Reports and Letters

Interaction of Molybdenum and Iron in Soils

The availability to plants of molybdenum in some acidic soils may be increased by raising the *p*H of the soil. This relation to *p*H is analogous to that of phosphate which is held in insoluble form by iron and aluminum, and it suggests a study of the interactions of molybdate with iron and aluminum. This paper (*1*) is concerned with interactions with iron in simple systems of ferric oxide as well as in soils.

A ferric oxide, which was amorphous to x-rays, was prepared by the method of Schuylenborgh and Arens (*2*) and ground to pass a 200 I.M.M. sieve. Solutions of sodium molybdate containing 100 μg of Mo were added to 100-mg samples of ferric oxide. The *p*H's of the suspensions were adjusted, and the total volume of each was brought to 50 ml. After mechanical shaking of the solutions for 15 hours, the *p*H's were determined, the suspensions were centrifuged, and the Mo remaining in solution was determined (*3*) by the colorimetric-dithiol method of Piper and Beckwith (*4*). The ferric oxide removed the following amounts of Mo from solution: 100 μg at *p*H 4, 100 μg at *p*H 5, 100 μg at *p*H 6, 98 μg at *p*H 7, 83 μg at *p*H 8, and 22 μg at *p*H 9.

In further experiments with ferric oxide, the amount of Mo adsorbed was determined as a function of the equilibrium concentration of Mo in solution for equilibrium *p*H 4.5. The adsorption isotherm had a high initial gradient and, at an equilibrium concentration of 50 μg of Mo in 50 ml of solution, it leveled off with a saturation value of about 7 mg of Mo per 100 mg of solid. An aluminum oxide (Böhmite) prepared by the method of Schuylenborgh (*5*) was found in similar experiments to be saturated with 3.5 mg of Mo per 100 mg of solid. The difference between the initial gradients was more marked, that for ferric oxide being about 50 times greater than that for aluminum oxide. The effectiveness of the clay minerals in adsorbing molybdate was less than that of the sesquioxides and decreased in the order halloysite, nontronite, and kaolinite.

Table 1. Molybdenum adsorbed (μg) from a total of 500 μg by 5-g samples of soils.

Soil	*p*H 4.0	5.0	6.0	7.0	8.0
Wollongbar, untreated	500	498	460	270	80
Wollongbar, minus Fe_2O_3	425	340	190	45	0
Elmhurst	450	310	100	20	0

The fact that ferric oxide adsorbs so much molybdate led to experiments with two soils that were, respectively, high and low in colloidal ferric oxide. The first soil was a krasnozem of *p*H 5.3 from Wollongbar, near Lismore in New South Wales. It contains 55 percent clay (particle size less than 2 μ) and 14.9 percent free ferric oxide. The other soil, from Elmhurst, near Ararat in Victoria, was a grey, gravelly loam of *p*H 5.9, overlying yellow clay at 10 in. It has 14 percent clay (particle size less than 2 μ) and 1.1 percent free ferric oxide.

The soils were air-dried and ground to pass a 60-mesh I.M.M. sieve. Samples of 5 g were shaken for 15 hours at adjusted *p*H's with solutions containing 500 μg of Mo in a total volume of 50 ml. After the suspension had been centrifuged, the Mo remaining in solution was determined as before. Parallel experiments were performed on 5-g samples of the Wollongbar soil after the free ferric oxide in them had been removed by Jeffries' method (*6*). In this method, the iron oxide is reduced by nascent hydrogen in oxalic acid, and the iron is then removed in solution.

The results (Table 1) show again that the greatest amounts of molybdate were adsorbed at low *p*H's, and that the amounts adsorbed decreased with increasing *p*H. The untreated Wollongbar soil adsorbed much more molybdate than the Elmhurst soil, and even at *p*H 7, the Wollongbar soil still adsorbed approximately half of the molybdate presented. The effect of removing the ferric oxide from this soil was striking. The amounts adsorbed were thereby reduced to amounts nearer those adsorbed by the Elmhurst soil. Thus, at *p*H 6, the adsorption by the Wollongbar soil was reduced from 460 μg to 190 μg, the amount adsorbed by the Elmhurst soil being 100 μg.

The importance of ferric oxide in soils is shown both by the relatively large amounts of molybdate that it adsorbs in simple systems and by the effect of removing it from the Wollongbar soil. Since adsorption is greatest in acidic systems and becomes less with increasing *p*H, it is suggested that Mo, in ferruginous soils, is held on the surface of colloidal ferric oxides as the molybdate anion, which is replaceable by hydroxyl ions.

This work fits in with the effect of lime on the availability of Mo to plants on some acidic, ferruginous soils and also with the principle used by Grigg (*7*) in his analysis for available Mo in soils—namely, that an amount of Mo which is sufficient for plants at *p*H 6 may be insufficient at *p*H 5. Another piece of compatible evidence is that presented by Williams and Moore (*8*) who, by means of chemical analyses of plants and soils, arrived at an equation relating Mo in plants to both *p*H and iron of soils. Their equation is of the form

$$\log \mathrm{Mo} = a\ p\mathrm{H} - b\ \mathrm{Fe} + c,$$

where the Fe was that dissolved by boiling the soil with 6*N* hydrochloric acid.

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References and Notes

1. I am indebted to the University of Melbourne and to S. M. Wadham for providing laboratory space and to G. W. Leeper for his interest in this work.
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3. The analyses and much of the experimental work were carried out by A. F. Sherrington.
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6 February 1956

Effect of Reserpine on Learning and Performance

Reserpine, an alkaloid extract of *Rauwolfia serpentina,* is now widely used in clinical psychiatry. It has been shown that it depresses well-established performance patterns of rhesus monkeys—for example, pressing a bar to avoid shock or to obtain food (*1*). The present study shows that reserpine can depress "discriminated" or "conditioned" re-