10. Publication authorized by the Director, U.S. Geological Survey. We thank C. H. Baltzo, Roy Hurd, Richard Hajny, and others of the U.S. Bureau of Commercial Fisheries for hospitality and cooperation. T.E. was supported by grants from the Arctic Institute of North America and the National Research Council of Iceland.

10 November 1965

Crystal Structure of Umangite, Cu_3Se_2

In the study of the phase relations of the copper-selenium system, single crystals of the composition Cu_3Se_2 have been synthesized. This compound, known as mineral umangite, is the only phase in the Cu-Se system for which the structure has not been elucidated. The structure determination has been carried out with the synthetic material.

A mixture of copper and selenium in the ratio 2.9 to 2.0 was enclosed in an evacuated silica tube and kept at 500°C for 2 days. The product was ground to fine powder, resealed in a new evacuated silica tube, kept first at 500°C for a week and then at 80°C for a month. After the run, the final product was covered with small crystals of Cu_3Se_2. The inner part of the product was, however, found to be an assemblage of crystals of two other phases, $Cu_{1.8}Se$ and CuSe.

The precession and Weissenberg methods were used to study the synthetic Cu_3Se_2 single crystals. The symmetry is tetragonal, with diffraction aspect P-2_1-, giving the possible space groups $P\bar{4}2_1m$ and $P42_12$. The cell dimensions obtained by the x-ray diffraction powder method are: $a = 6.406 \pm 0.002$ Å and $c = 4.279 \pm 0.002$ Å. With a cell content of Cu_6Se_4, the density is calculated as 6.590—in good agreement with the measured values 6.44 to 6.49 for the artificial compound (*1*).

The crystallographic data given by Berry and Thompson (*2*) are as follows: $a = 6.402$ Å and $c = 4.276$ Å, with space group $P4/mmm$. In order to elucidate the conflict between the diffraction aspects of the synthetic and natural materials, single crystals of umangite, Sierra de Umango, Argentina (*3*), were studied. The diffraction aspect of the natural specimens is P-2_1- as in the case of the synthetic crystals.

The intensities were measured visually on the Weissenberg films for the synthetic crystals. They were corrected for Lorentz and polarization factors. No absorption correction was made. Interpretations of the Patterson projections on (001) and (100) gave a structure uniquely based on the space group $P\bar{4}2_1m$. The atomic parameters obtained by the two-dimensional difference Fourier method are as follows: 2 Cu(I) in equipoint *a* at 0,0,0; 4 Cu(II) in equipoint *e* at $x, \frac{1}{2} - x, z$, with $x = 0.147$ and $z = 0.750$; 4 Se in *e* at $x, \frac{1}{2} - x, z$, with $x = 0.275$ and $z = 0.250$. The *R*-factors are 0.12 and 0.13 for (*hk*0) and (*h*0*l*), respectively.

The structure is projected on (001) and on (100) in Fig. 1, *A* and *B*, respectively. In this structure, as in typically intermetallic compounds, Cu atoms are as closely bonded with one another as with Se atoms. On the basis of the distribution of these bonds, the structure is considered to consist of sheets extending parallel to (001). All the Cu—Cu bonds are included inside the sheets, and their bond distances of 2.63 or 2.66 Å are slightly longer than the atomic distance found in metal copper 2.56 Å. Each Cu(I) is surrounded by four Se at 2.49 Å and four Cu(II) at 2.63 Å; and each Cu(II) by four Se at 2.43 and 2.37 Å, and by two Cu(I) at 2.63 Å and by one Cu(II) at 2.66 Å. Each Se is surrounded by two Cu(I) at 2.49 Å and by four Cu(II) at 2.43 and 2.37 Å.

