been used to determine what clay mineral surfaces are involved in the selective bonding of Co: (a) polyphosphate ions were used to block edge surfaces of montmorillonite and vermiculite from Co, (b) collapse of the interlamellar spaces with potassium saturation was used to block internal basal surfaces of vermiculite from Co, and (c) autoradiographs were prepared of vermiculite and mica particles that had reacted with Co⁵⁹. In each case Co in low concentration was allowed to combine with the mineral in the presence of high concentrations of CaCl₂.

The preliminary sorption of polyphosphate ions had no appreciable effect on the sorption of Co by the minerals studied, indicating that the edge surfaces were not likely to be involved in the Co reaction. The blocking of internal basal areas had only a very slight effect suggesting that these surfaces were involved in the sorption of Co, but only to a limited extent. Autoradiographs of naturally occurring vermiculite particles revealed a somewhat uneven distribution of Co over the planar surface of the particles. Removal of the outer layers of the crystals, either before or after the material had combined with Co but before autoradiography, resulted in a concentration of the metal along edges and cracks.

Apparently the external basal surfaces are principally involved in the specific sorption of Co by layer silicates. It is suggested that chemical weathering and physical abrasion of the surfaces introduce defect structures which favor the chemical bonding of heavy metals.

INTRODUCTION

Heavy metals may be attracted to clay mineral surfaces by forces other than those resulting from the negative charge on the mineral. This conclusion is inherent in the observation of many workers that heavy metal cations that have combined with clay minerals will not completely exchange with other cations or may exchange only with cations of certain heavy metals.

¹ Present address: Division of Soils, C.S.I.R.O., Adelaide, South Australia.

A few attempts have been made to develop hypotheses regarding the nature of the linkage formed between heavy metals and clay minerals. Bower and Truog (1940) concluded from measurements of exchange capacity using different cations that hydrolysis was a factor in the base exchange reactions of certain cations. Menzel and Jackson (1951) and also Spencer and Giesecking (1954) have further suggested that the formation of basic ions was involved in the combination of Cu and Co with clays. However, it is not essential to invoke the concept of basic ion formation to explain the results in either case since specific exchange reactions involving H or possibly Al could also give the observed results. Infrared analysis has been used (DeMumbrum and Jackson, 1956) to implicate lattice hydroxyls in Cu-clay reactions. The selective nature of heavy metal sorption by clay minerals was presented in support of the contention that a chemical bond must be involved in these reactions and that they are in part made up of exchange reactions specific for a certain group of cations (Hodgson, 1960). Solid state diffusion into the crystal lattice also has been suggested as a factor in heavy metal-clay systems (Elgabaly and Jenny, 1943; Hodgson, 1960).

This paper investigates the nature of the clay mineral surfaces that are involved in selective bonding of Co. The problem has been approached in three ways: (a) blocking edge surfaces by the use of sodium polyphosphate (Calgon); (b) blocking internal basal surfaces of vermiculite by collapsing the interlayers with K saturation; and (c) preparing and visually observing autoradiographs of individual particles of vermiculite and mica that had sorbed radioactive Co⁵⁸.

EXPERIMENTAL METHODS

Blocking of Edge Surface

Two expanding lattice minerals were selected for treatment with sodium polyphosphate: the $< 2 \mu$ fraction of Wyoming bentonite and the 2–20 μ fraction of a Montana vermiculite were collected by sedimentation and centrifugation. The vermiculite was ground in a mortar before fractionation. Three replications having 30 mg of mineral each were washed four times in 15 ml centrifuge tubes with 0.5 N NaCl, and the treated samples allowed to react with 1 and 5 percent sodium polyphosphate (Calgon) overnight. The samples were washed rapidly, five more times, with 0.5 N NaCl before adding 0.8 μg of Co⁵⁸ (67 ppb, 1.1×10^{-6} M) to each tube. The samples were shaken at 24 °C for 3 days. After removing the supernatant liquid the samples were extracted twice for 3-day periods with 2.5 percent acetic acid. The amount of Co in extract and residue was determined by assaying for radioactive content with a scintillation counter.

