Oxidation of Ferrous Iron in Vermiculite and Biotite Alters Fixation and Replaceability of Potassium

Abstract. *Oxidation of octahedral ferrous to ferric iron in soil vermiculite clays and biotites increases the potassium-fixation capacity of vermiculites and increases the difficulty of replacing interlayer potassium in biotites. This unexpected effect is believed to be related to an increase in the attractive forces between potassium ions and oxygen ions of the surface layers which is brought about by a tilting of the dipole of the octahedral hydroxyl ions from a perpendicular position to an inclined position with respect to the cleavage plane.*

One of the factors affecting fixation of potassium by vermiculite and replaceability of potassium from biotite (*1–3*) is the total layer charge at the cleavage planes of the crystals: thus the higher the charge, the more strongly potassium is fixed, and the more difficult it is to replace. We here report results of a study of fixation by soil clay vermiculites, which were contrary to the foregoing finding. When Fe^{3+} in the crystal lattice of several samples had been reduced to Fe^{2+} by removal of free Fe_2O_3 from clays (*4*), the samples exhibited a decrease in potassium fixation (Table 1), even though there was an increase in layer charge. Those samples with Fe^{2+} iron which remained wet after being saturated with K^+ exhibited almost no K^+ fixation, whereas those with Fe^{3+} iron did. Furthermore, after changing the potassium-saturated samples from an air-dry to an oven-dry condition, those with Fe^{3+} iron exhibited a larger increase in K^+ fixation than did those with Fe^{2+} iron.

The increase in K^+ fixation resulting from oxidation led us to suspect that the ease of replaceability of the interlayer K^+ from biotites with a cation which is capable of replacement (*5*), such as Mg^{2+}, might decrease upon oxidation of the octahedral Fe^{2+} to Fe^{3+}—a reaction which occurs in nature. In order to investigate this possibility, the Fe^{2+} iron of two powdered biotite samples (*1*), whose particles had the dimensions of silt, was artificially oxidized by repeated treatment with a hot (70° to 80°C) 5 percent (by weight) solution of sodium hypochlorite at *p*H 11.4 until the green or black color of the samples changed to reddish-brown. Chemical analysis of the treated samples disclosed that, even though most of the Fe^{2+} was oxidized to Fe^{3+}, the layer charge remained nearly the same as in the untreated samples; however, x-ray analysis disclosed that the samples became partially converted to vermiculite owing to the replacement of some of the K^+ with Na^+. The retention by the treated samples of a layer charge which was nearly equal to that of the untreated samples rendered them ideal for the proposed study. The complication of a lower layer charge, which can occur when Fe^{2+} is oxidized to Fe^{3+} under certain *p*H conditions (*6*), was avoided. In order to carry out the replaceability experiment, it was only necessary to resaturate the samples with K^+. This was readily accomplished by leaching with a normal KCl solution and then elutriating the soluble salts with methanol. X-ray analysis of these potassium-saturated samples disclosed that they reverted to the crystal structure of biotite and that they were identical in form to the original samples. No evidence was found by any test that the biotite was destroyed by treatment with sodium hypochlorite.

Table 1. Potassium-fixation capacities (amount of adsorbed K^+ which is not replaceable by NH_4^+ expressed as the percent of total adsorbed K^+) of soil clays in relation to the state of oxidation of octahedral Fe. Prior to extraction with $1N$ $NH_4C_2H_3O_2$, the potassium-saturated samples were either water-wet, or dried at room temperature, or oven-dried at 110°C. Total K^+ in the vermiculite sample is expressed as milliequivalents per 100 grams (ignited weight basis).

Sample name	Total K^+ in vermiculite fraction (meq)	K^+ fixation capacity (%)			Increase in fixation by oven drying (%)
		Wet state	Air dry	Oven dry	
Fe in Fe^{2+} state					
Neuns	66	0	51	64	13
Aiken	56	15	57	64	7
Sweeney	64	0	67	78	11
Boomer	78	2	69	79	10
Fe in Fe^{3+} state					
Neuns	51	43	43	69	26
Aiken	46	20	42	66	24
Sweeney	46	23	47	83	36
Boomer	49	13	38	52	14

To measure the ease of replaceability of fixed K^+, that is, K^+ which cannot be replaced by NH_4^+, equal amounts of samples (15 mg) were equilibrated with equal volumes of either neutral $0.1N$ $MgCl_2$ solution or neutral $0.2N$ $NH_4C_2H_3O_2$ solution (15 ml) in centrifuge tubes. After a period of contact between sample and solution (varying from a few minutes to 5 days), the K^+ content of the solution was determined. The equilibrated solution was then carefully removed without loss of sample and replaced with a fresh solution. This procedure was repeated for each sample four times over a period of 2 weeks.

