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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  $\text{SO}_4^{2-}$  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  $\text{SO}_4$ ) 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  $\nu_2$  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  $\nu_2$  degeneracy which is inherent in all molecules having  $C_\infty$  symmetry.

THE CRYSTAL STRUCTURE OF MELANOPHLOGITE,  
A CUBIC POLYMORPH OF  $\text{SiO}_2$

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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  $\text{SiO}_4$  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  $\beta$ . 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

intergrowth is clearly that of an amphibole, but there were extra weak intergrowth spots which could only be indexed by assuming a primitive lattice. No spots found were inconsistent with the space-group  $P 2_1/m$ .

Electron-probe analysis (by courtesy of J. V. P. Long) showed CaO content of the tremolite to be 12.0 wt.%, a typical tremolite value. The extreme fineness of the lamellae prevented an accurate analysis, but it could be established that they were poorer in CaO than the tremolite, with an upper limit of 7.5 wt.%.

It is suggested that these lamellae are clino-anthophyllite.

#### EVALUATION OF THERMAL PARAMETERS FOR SILICON, ALUMINUM AND OXYGEN ATOMS IN SILICATES

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Values of thermal parameters derived from x-ray diffraction data are strongly affected by systematic experimental errors and by non-thermal physical and chemical properties of the crystals. Effects of anomalous dispersion corrections, changes of ionization state, and variation of diffraction conditions on thermal parameters for Si, Al, and O in several structures refined to R values between 3 and 5% have been evaluated as part of an overall attempt to determine true atomic thermal models for silicates.

When anomalous dispersion corrections (real and imaginary) were applied to  $\text{CuK}\alpha$  data, isotropic temperature factors for 4-coordinated Si and Al atoms increased 10 to 30% to values ranging from 0.40 to 0.43 for order sites, and 0.63 to 0.65 for disordered sites. Oxygen temperature factors were reduced by 12% or less. Substitution of neutral scattering factors for fully ionized ones caused no significant changes in cation temperature factors, but increased oxygen temperature factors to values higher than those obtained when neglecting anomalous dispersion. When the scattering curve for  $\text{Al}^{3+}$  rather than  $\text{Si}^{4+}$  was applied to pure Si sites, the temperature factors immediately refined to negative values. Throughout these tests positional parameter changes were less than 0.0003.

Least-squares refinement of  $\alpha$ -quartz using Nb-filtered  $\text{MoK}\alpha$  counter-diffractometer data for 106 reflections (corresponding to those within the  $\text{CuK}\alpha$  sphere of reflection) yielded thermal ellipsoids whose orientations agree with previous determinations, but whose principal axes are significantly shorter. Equivalent isotropic temperature factors are 0.26 for Si and 0.65 for O, compared with 0.43–0.48 for Si and 0.92–0.99 for O obtained by previous workers using  $\text{CuK}\alpha$  radiation.

Although the anisotropy of thermal ellipsoids for disordered Si, Al sites suggests that the Si and Al atoms may take up slightly different positions, comparison of these ellipsoids with those for cations in ordered sites shows that rms displacements are larger in all directions rather than just one direction.

#### ORIGIN OF PLEOCHROISM IN "HYPERSTHENES"

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Measurements of polarized absorption spectra of silicates yield information on the origin of color and pleochroism in minerals. Most ferromagnesian silicates (olivines, orthopyroxenes, clinopyroxenes, pigeonites, actinolites, cummingtonites) are distinctly pleochroic in the short-wave infrared region (7000–14,000 Å), but the effects are frequently not apparent optically. The green color observed in these minerals (for example, "hypersthene" in Z polarized light) and Fe (II) compounds in general is due to absorption of light in the

red region by shoulders of bands with absorption maxima in the infrared, giving rise to green transmitted light. Absorption of radiation induces d electron transitions within the  $\text{Fe}^{2+}$  ion. Pleochroism results from the presence of  $\text{Fe}^{2+}$  ions in distorted coordination sites, and from strong next-nearest neighbor interaction in a specific direction.