Blocking of Interlayer Surfaces

Vermiculite fractions of $< 2 \mu$ and $2-20 \mu$ were collected by sedimentation and centrifugation from the source mentioned above. Each fraction was divided into three treatments of three samples each. The first treatment was Na saturated before adding Co and washed five times with 0.5 N NaCl after the mineral had reacted with Co. The second was K saturated before adding Co and washed five times with 0.5 N KCl after the Co reaction. The third was sodium saturated initially but washed five times with 0.5 N KCl

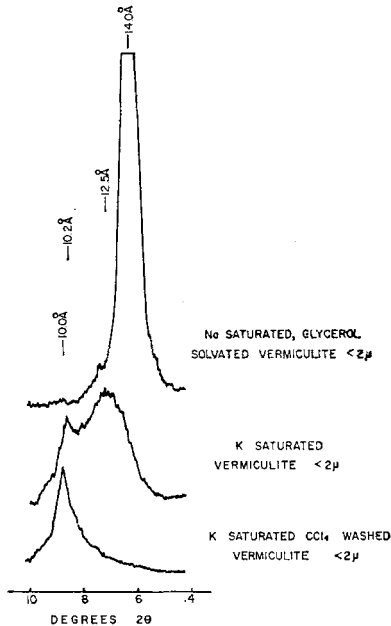


FIGURE 1.—Effect of saturating with K and washing with organic solvents on the basal spacing of the vermiculite used in these studies. The curve labelled “ CCl_4 washed” included washes with isopropyl and isobutyl alcohols.

after the Co reaction. Immediately following a group of salt washings the samples were washed two times each with isopropyl alcohol, isobutyl alcohol, carbon tetrachloride and again with isopropyl alcohol. This treatment promoted collapse of the K-saturated interlayers (Fig. 1). Each treatment was extracted twice with 2.5 percent acetic acid after the last salt wash.

Preparation of Autoradiographs

Autoradiographs were prepared for from four to six particles from each of three samples of vermiculite and eight samples of mica. The mica particles were separated from both mineralogical deposits and soils. Individual

particles 1–10 mm across were allowed to combine with solutions that were 10^{-6} M with respect to Co^{58} (specific activity of 200 c per g) and 5×10^{-2} M with respect to CaCl_2 . The pH of the solutions was maintained at values ranging from 6.2 to 6.7. The mineral particles were allowed to combine with the Co for a period of one week at which time they were washed five times with 5×10^{-2} M CaCl_2 , transferred to a Buchner funnel, washed with distilled water, then alcohol, and dried. Each particle was then affixed to a lucite slide by first dipping the slide into chloroform and then placing the particle on the slide before the solvent had evaporated completely.

Autoradiographs were prepared by the stripping emulsion technique with Kodak AR.10 photographic emulsion supplied on glass plates (Pelc, 1947; Boyd, 1955). Exposure varied from 8 hr to 3 weeks. The stripping emulsion was removed from the vermiculite particle after developing so that the photographs include only the exposure of the autoradiograph and a few bits of mineral that broke off with the emulsion. Autoradiographs of mica illustrated in this paper include the mineral particle as well.

RESULTS

Effect of Edge Blocking

The sodium polyphosphate did not decrease the retention of Co as would be expected if it had blocked the edge surface against the entry of Co (Table 1). A small increase in the sorption of Co was noted but the physical significance of this increase is doubtful, especially as it was not observed on a smaller, preliminary, experiment. If the polyphosphate ion can be assumed to have blocked the edge surface against the entry of Co ions to any appreci-

TABLE 1.—EFFECT OF POLYPHOSPHATE PRETREATMENT ON THE SORPTION OF CO BY MONTMORILLONITE AND VERMICULITE

| Polyphosphate Concentration (percent) | pH | μg Co per 100 mg mineral | |
|---------------------------------------|-----------------|-------------------------------------|-------------------------------------|
| | | Extractable by 2.5% Acetic Acid | Not Extractable by 2.5% Acetic Acid |
| | Montmorillonite | | |
| 0 | 6.32 | 0.85 | 0.0070 |
| 1 | 6.31 | 0.99 | 0.0070 |
| 5 | 6.35 | 0.98 | 0.0076 |
| | Vermiculite | | |
| 0 | 6.62 | 2.4 | 0.0064 |
| 1 | 6.64 | 2.5 | 0.0080 |
| 5 | 6.68 | 2.5 | 0.0070 |

able degree, these results would indicate that edges of layer silicates are not involved in the bonding of Co.

