conclude that there is not much s-d scattering in W and that s-d scattering is the major process leading to normal-state resistivity in Nb.

To summarize our previous arguments and extend them somewhat, we consider that while there is a large s-d interaction in V, Nb, and Ta, in Mo and W this interaction is small, owing to the intrinsic stability of a half-filled d-shell along with its involvement in strong lattice bonding. There is the correlation between generally high superconducting transition temperatures in the column headed V (Table 2) and a large s-d interaction; for W and near Mo there is a low T_c, together with low s-d interaction and a high lattice stability. Because of the maximum stability of the crystal lattice and electron configuration near column VI, we interpret the large s-d interactions in column V to be caused by the tendency of the valence electrons in these elements to assume the configuration of column VI. This leads us immediately to a picture for the occurrence of superconductivity in the transition metals.

Of all the rare earths along with Sc and Y only La becomes superconducting. La has a T^3 dependence of resistivity (*14*) at low temperatures as compared to Y, which has a T^5 dependence (*11*). This further substantiates the contention of Hamilton and Jensen that an incipient f level exists for La (*15*).

Superconductivity has not been observed in Pd or Pt. These elements are highly paramagnetic and close to ferromagnetic when doped with small amounts of magnetic elements (*16*). The resistivity behavior of Pd and Pt is nearly T^3, very much like the T^3 behavior observed in the magnetic elements from Cr to Ni.

Let us again consider Nb, since it has the highest T_c. In our picture, the d electrons are rather localized and also strongly involved in lattice bonding, while the s electrons are itinerant as usual. Although distinguishing between electrons this way is rather artificial, it is useful for the discussion. Our model is somewhat different from that of Zener (*17*), in which he describes some properties of transition elements. We think that bonding between adjacent Nb d-shells would be stronger if there were more d electrons, since they would be approaching the cohesion maximum that is between columns V and VI (Table 2). For the ground state configuration of Nb the s electron wave function, whatever it may be, will reflect the involvement of the s electrons in the d bonding. A measure of this involvement is the s-d scattering as deduced from resistivity data. The wave function of the free electrons is thus modified. We may view this process in a time-dependent scale as follows: Metastable d state configurations are constantly being formed by s-d scattering. It is possible that when two s-d scatterings occur on adjacent Nb atoms at nearly the same time, the pair of metastable states will live longer than a single state because of the enhanced cohesion between them. On a time average, this will be manifested as an attractive interaction between pairs of s electrons. Schematically this would be written $s \rightarrow d^5 = d^5 \leftarrow s$ where the double line indicates additional lattice bonding. This results in correlation and attractive interaction between s electrons as required for superconductivity.

Resistivity data indicate a large s-d scattering also in V and Ta. Thus the same process would apply to these elements as to Nb. In column VII (heading VII in Table 2), although the evidence is not as complete, an essentially similar process presumably will occur as in column V. A crystal structure change on going from column VI to VII further complicates this situation.

In our model we try to show that for the transition metals the interaction between d-shells is essential for providing a correlation between s electrons and hence superconductivity. At the extreme right of the transition elements, Pd and Pt have a ground state configuration somewhere between d^9s^1 and d^{10}. A tendency for the itinerant electrons to scatter into the d-shell and form a somewhat stable d^{10} configuration would account for the strong s-d scattering as deduced from the resistivity data. However, the result of this configuration will not be enhanced bonding nor will any attractive interaction between s electrons follow.

In conclusion we have been able for the first time to establish a connection between high-temperature superconductivity and bonding electrons—in particular, the half-filled d-shell. An insight into the instability of the high-temperature superconductors thus might emerge.