The replaceability of the fixed K^+ was calculated (Table 2) by subtracting the amount of K^+ replaced by NH_4^+ from that replaced by Mg^{2+}. The sums of the four determinations for each sample are reported in Table 2. Oxidation of Fe^{2+} to Fe^{3+} causes a great reduction in the amount of K^+ replaced by Mg^{2+}. Other results (*6*) indicate that, even when there is a loss in surface charge upon oxidation, the replaceability of the interlayer K^+ is less than that in samples with a higher charge which contain Fe^{2+} iron. Furthermore, this effect is reversible: upon reducing the Fe^{3+} to Fe^{2+}, the replaceability of K^+ by Mg^{2+} is again enhanced.

We propose an explanation for this effect which is associated with a change in the orientation of the dipole of the octahedral hydroxyl ions from a position perpendicular to the cleavage plane when iron is in the Fe^{2+} state to an inclined position with respect to the cleavage plane when iron is in the Fe^{3+} state. Such a change places the interlayer K^+, which occupies the hexagonal cavity just above and below the hydroxyl ions, in a more electrically negative environment when the dipole of the hydroxyl ion is in an inclined position than when it is in a perpendicular position with respect to the cleavage plane; as a consequence, the K^+ becomes more strongly held by the surrounding oxygens and more difficult

Table 2. Potassium replaced from biotites (samples dried at room temperature) by NH_4^+ or Mg^{2+} in relation to the state of oxidation of octahedral Fe. Total K^+ was determined by dissolving the sample and determining K^+ in solution. Amount of K^+ is expressed as milliequivalents per 100 grams [oven-dry (100°C) basis].

Sample No.*	Total K^+ (meq)	K^+ replaced by		Fixed K^+ replaced by Mg^{2+} (meq)
		NH_4^+ (meq)	Mg^{2+} (meq)	
Fe in Fe^{2+} state				
16	164.5	20.4	114.4	94.0
19	188.5	3.1	136.3	133.2
Fe in Fe^{3+} state				
16	158.0	7.3	24.9	17.6
19	173.0	7.3	26.2	18.9

* From Barshad (*1*).

to replace. Serratosa and Bradley (*7*) and Bassett (*8*) have shown that, as long as the attractive electrical forces in the three octahedral positions which surround each hydroxyl ion are of equal strength (as in the trioctahedral micas with divalent octahedral ions), the dipole is perpendicular to the cleavage surface. But when the forces become unequal, owing to the presence of an empty octahedron [as in dioctahedral micas (muscovite)], the dipole is inclined with respect to the cleavage surface. In biotite, where one of the octahedrons may be occupied by Fe^{2+} (as in the samples studied), oxidation to Fe^{3+} disturbs the electrical balance and thus brings about a change in the inclination of the dipole.

That the difference in inclination of the dipole could cause a greater difficulty in the replaceability of K^+ from muscovite than from trioctahedral micas of equal layer charge was suggested by Bassett (*8*) and confirmed by Rausell-Colom and co-workers (*9*) and by Scott and Smith (*2*). Furthermore, the idea that this difference may be related to a greater negative environment surrounding the K^+ was also suggested (*9*); in micas which contain F^- as a replacement for OH^-, the replaceability of K^+ is inversely proportional to the F^- content, even though the layer charge is of equal magnitude.

Several important conclusions emerge from these findings: (i) Changes in the replaceability of K^+ are only an exaggerated expression of changes in the exchange characteristics of other cations in general, as measured by adsorption isotherms and equilibrium constants. (ii) In preparation for cation exchange studies, clay minerals are frequently treated with solutions which may cause either an oxidation or a reduction of the iron in the crystal lattice. Differences in results on similar materials could be accounted for by sample treatment rather than by experimental variations or errors. (iii) The persistence of species of biotite micas in many highly weathered soils could be partially accounted for by the finding that oxidation of Fe^{2+} to Fe^{3+} renders the K^+ more difficult to replace and increases the fixation capacity for K^+ by that part of the biotite which became converted to vermiculite and which thereby helps to preserve the biotite (*4*). Oxidation of octahedral Fe^{2+} to Fe^{3+} is an important factor in the preservation of the K^+ content of soils, even though at times K^+ may become less available for plant uptake. Under such circumstances, however, it would appear possible that the replaceability of K^+ and its availability to plants might be artificially increased without fertilization by the production of a reducing environment in the soil. This could be done by waterlogging, as frequently practiced in rice culture.