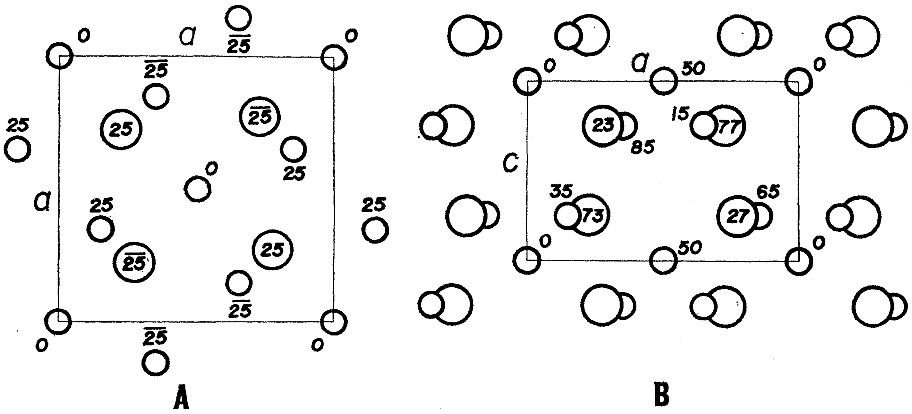

Fig. 1. (*A* and *B*) The structure of Cu_3Se_2 projected on (001) and (100), respectively. Large circles represent Se atoms and small circles Cu atoms. Numbers give *z*-parameters in *A*, and *x*-parameters in *B*.

Preliminary experiments on the electric properties of this synthetic Cu_3Se_2 indicate that the conductivity decreases with increasing temperature. The mechanism of conduction is, therefore, metallic.

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Infrared Spectra from Fine Particulate Surfaces

Abstract. *Characteristic spectral information can be obtained from a surface composed of fine particles either if the spectrum is observed at sufficiently high signal-to-noise ratio or if the particles are well compacted.*

Recent publications (*1*) concerning spectral reflectance or emittance by particulate surfaces have indicated that the surface tends to appear black when the particle size is small compared with the wavelength. Thus it is generally concluded that little or no characteristic spectral information can be gained by remote sensing of lunar or planetary surfaces if the surfaces are composed of fine particles. We now show both theoretically and experimentally that most of the spectral information is not really lost under these circumstances if one observes the spectrum at sufficiently high signal-to-noise ratio or if the surface is well compacted.

We consider first the case of a semi-infinite medium having a smooth surface and composed of uniformly distributed particles of diameter and spacing much less than a wavelength. Under these conditions the reflection by the medium of a beam of radiation is predominantly a coherent surface effect caused by the discontinuity at the surface of the average values of the optical

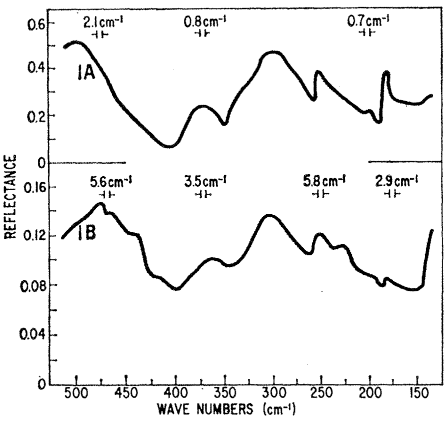

Fig. 1. Far-infrared spectra of fayalite in bulk (*A*) and powdered (*B*). The spectral slit widths used for various parts of the spectra are shown. The difference between the vertical scales of the two spectra accentuates minor features, possibly spurious, near 450 and 230 cm⁻¹ in the lower spectrum.

constants of the medium. The incoherent volume scattering by the individual particles (that is, the Rayleigh scattering) is negligible compared with the surface reflection when the particles are very small compared with the wavelength. The reflectance at normal incidence is given by the modified Fresnel formula (*2*):

$$R = [(n - 1)^2 + k^2]/\{[n + (2/f) - 1]^2 + k^2\} \quad (1)$$

where $n - ik$ is the complex refractive index of the material constituting the particles, and f is the fraction of the volume occupied by the particles. Equation 1 is valid only when the complex index is in the neighborhood of unity. We have derived a more general formula (based on the Lorentz-Lorenz theory) which is now under experimental test; the results will be published shortly.