Effect of Interlayer Collapse

The effect of potassium saturation and collapse of the interlayers on the Co-mineral reaction was also very small (Table 2). If the internal basal surfaces were involved to any significant degree in the retention of Co by vermiculite, the initial collapse of the lattice should seriously reduce the subsequent reaction of the mineral with Co. No such reduction was noted.

TABLE 2.—EFFECT OF K COLLAPSE ON THE REACTION OF COBALT WITH VERMICULITE

| Base Saturation | | $\mu\text{g Co per 100 mg Clay}$ | | | | |
|-------------------------------|-------------------|----------------------------------|-------|-------|---------------------------|--------------------------|
| Before and During Co Reaction | After Co Reaction | Acid Extractions | | | Total Acid Extractable Co | Co not Extracted by Acid |
| | | 1 | 2 | 3 | | |
| | | Less than 2μ vermiculite | | | | |
| Na | Na | 2.0 | 0.078 | 0.016 | 2.1 | 0.007 |
| K | K | 2.1 | 0.093 | 0.023 | 2.2 | 0.023 |
| Na | K | 1.7 | 0.093 | 0.033 | 1.8 | 0.12 |
| | | 2–20 μ vermiculite | | | | |
| Na | Na | 2.1 | 0.057 | 0.011 | 2.2 | 0.005 |
| K | K | 2.0 | 0.070 | 0.025 | 2.1 | 0.023 |
| Na | K | 1.9 | 0.090 | 0.026 | 2.0 | 0.104 |

Similarly, if these surfaces were responsible for the sorption of Co when the interlayers were expanded, bound Co should have been trapped when the mineral was K saturated and rendered much less available for extraction with acetic acid. Collapse of the lattice did not seriously alter the amount of Co extracted with acetic acid. Examination of the residue, however, reveals that when the interlayers are closed down there is a significant increase in that fraction of Co which cannot be extracted with acetic acid. Furthermore the distribution of Co in the successive acid extractions of K-collapsed vermiculite is slightly smaller in the first extraction and slightly larger in subsequent extractions. Thus a portion of the Co normally brought into solution with acetic acid appears to be more difficult to extract after K saturation and was presumably sorbed on the interlamellar surfaces. However, only a small amount of the total Co sorbed seems to be influenced in any way by closure of the interlayers.

Autoradiographs of Vermiculite

Examination of autoradiographs of naturally occurring particles of vermiculite that had sorbed Co^{58} indicated relatively uneven distribution of Co over the basal surface of the mineral (Plate 1). In certain cases Co is con-

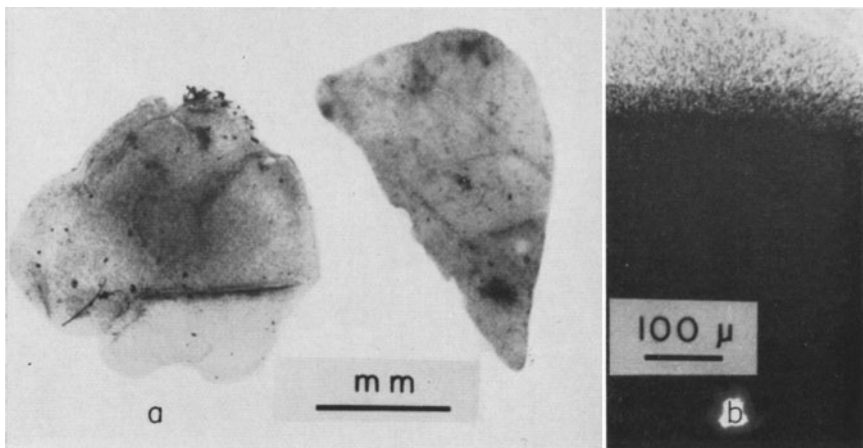


PLATE 1.—Autoradiographs of vermiculite particles that have adsorbed Co^{58} in the presence of large amounts of CaCl_2 . (a) Viewed under low magnification; (b) enlargement of an area at edge of a particle.