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References and Notes

1. I. Barshad, *Soil Sci.* **78**, 57 (1954).
2. A. D. Scott and S. J. Smith, *Proc. Nat. Conf. Clays Clay Mineral.* **26**, 69 (1966).
3. G. F. Walker, in *X-Ray Identification and Crystal Structure of Clay Minerals*, G. Brown, Ed. (Mineralogical Society, London, 1961), p. 297.
4. O. P. Mehra and M. L. Jackson, *Proc. Nat. Conf. Clays Clay Mineral.* **5**, 317 (1960).
5. I. Barshad, *Soil Sci.* **77**, 463 (1954).
6. ———, unpublished data.
7. J. M. Serratosa and W. F. Bradley, *J. Phys. Chem.* **62**, 1164 (1958).
8. W. A. Bassett, *Bull. Geol. Soc. Amer.* **71**, 449 (1960).
9. J. A. Rausell-Colom, T. R. Sweatman, C. B. Wells, W. Norrish, in *Experimental Pedology*, E. G. Hallsworth and D. V. Crawford, Eds. (Butterworth, London, 1964), p. 40.

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Mascons Interpreted

Iron Meteorites as Mascons

The discovery by Muller and Sjogren (*1*) of mascons in the moon is of great interest. My investigations (*2*) allow a calculation to be made of the size and depth of the mascons in terms of the size of the mare formed by low-velocity impact of an iron meteorite. The results of these calculations are in reasonable agreement with the results reported by Muller and Sjogren.

I am currently completing an analysis of penetration and cratering of concrete and soils by steel projectiles ranging, in diameter, from 1.27 to 15.5 cm and, in mass, from 8.35 g to 44 kg. Spherical projectiles are included. At velocities of 1.0 km/sec, the projectiles do not deform in concrete but suffer only minor scratches, and they are not heated excessively when stopped in the target. One result of the analysis is that, over the range of variables in the tests, the force resisting the projectile motion increases to a constant value. For this reason, it is believed that the results may safely be extrapolated to somewhat higher velocities without difficulties due to projectile deformation and heating.

A result of the analysis is that the depth of penetration x by a projectile of diameter d and mass m striking a target of compressive strength S and density ρ, with a velocity V, is

$$\left(\frac{x}{d}\right) = 0.0615\left(\frac{\tfrac{1}{2}mV^2}{Sd^3}\right) + 1.10\left(\frac{m}{\rho d^3}\right)^{1/3} \tag{1}$$

where the units are such that each term in parentheses is dimensionless. This equation is the limiting case of a more complex relation and is valid at velocities so great that an exponential term in the complex relation may be neglected. At these higher velocities Eq. 1 fits more than 80 percent of 140 data points within ± 10 percent. The data include values of ($\tfrac{1}{2}mV^2/Sd^3$) up to 218. For iron spheres striking the lunar surface with a velocity of 2.4 km/sec and with an assumed value of S = 3500 newton/cm² (= 5000 pounds per square inch), the value of ($\tfrac{1}{2}mV^2/Sd^3$) is 336. This is only one and one-half times the maximum value in the tests being analyzed, and it is assumed that the results may safely be extrapolated this far. In the second term on the right we take m/d^3 for an iron sphere and assume a density of 3.0 to 3.5 g/cm³ for the target material. The predicted penetration of a smooth sphere, with data as given here, is x/d = 22.

We should not expect a meteorite, having irregular shape and a rough surface and probably striking with obliquity, to penetrate as far as a smooth steel projectile striking normally. Projectiles fired normally into concrete go straight in, but those fired normally into soils often turn sideways and penetrate about 70 to 50 percent as deep as those that go straight in. Some projectiles fired into soil break into two or three pieces, and these pieces penetrate less than half as far as unbroken projectiles which go straight in. Projectiles striking at an angle from the normal may ricochet, and the limiting angle for ricochet increases with velocity. Projectiles that strike with obliquity and do not ricochet penetrate less deeply than those that strike normally. At the highest velocities used in the tests, projectiles striking with