Equation 1 shows that the reflectance has the usual bulk value when $f = 1$ and becomes smaller as f decreases. However, the shape of the spectral reflectance curve does not change significantly as the packing density decreases. For example, consider the change in R when k varies from 0 to 1, for a fixed value $n = 1.5$. When $f = 1$, R changes by a factor of 4.3; when $f = \frac{1}{2}$, R changes by a factor of 4.8.

These conclusions are well demonstrated by the experimental results (*3*) shown in Fig. 1, which were obtained during a study of the far-infrared spectra (15 to 200 μ) of silicate minerals. The silicate in question was fayalite (Fe_2SiO_4), the iron-end member of the olivine series; the reflectance spectrum of a polished polycrystalline sample appears in Fig. 1*A*. When this material was ground to particles finer than 2.6 μ, with most particles smaller than 1 μ, and a surface was prepared from this powder, the reflection spectrum shown in Fig. 1*B* was obtained. The general reflectance level has clearly decreased, but the spectral shape has not greatly changed, although small shifts in some bands are apparent. In order to obtain this spectrum, it was necessary only to open the slits so as to increase the signal in comparison to the noise. As we have just shown, the less dense the material (that is, the smaller is f) the more this is necessary. The density of our material measured roughly 2.5 g/cm³; the bulk density of fayalite is 4.14.

These conclusions also apply when the surface of the fine-grained medium is undulating rather than flat; the reflected radiation is then merely redistributed in angle, while the reflectance is unchanged. However, if the surface of the medium is covered with steep-walled cavities with dimensions of the order of the wavelength or larger, reflectance will be reduced because of multiple reflection. On the other hand, large internal cavities within the medium will in general enhance the reflectance by providing an incoherent volume scattering that adds to the surface Fresnel reflection. A reflectance formula has been given (*2*) that combines the effects of surface and volume reflection, whether the latter results from the presence of internal cavities or of large particles.

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Tracers Determine Movement of Soil Moisture and Evapotranspiration

Abstract. *The downward movement of water in soil is a layered one. Marking a certain layer with hydrogen-isotope tracer, and watching its displacement, makes possible a water balance and gives information on evaporation and groundwater recharge.*

An investigation with natural deuterium and bomb tritium in groundwater, lysimeter-measured seepage water, and soil moisture (*1*, *2*) has suggested that downward transport of water in soil is a very slow process and that the water may take years to reach the water table. Theoretical considerations (*2*) also led to the expectation that water seeping through larger pores has sufficient time for exchange with the stationary (capillary) water; lateral molecular diffusion provides for this exchange between draining and capil-

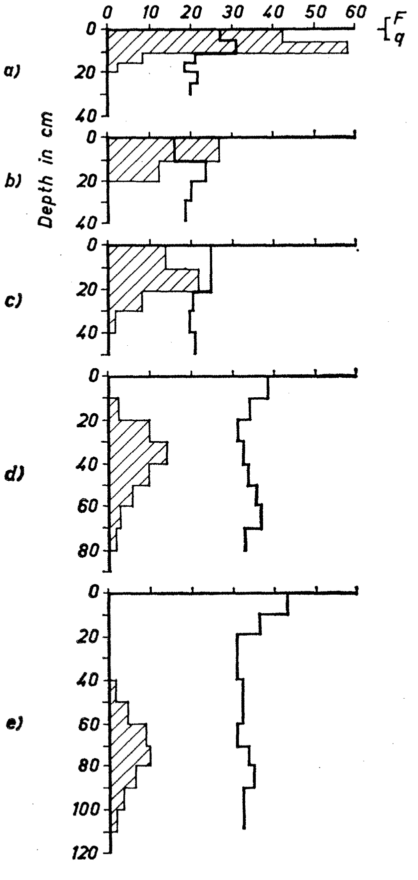

Fig. 1 (to be read in conjunction with Table 1). Loamy soil without vegetation, labeled 9 July 1964. *F* (heavy line), soil moisture (volume percentage); *q* (boundary of hatched area), amount of tracer per 10-cm layer of soil, as a percentage of the amount of tracer originally deposited in the soil; *a* to *e*, samplings 4, 26, 82, 152, and 214 days after labeling, respectively.