

ABSTRACTS OF PAPERS

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INFRARED SPECTROSCOPY AND HYDROGEN BONDING—FREQUENCY
SHIFTS AND BAND SPLITTING IN MINERAL SPECTRA

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Differences in vibration frequency of congeneric modes of the SO_4^{2-} ion in the tetra-hydrated sulfates of Hf and Zr and in isomorphous sulfate mineral groups can be attributed to cation substitution in extramolecular lattice positions. The magnitude and direction of frequency shift are found to be reasonable if attributed to a change in radius of the substitutional cation but cannot be satisfactorily correlated with the mass change. An increase in the vibrational frequency of the functional group may be explained as resulting from shortening of the S-O bond caused by increased repulsion between neighboring sulfate ions as the cation-oxygen distance diminishes.

The shift of the stretching mode absorption of OH to lower frequency with decreasing cation size reflects an increase in the H-bond strength as well as a decrease in the H-bonded oxygen-oxygen distance. Both polyatomic vibrational systems (OH and SO_4) respond to the change in cation radius. Hence, the strength of the binding of oxygen atoms by hydrogen in isomorphous systems appears to be a function of the size and nature of the metallic ion.

Splitting of the ν_2 bending mode of OH is interpreted as arising from an unsymmetrical linear O-H...O group occupying a site of orthorhombic or lower symmetry. This favors removal of the ν_2 degeneracy which is inherent in all molecules having C_∞ symmetry.

THE CRYSTAL STRUCTURE OF MELANOPHLOGITE,
A CUBIC POLYMORPH OF SiO_2

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The crystal structure of melanophlogite has been solved by the application of the symbolic addition procedure described by J. Karle and I. Karle. The phases of the 99 largest normalized structure factors were determined directly and used to compute an E-map which resolved most of the atoms. The structure consists of SiO_4 tetrahedra sharing corners to form five- and six-membered rings, which delimit large polyhedral cages in the shapes of pentagonal dodecahedra and tetrakaidecahedra. The atomic arrangement is analogous to that of the 12 Å gas-hydrate clathrate structure. Organic material is included as a "guest" in the cages.

THE ARSENATE ANALOG OF TSUMEBITE, A NEW MINERAL

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The new arsenate has been found on a single specimen from Tsumeb, South West Africa. It occurs as a crust of distorted crystals on malachite, associated with iron ox-

ides, wulfenite, cerussite and quartz. Color Ridgeway zinc green, biaxial (-), $2V=88^\circ$, $\alpha=1.970$, $\beta=1.992$, $\gamma=2.011$. Pleochroism $Z=Y$ =bottle green, X =pale pistachio green. G (meas)=6.46. The unit cell derived from analogy to tsumebite is monoclinic, $a=8.85$, $b=5.92$, $c=7.84 \text{ \AA}$, $\beta=112.6^\circ$.

Tsumebite occurs at Morenci, Arizona predominantly as twinned crystals associated with wulfenite, olivenite and hyalite. Color Ridgeway sulfate green, biaxial (+), $2V=88^\circ$, $\alpha=1.900$, $\beta=1.920$, $\gamma=1.942$. Pleochroism Z =robin's egg blue, $X=Y$ =very pale blue to colorless. G (meas)=6.01. Several untwinned crystals were studied by Weissenberg and precession methods. Monoclinic, $P2_1/m$, $a=8.70$, $b=5.80$, $c=7.85 \text{ \AA}$, $\beta=111.5^\circ$. Structural study of tsumebite indicates the chemical formula $Pb_2Cu(PO_4)(OH)_3 \cdot 3H_2O$ is in error. X-ray fluorescence analysis has shown the formula is more likely $Pb_2Cu(PO_4)(SO_4)(OH)$.

DIFFERENTIAL GRAVIMETRIC HYPSONOMETRY

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Differential gravimetric hypsonometry allows control and measurement of the temperature and vapor pressure during dissociations of non-volatile solid phases with condensable vapors. The apparatus consists of a tube suspended within a furnace from each end of a balance by a thermocouple. Weight loss by dissociation is differentially recorded against weight gain by condensation at the other end of the tube.

Required conditions of the experiment are: (1) measurement of the temperature of the coldest point of the tube, determines the vapor pressure, (2) measurement of the temperature of the solid phase, and (3) maintenance of the remainder of the system at a higher temperature. Furnace temperature and losses assure that the center of the tube is the hottest point in the system. A heat sink at the vapor end of the tube maintains this point as the coldest part of the system.

Measurement does not disturb equilibrium, is amenable to systems with rapid or slow reactions, and repeated analyses may be made approaching the reaction from higher or lower temperatures or vapor pressures. Since the method may be programmed isothermally or at a variable rate of temperature or vapor pressure, kinetics of the reactions may be determined.

A NEW AMPHIBOLE POLYMORPH IN INTERGROWTH WITH TREMOLITE: CLINO-ANTHOPHYLLITE?

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Tremolite and anthophyllite are well known to be the amphibole equivalents of the pyroxenes diopside and enstatite, and recently Gibbs, Bloss and Shell have synthesized proto-amphibole, the structural equivalent of proto-enstatite. So far there has been no certain discovery of an amphibole equivalent to the calcium-poor clinopyroxenes, pigeonite and clinoenstatite. From structural considerations it can be expected that such an amphibole would have space group $P 2_1/m$, in place of the $I 2/m$ of tremolite.

In thin sections cut from specimens of tremolite-anthophyllite-talc rocks collected by S. O. Agrell from the Wight Talc Mine, Adirondacks, the tremolite shows extremely fine (001) lamellae. These tremolites were examined by single-crystal x-ray diffraction using oscillating-crystal and Weissenberg techniques. The spots from the tremolite could be indexed on a unit cell $a=9.88$, $b=17.95$, $c=5.27 \text{ \AA}$, $\beta=106.3^\circ$, with $I 2/m$ space-group. The weaker intergrowth spots indicated a monoclinic unit cell with $a=9.87$, $b=17.95$, $c=5.27 \text{ \AA}$, $\beta=109.5^\circ$, differing from tremolite mainly in the angle β . The mutual orientation of the two phases was such that the diad y axes and the z^* axes were in common. The unit cell of the