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Biotite Flakes: Alteration by Chemical and Biological Treatment

Abstract. *Biotite alteration under acid conditions proceeds differently from the generally accepted pathway of transformation to vermiculite in which hydrated cations cause interlayer expansion, resulting in a dark-colored peripheral band on mica particles. Acid solutions of synthetic or biologic origin remove octahedral ions, leaving a fragile matrix of amorphous material.*

Most discussions of primary mineral alteration and clay mineral formation in the biosphere are restricted to consideration of inorganic chemical reactions. Such reactions are of significance in explaining the continuum of processes that may take place between magmatic crystallization and ultimate degradation of lattice minerals.

Frequently overlooked, however, is the fact that energy for initiating and propagating mineral alteration comes mainly from solar radiation transported to the reaction site by biochemical intermediaries resulting from metabolism of higher and lower plants. Only a few studies have considered these metabolites in mineral breakdown (*1*). This report presents some specific examples of changes induced in biotite mica particles by chemical or biological agents.

Biotite sheets were cleaved under a microscope, and uniform rectangular flakes about 0.5 by 0.7 mm and about 20 μ thick were cut with a razor blade. Flakes having smooth faces with no cutting cracks were used in subsequent treatments. In a few cases larger flakes, 2 by 2 mm, were used. Individual flakes were placed in solutions of salts, organic acids or HCl of different concentrations, or in an 8 percent glucose solution inoculated with *Aspergillus niger* or with suspensions of soil from different forest ecosystems. Flakes were kept in the appropriate solution for periods ranging from 24 hours to 6 months at temperatures from 22° to 50°C. In some cases the solutions were renewed daily and in others the same solution was used throughout the treatment. At the end of each treatment flakes were examined microscopically with ordinary transmitted light or by phase contrast and were photographed. Typical results are shown in Fig. 1.

In all cases weathering was most obvious at the edges of the flake. A border of altered material appeared after a few hours with some treatments and grew progressively wider with time, and eventually covered the entire flake. In solutions of NaCl, $CaCl_2$, $MgCl_2$, and $AlCl_3$ the band was darker in color than the original mineral. The altered border was also thicker than the unaltered portion of the mica particle. These changes parallel the observations of Rausell-Colom *et al.* (*2*) who attributed alterations in color and dimensions to interlayer replacement of potassium by hydrated ions. The net result is a considerable swelling of the affected portion of the particle. Interlayer spacing of micas may increase as much as 40 percent with solvated substitution (*3*).

Distinct differences were observed between the effects caused by NaCl and $CaCl_2$. The rate at which the width of the band developed was considerably more rapid with NaCl than with $CaCl_2$, and the surface of the band that developed in NaCl tended to be smooth, whereas that resulting from treatment with $CaCl_2$ sometimes showed cracks perpendicular to the edge, giving the band a characteristic reticulated appearance. These patterns may be related to diffusion rates and ionic radii.

Alteration of biotite by acid solutions or by biological activity was different from alteration caused by salt solutions. Although the rate of expansion of the band width in acid solutions was approximately equal to that in salt solutions of equal concentration, the altered band was transparent or translucent in acids, whereas in salt solutions the band was darker than the original biotite. Color differences are apparently associated with hydration of interlayer ions as well as with removal of iron and magnesium by acid solutions.

Upper and lower surfaces of the flakes sometimes showed evidence of alteration along flaws or scratches, and, with time, these would coalesce with the advancing front from the edge. In cultures of *A. niger* individual hyphal strands occasionally penetrated edges of flakes, causing invaginations in the weathering front. Aside from these variations, however, the weathering front in all treatments was almost precisely parallel to the edge of the flake (Fig. 1, B and E) until about half of it had been altered. At this stage the edge began to show some undulation (Fig. 1, C and D), particularly in the larger flakes.