The red color observed with X polarized light in some orthopyroxenes ("hypersthènes"), notably those occurring in granulite facies rocks, is caused by absorption of light in the blue region by shoulders of charge transfer bands located in the ultraviolet region. Charge transfer is facilitated along the X vibration (*b* crystallographic) axis by the presence of aluminum in the orthopyroxene structure. Necessary conditions for optical pleochroism in "hypersthènes" are: (1.) ordering of  $\text{Fe}^{2+}$  ions in the structure ( $M_2$  positions); (2.) entry of  $\text{Al}^{3+}$  ions into  $M_1$  positions; (3.) substitution of silicon by aluminum in  $[\text{SiO}_4]$  tetrahedra; (4.) the  $\text{Fe}^{2+}$  ion concentration must exceed a minimum value (ca. 15 mole % ferrosilite). Crystal growth under granulite facies temperatures and pressures best fulfills these conditions.

#### CRYSTAL CHEMISTRY OF MANGANESE NODULES FROM ELECTRON-PROBE MEASUREMENTS

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Manganese nodules from the sea-floor are strongly enriched in certain elements (notably: manganese, iron, cobalt, nickel, copper, zinc, titanium, molybdenum, barium, lead, rare earths) relative to sea water. Electron-probe measurements yield information on interelement relationships and phase enrichments of these elements.

The results indicate that manganese nodules fall into two broad categories. Nodules composed predominantly of "manganite" phases show relative enrichment of Ni, Cu, Zn, Mg, Al, K, and Ba, together with Mn, in the "10 Å manganite" and "7 Å manganite" layers. Cobalt and iron are depleted in these layers. Manganese nodules which formed in more highly oxidizing environments are composed of an intimate mixture of  $\delta\text{-MnO}_2$  and hydrated iron oxide, with sporadic bands of "7 Å manganite". These nodules generally contain higher concentrations of Pb, Ce, Zr, Mo and Co. The elements Pb, Ce, Zr and Mo are enriched with Ti in the  $\delta\text{-MnO}_2$  phase, and Co is enriched with Fe in hydrated iron oxide. The sparse bands of "7 Å manganite" are strongly enriched in Ni, Cu and Zn.

It is concluded that solid solution phenomena are important factors controlling minor element distribution in manganese nodules.

#### VONSENITE OF MONTEREY COUNTY, CALIFORNIA

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Vonsenite, an iron-magnesian borate, is one of the main constituents of a vonsenite-magnetite-calcite rock which occurs as a lens about 10 feet long at the contact between calc-silicate hornfels and quartz monzonite near the crest of the Gabilan Range, eastern Monterey County, California. The vonsenite is black, has a brilliant glossy luster and occurs as equant grains and short prismatic crystals in calcite and as intergrowths with magnetite. Other associated minerals include salite, grossularite, barite and minor ludwigite. Studies of thin sections and polished mounts of the vonsenite-bearing rock indicate that the vonsenite and magnetite formed late, and that the vonsenite is later than the magnetite which it replaces in part. The presence of tourmaline-bearing pegmatite dikes intruding the vonsenite-magnetite-calcite rock, the calc-silicate hornfels and quartz mon-

zonite support the thesis that sufficient boron to form both the vonsenite and ludwigite could have been introduced by the pegmatites.

THE CHEMICAL EROSION OF DIAMOND BY BORON:  
AN ANALOGY TO GRAPHITIZATION

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Some pertinent conclusions concerning the deleterious effects of extreme pressure, temperature, and chemical environments on diamond crystals were formulated during a research project designed to synthetically create conductivity in non-conducting diamonds. The encountered phenomena which were interpreted on the basis of crystallographic mechanisms include chemical reactions, graphitization and oxidation or thermal etching.