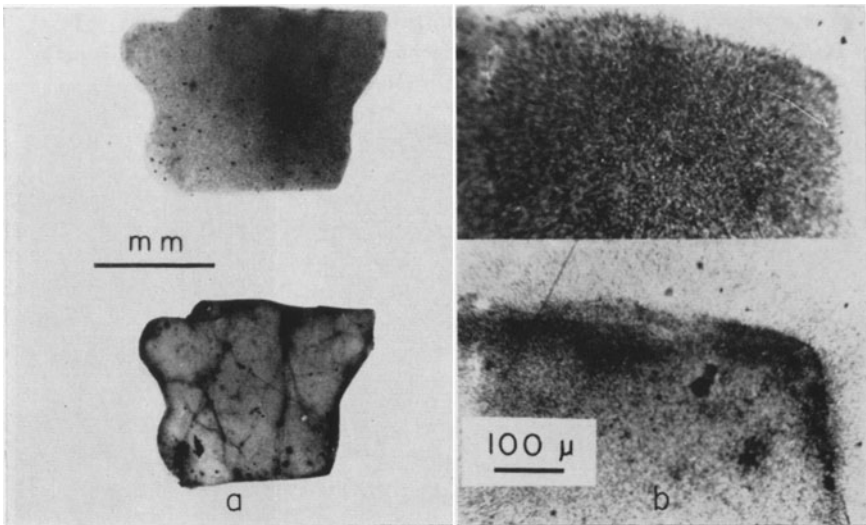


PLATE 2.—Autoradiographs of vermiculite particles that have adsorbed Co^{58} in the presence of large amounts of CaCl_2 . The lower autoradiograph in each case was made after the basal surfaces of the particle had been stripped off.