X-ray diffraction analyses of altered flakes further support the differences in biotite weathering by salts and acids that were observed under the microscope. X-ray diffraction patterns of biotite treated with salts agree with the generally accepted conclusions that salt solutions cause biotite to expand to vermiculite (*4*). In contrast, biotite altered by acids or by biological ac-

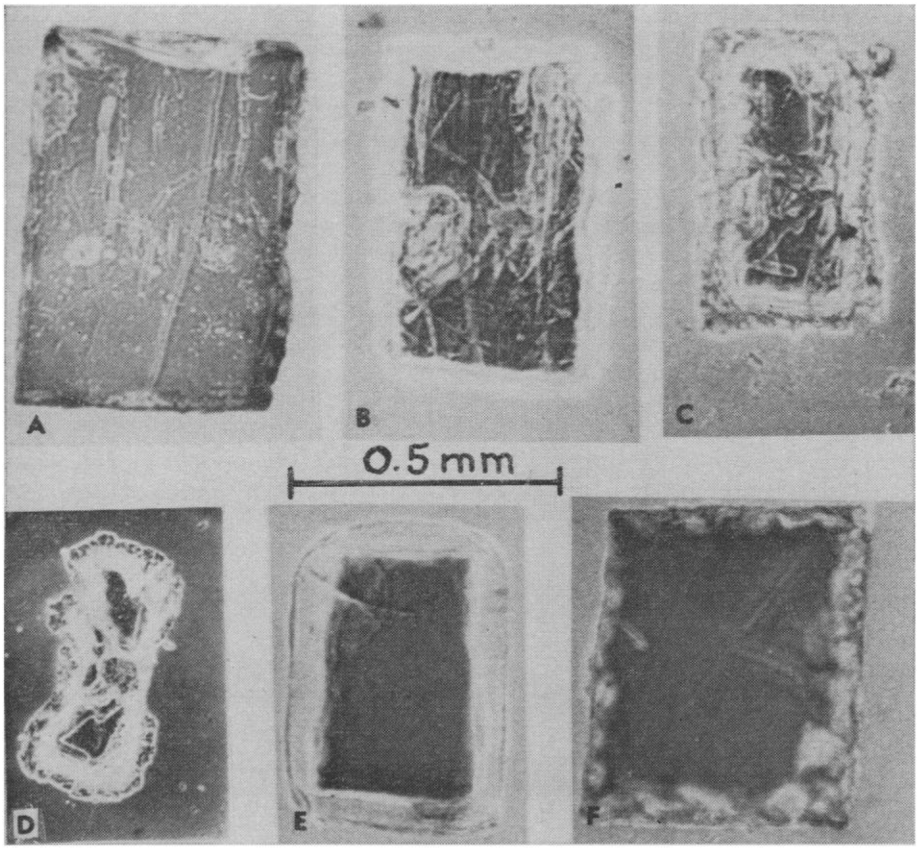

Fig. 1. Changes in biotite flakes induced by acids and microbial cultures. (A) Original flake. (B, C, and D). Same flake kept in 1*M* oxalic acid for 1, 2, and 3 weeks, respectively. Note progressive increase in width of light-colored band and progressive decrease in size of flake due to fragmentation. (E) Flake from 8 percent glucose solution 8 weeks after inoculation with *Aspergillus niger*. (F) Flake from 8 percent glucose solution 8 weeks after inoculation with a suspension of soil from a *Liriodendron tulipifera* ecosystem. Note conchoidal appearance of edge resulting from scrolling and curling. Similar effects were caused by citric acid. Scrolling has been observed on surfaces of vermiculite particles treated with KF (*7*).

tivity showed no expansion of interlayers during the entire treatment. Similarly, no interlayer expansion was detected when biotite particles less than 50 μ in diameter were kept in $0.1N$ or $0.01N$ oxalic acid solutions that were changed frequently. The apparent initial stage of acid alteration was removal of iron, resulting in a light-colored weathering edge that gradually advanced inward. The bleached fragile matrix disintegrated with shaking and dissolved in the acid, thus reducing the size of the particle (Fig. 1, B, C, and D). Chemical analyses of the acid extracts at varying periods of the reaction showed that the constituents released were in the same proportion as in the original biotite, except that slightly larger amounts of iron and aluminum were extracted. This is attributed to the chelating abilities of the acids we used. Indeed, the greater the chelating ability of the acid, the more iron and aluminum it removed. Thus, acid alteration of biotite involves breakdown of the edges and not expansion of interlayers, as is attained by alteration with salts. This conclusion is supported by recent work of Marshall and McDowell (*5*) and Sawhney and Frink (*6*), which suggests that edges of lattice minerals break down in acid solutions.