Natural cubes, table stones and brilliant-cut gem stones were used in the investigation, as well as synthetic cubo-octahedra. Experiments with brilliant-cut crystals were especially rewarding because the anisotropic behavior of unnatural crystallographic surfaces could be readily observed.

Electron diffraction, Laue back reflection, and optical goniometry, as well as standard optical microscopy and x-ray diffraction techniques were utilized. Experimental conditions involved pressures of 1 bar and 50–80 kilobars, temperatures of 1000–2000 degrees centigrade, and times of 5–10 minutes and 1–12 hours. Several chemical environments were employed; however, this paper emphasizes boron, carbon and argon.

The chemical erosion of diamond crystals by boron and the consequent formation of rhombohedral boron carbide ( $B_4C$ ) is described. The similarity to graphitization in crystallo-chemical mechanism of formation is explained. Evidence is developed to support the theory that in cases where the diamond structure exerts influence over the orientation of the graphite crystallites, the  $\langle 110 \rangle$  control of the  $a$ -axis prevails over the  $\langle 111 \rangle$  control of the  $c$ -axis.

FURTHER CONSIDERATIONS OF THE APPARENT DEARTH OF  
K-FELDSPARS WITH INTERMEDIATE  $\Delta$ -VALUES

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If the Al-Si order-disorder relationships in K-feldspar are dealt with on the basis of the hypothesis that there are two order-disorder series—a long-range, microcline series and an apparently shorter-range, sanidine series—several observations, previously considered anomalous, may be resolved. For example, under this two-series hypothesis, the apparent dearth of K-feldspars with intermediate  $\Delta$ -values no longer exists because most of the feldspars thus far reported to have  $\Delta$ -values of less than approximately .20 should probably be referred to the sanidine series.

The  $\Delta = 12.5 [d_{131} - d_{1\bar{3}1}]$  method for defining degree of disorder is at best valid for only the microcline series and even for this series may require modification, as well as the already well-recognized, rather restricted use. Preliminary studies suggest that utilization of infrared adsorption measurements, nuclear magnetic resonance, or possibly refined cell-edge measurements may prove useful in defining degree of disorder in both series.

Too few data have thus far been reported to indicate any regular distribution of degree of disorder values for feldspars of the sanidine series. The distribution curve of  $\Delta$ -values for measured and reported feldspars of the microcline series exhibits a high near its high  $\Delta$ -value end. This latter distribution is what one might expect on the basis of considerations relating probability of formation to available temperature-range for formation (under equilibrium conditions) as indicated by a statistically established state-temperature diagram.

## X-RAY DIFFRACTION AT ULTRA-HIGH PRESSURE AND TEMPERATURE

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X-ray diffraction studies have been carried out at pressures up to 100 Kb. and temperatures to 1000° C. by the combination of a high power rotating-anode x-ray tube and a tetrahedral anvil press. Due to the press geometry the technique is limited to the type of information obtained by powder techniques. The x-ray tube is operated at voltages up to 50 Kv. with anode currents up to 150 ma. depending upon the target material used. The applied voltage is essentially direct current. Measurements indicate that the tube power may be doubled with certain modifications. The sample is contained in a gasketing material used to confine the pressure. At present, the x-ray absorption of this material limits the maximum pressure and temperature. The press itself is capable of operation to 150 Kb. and 2500° C. Data are recorded either by a film camera or counter, as desired. As the sample is confined by the gasketing material, experiments can start with the liquid phase. Specimen size is no limitation, and adequate material may be used for x-ray studies together with provisions for heating the sample. Thermocouples or other electrical connections may also be included for various purposes. A number of suitable gasketing materials has been found—the proper choice depending upon the experiment to be carried out. To date experiments have been confined to compressibility studies of the alkali halides and evaluation of the potential usefulness of theoretically calculated compressibility as a pressure standard. The magnitude of the pressure permits compressibility data to be obtained on essentially any material. The pressure and temperature range are also of sufficient magnitude to permit studies of vital interest to mineralogists and geophysicists.