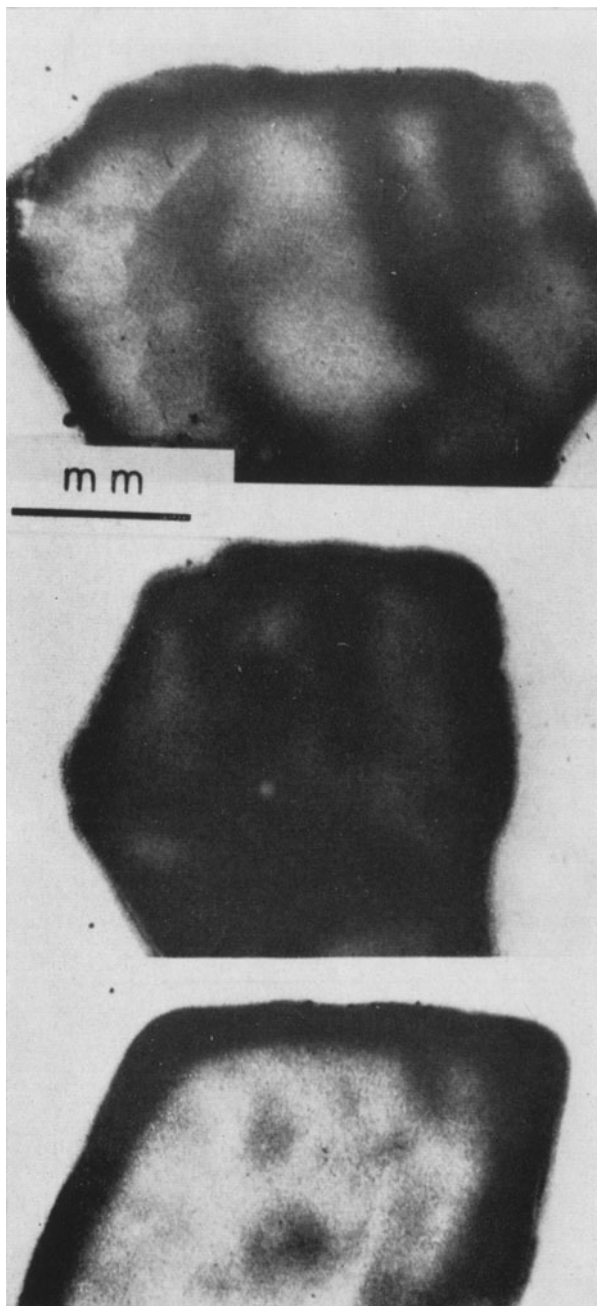


PLATE 3.—Autoradiographs of vermiculite particles that have adsorbed low specific activities of Co^{60} in the absence of CaCl_2 .

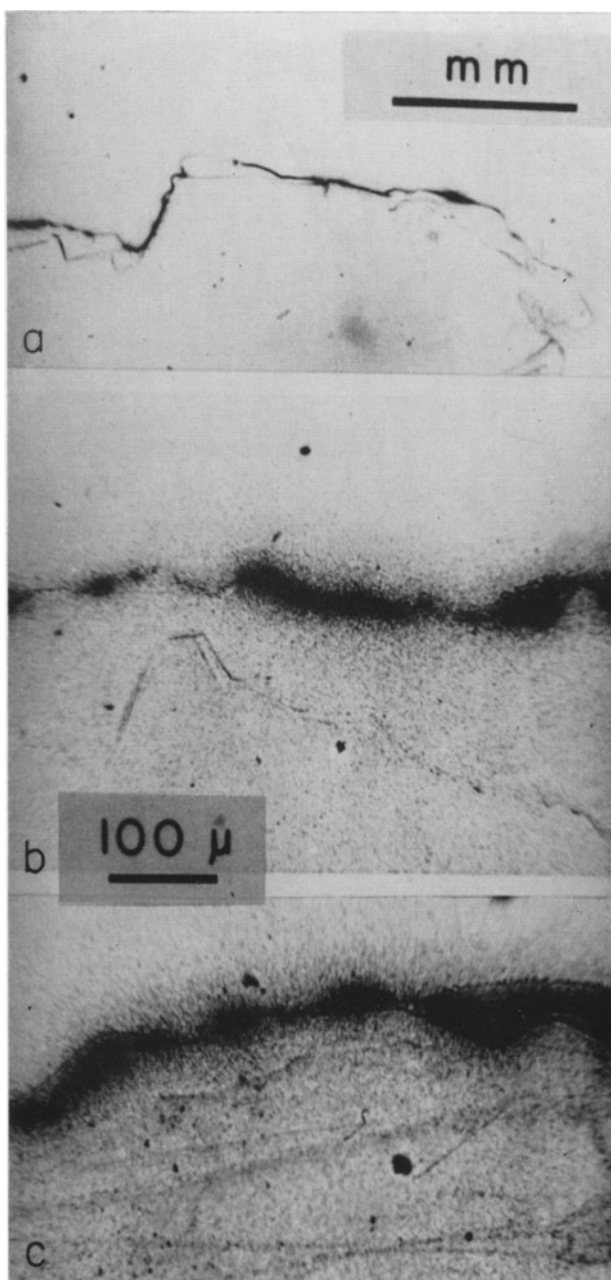


PLATE 4.—Autoradiographs of mica particles that have adsorbed Co^{58} in the presence of excess CaCl_2 . (*a*, *b*) muscovite; (*c*) biotite

centrated near the edges or cracks of the crystal and occasionally in isolated spots, but the association of the metal with the basal surface is the most striking feature.

Results presented thus far suggest that edges are not appreciably involved in the selective sorption of Co by layer silicates and that internal basal surfaces are involved only slightly. Yet in the autoradiographs there appears to be a relatively even smearing of the Co over the planar surface of the crystal. To investigate the possibility that the external basal surfaces were principally responsible for the sorption of Co by vermiculite, a method was developed to strip off the outer layer of the crystal.