The rate at which alteration proceeded was primarily a function of the concentration of acid or salt at a given temperature. In some instances treatments were carried out at elevated temperatures, and substantial rate increases in alteration for a given concentration of salt or acid solution were noted. Cultures inoculated with soil suspensions were much slower in producing weathering edges than those inoculated with *A. niger*, indicating differences among different groups of soil organisms. Chromatographic analysis indicated that *A. niger* produced both oxalic and citric acids from the glucose medium. Alteration of biotite by this organism, however, was more closely related to changes caused by oxalic than by citric acid. Similar alterations were observed on biotite particles in close contact with tree roots, both in soil and in inoculated quartz sand cultures.

The contribution of the observed alteration of biotite particles to pedogenesis or to the maintenance of ecosystem nutrient status cannot be assessed at present. However, acid weathering occurs in varying degrees wherever plant roots and their associated microorganisms permeate the substratum and thus constitutes an important mechanism for mineral weathering.

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Detergents in Membrane Filters

Abstract. *Membrane filters from several manufacturers contain detergents. Cells cultured in media filtered through washed filters had higher plating efficiencies and a higher percentage of differentiation than cells cultured in media filtered through unwashed filters.*

Membrane filters from several manufacturers (Millipore, Gelman, and Schleicher and Schuell) are widely used in many areas of biology, biochemistry, and pharmacology. These filters contain 2 to 3 percent of their dry weight as detergent, a fact not contained in the descriptive brochures of any of the manufacturers. Millipore filters contain Triton X-100 or a similar detergent. The type of detergent used in the other filters has not been determined. The manufacturers state that the detergent is added to promote efficiency of filtration and to allow filters to be sterilized by autoclaving. Without the detergent, the filters are unwettable, and excessive pressures are needed to effect filtration. I wish to point out the presence of detergent in the filters and to demonstrate at least one toxic effect of eluates from unwashed filters containing detergent.

The fact that the filters contain a detergent is not immediately obvious when media containing serum or solutions containing proteins are filtered, but it becomes immediately recognizable when distilled water or a saline solution is filtered. The resulting filtrates develop a persistent foam not obtained with the solutions before filtration. The concentration of detergent in eluates of the filters is high enough to cause damage to cells cultured in filtered media and probably has as yet unrecognized effects on other biological systems.

Millipore filters (Millipore Filter Corp., Bedford, Mass.) were used in pressure or vacuum filtration apparatuses as described by the manufacturer. The filters were assembled and autoclaved before use. They were then extracted with 200 ml of glass-distilled water (90° to 100°C) and rinsed with 100 ml of ice-cold saline before use. These eluates were discarded. The hot water effectively removes most of the detergent in the filter. Saline was used simply to cool the apparatus. This treatment does not remove all the detergent from these filters, but if filtration is carried out rapidly after the extraction a negligible amount of detergent is included in subsequent filtrates. It is important that the actual filtration be carried out cold to minimize extraction of detergent.

Although the manufacturers would not disclose the process of incorporation of the detergent into the filters, it is likely that the filters of some manufacturers contain detergent within the substance of the filter and not just on its surface. This may account for the continued, slow leaching of detergent into later filtrates. Filters free of detergent may be obtained from some manufacturers (Millipore, Gelman) upon special request. These filters are not wettable with physiological solutions and must be wet with 50 percent ethanol before use. The use of these filters may eliminate the necessity for the procedure of extraction described above. However, filters made without detergent are difficult to sterilize. They buckle and are considerably weakened after being autoclaved. Furthermore, ethanol is quite toxic to most cultured cells.