## A PHENACITE—SPINEL INVERSION IN LITHIUM ALUMINUM GERMANATE

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Lithium aluminum germanate undergoes a reconstructive transition at elevated temperatures and pressures from the hexagonal phenacite structure ( $a = 13.751$ ,  $c = 9.220$  Å) to a spinel structure ( $a = 7.997$  Å). The equilibrium phase boundary is given by  $P(\text{kb}) = 0.015T$  (° C.) - 1.75.  $\Delta H^\circ$  for the transition is calculated to be  $1300 \pm 200$  cal./mole. The silicate analog eucryptite ( $\text{LiAlSiO}_4$ ) also undergoes a transition at slightly higher pressures, but does not yield the spinel structure directly.

HUEMULITE,  $\text{Na}_4\text{MgV}_{10}\text{O}_{28} \cdot 24\text{H}_2\text{O}$ , A NEW HYDROUS SODIUM AND  
MAGNESIUM VANADATE FROM HUEMUL MINE, MENDOZA  
PROVINCE, ARGENTINA

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Huemulite, a new mineral with the formula  $\text{Na}_4\text{MgV}_{10}\text{O}_{28} \cdot 24\text{H}_2\text{O}$ , was found in several uraniumiferous ore-bodies of the "sandstone-type deposits" in the southwestern part of Mendoza province, Argentina.

Huemulite appears in botryoidal masses, thin films, or as interstitial filling in the sandstone that is the host rock. It is soft, yellowish orange to orange in color, with a dull luster and specific gravity of  $2.39 \text{ g/cm}^3$ . It is not fluorescent.

The mineral is easily soluble in cold water, giving an orange solution of pH 5.5 to 6.5.

From this solution the mineral recrystallizes, giving tabular crystals elongated parallel to (010), with a perfect cleavage parallel to (001) and less perfect parallel to (010).

The optical properties determined in the recrystallized material show that the mineral is biaxial negative,  $2V = 25^\circ - 30^\circ$ , pleochroic with X light yellow, Y golden yellow and Z yellowish orange. The indices of refraction measured with sodium light are  $\alpha = 1.679$ ,  $\beta = 1.734$ , and  $\gamma = 1.742$ . The dispersion is strong with  $r > v$ .

Chemical analyses were performed on both natural and recrystallized material. A synthetic compound was prepared which gives a  $x$ -ray powder, and single crystal data similar to those of huemulite.

Huemulite is triclinic, space group  $P1$  or  $P\bar{1}$ . Unit cell data obtained on the recrystallized material are:  $a = 11.770 \pm .019$ ,  $b = 11.838 \pm .008$ ,  $c = 9.018 \pm .009$  Å,  $\alpha = 107^\circ 13' \pm 05'$ ,  $\beta = 112^\circ 10' \pm 06'$ , and  $\gamma = 101^\circ 30' \pm 05'$ ,  $a:b:c = 0.9943:1:0.7618$ .  $V = 1040.67$  Å<sup>3</sup>  $\pm 2.70$ . Cell contents  $\text{Na}_4\text{MgV}_{10}\text{O}_{28} \cdot 24\text{H}_2\text{O}$  give a calculated density of 2.40 g/cm<sup>3</sup>.

The strongest lines of the  $x$ -ray powder diffraction pattern are: 7.6 (100), 10.6 (90), 9.1 (60), 10.2 (55), 8.2 (35), 2.88 (35), 3.05 (30), 5.26 (25).

The name huemulite comes from the Huemul mine, the most important deposit of the area where the mineral was discovered.