It was noted that when the autoradiographic stripping emulsion with its gelatin base was fully hydrated, it could be removed from the mineral particle without noticeably damaging the particle. On the other hand, when the stripping emulsion was removed dry, it would cleave the particle approximately into two equal parts. As the emulsion layer became partly hydrated it tended to strip off thinner sheets of vermiculite. By immersing the slide with affixed particle covered by dry stripping emulsion for 3 min in water, the emulsion could be stripped off cleaving the particle in such a way as to remove only a very thin flake of vermiculite.

When the preceding technique was employed and the remainder of the particle autoradiographed for a second time, an entirely different distribution was noted (Plate 2). These second autoradiographs, because of their lowered activity, were exposed approximately twice as long as the originals of the same particle. Plate 2 shows that the Co is no longer distributed evenly over the surface but is concentrated near the edges and cracks. The pattern does not suggest that Co is concentrated at the edge or crack but rather is distributed back from these features for some distance.

When flakes of vermiculite were broken away from larger crystals of Montana vermiculite (supplied by Ward's Natural Science Establishment) and these flakes allowed to react with small amounts of Co, they gave autoradiographs very similar to those obtained from naturally occurring particles that had been cleaved after they had combined with Co. These would indicate that the cleaved surface is less reactive than the one occurring naturally. Any abrasion or distortion of that surface markedly increases the retention of specifically bound Co.

Interpretation of these data must be moderated to some extent by the distribution of Co when it is added to the system in high concentration using low specific activity Co in the absence of Ca. Under these conditions the Co is presumably associated with the mineral principally by electrostatic forces. The specific activity was sufficiently low that selective exchange reactions studied up to this point could barely be detected. When autoradiographs are made of these particles an even different distribution is noted (Plate 3). The Co still is concentrated near cracks and edges but

there is less variation from one particle to another and from one portion of the edge to another when the Co is bound by coulombic forces.

Autoradiographs of Mica

Autoradiographs of portions of mica flakes that were cleaved from large muscovite and biotite crystals are shown in Plate 4. Here the Co appears immediately at the edge of the crystal. The stripping emulsion was not removed from the particles for these photographs, so that the exposure of the emulsion is superimposed on the mica itself. In the center particle of Plate 4 there are successive steps to the edge, but only one of these steps has reacted with Co.

In contrast, when crystals of muscovite and biotite were separated from soils, Co seemed to be distributed over the planar surface as in the naturally occurring vermiculite particles. Unfortunately autoradiographs that were made of naturally occurring micas were very difficult to evaluate qualitatively because the surface of the mineral broke up and came off with the stripping emulsion. The autoradiographs in this case could be evaluated only by noting the density of silver bromide grains in small fields of vision through the particle in contrast with the background.

CONCLUSIONS

From the foregoing results the following model is proposed: External basal surfaces of layer silicates are principally involved in the selective retention of Co, but all planar surfaces are reactive to a lesser degree. In micas, weathering and physical fraying of the edges during handling allows the Co to come in contact with interlamellar surfaces immediately adjoining the edge. The resolution of the autoradiographs is such that if the Co were distributed as far back as 8–10 μ from the edge it could not be distinguished from that sorbed on the edge surface itself.

Since the exposure of internal basal surfaces of vermiculite through cleavage does not noticeably increase their reactivity, the disproportionately high retention of Co by the naturally occurring external surfaces must be the result of interactions between the particle and its environment, either through the weathering of that surface or the sorption of foreign materials which in turn contribute to the sorption of Co. Tiller's (1961) data suggest that the presence of foreign matter is not a major factor in the reactivity of the mineral. From the influence of physical abrasion on the reactivity of vermiculite together with the pattern of reactivity of other minerals, as noted in the previous paper (these Proceedings), it is considered likely that crystal strain or defect structure provides the conditions that result in a specific chemical combination of heavy metals with the basal surfaces of

layer silicates. Such defects may be formed in the original mineral structure owing in part to strain arising from certain isomorphic substitution, or they may result from physical abrasion or chemical weathering.

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