#### THE CRYSTAL STRUCTURE OF THE ZEOLITE

##### EPISTILBITE, $\text{Ca}_3\text{Al}_6\text{Si}_{18}\text{O}_{48} \cdot 15\text{H}_2\text{O}$ <sup>1</sup>

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Epistilbite, a member of the common stilbite group has space group  $Cm$ ,  $a = 10.09$ ,  $b = 17.77$ ,  $c = 9.10$  Å,  $\beta = 111^\circ$ . There are approximately 30 independent atoms per unit cell. The silica-alumina framework is a variant of its nearest compositional relatives mordenite and dachiardite. Ten membered rings, as in dachiardite, are arranged as are the twelve membered ring-groups of mordenite. Two normal intersecting channels are occupied by calcium disordered in four sites away from the channel centers. Water positions are also disordered. Marked ordering of aluminums is not evident. Disordering in the epistilbite structure is statistical.

#### A REFINEMENT OF THE STRUCTURE OF LORANDITE, $\text{TlAsS}_2$

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The crystal structure of lorandite ( $8 \text{TlAsS}_2$ ,  $P2_1/a$ ,  $a = 12.239$ ,  $b = 11.338$ ,  $c = 6.144$  Å  $\pm 0.1\%$ ,  $\beta = 104^\circ 36' \pm 0.6'$ ) was determined by three-dimensional least-squares technique. The refinement was done on 1141 reflections giving a final residual of 12%. The framework is essentially infinite chains of trigonal pyramidally coordinated As atoms running parallel to the  $b$ -axis. These chains are joined together by 2-fold coordinated Tl atoms with Tl-S distances of 2.96 to 3.09 Å. The pyramids have As-S distances from 2.18 to 2.34 Å and S-S distances from 3.44 to 3.52 Å. These distances show a considerable deviation from the original work of Zemann and Zemann (1959) which was done with (h0l) and (hk0) reflections only. The thermal displacement of the S atoms, as shown by the anisotropic temperature factors, gave an ellipsoid of vibration with the three principal axes having an average vibration of 0.10, 0.16 and 0.21 Å.

ZEMANN, A. AND J. ZEMANN (1959) Zur Kenntnis der Kristallstruktur von Lorandite,  $\text{TlAsS}_2$ . *Acta Cryst.* **12**, 1002-1006.

<sup>1</sup> Work supported by the National Science Foundation (NSF-GP 470).

## PHASE RELATIONS IN THE SILVER-TELLURIUM SYSTEM

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In the Te-Ag<sub>2</sub>Te part of the system the liquidus falls from the melting point of Te, 449.8° C., to an eutectic at 353.0° C., 33.3 at. % Ag, and then rises in several steps to the melting point of Ag<sub>2</sub>Te at 960° C. At 420° C. the Ag<sub>5-x</sub>Te<sub>3</sub> compound melts incongruently to crystals of  $\gamma$ -phase and a melt of 44.4 at. % Ag. Ag<sub>5-x</sub>Te<sub>3</sub> has a transition at 295° C. in the presence of Te and at 265° C. in the presence of a more silver-rich phase. This transition has the characteristics of an order-disorder reaction. At 460° C. a peritectic reaction occurs, as the incongruently melting  $\gamma$ -phase dissociates into crystals of Ag<sub>2</sub>Te and a melt of 48.7 at. % Ag.  $\gamma$ -phase is not stable below 120° C. and has a transition at about 178° C.

In the Ag<sub>2</sub>Te-Ag part of the system two immiscible liquids coexist with crystals of Ag<sub>2</sub>Te at 881° C., the two liquids having the composition 69.6 and 87.5 at. % Ag; there is an eutectic of Ag<sub>2</sub>Te, Ag, and melt at 869° C., 87.5 at. % Ag.

Ag<sub>2</sub>Te has two transitions. The lower transition, monoclinic to face-centered cubic, occurs at 145° C. The upper transition, to body-centered cubic, occurs at 689° C. on the Te side of Ag<sub>2</sub>Te, and at 802° C. on the Ag side.

## X-RAY DIFFRACTION STUDY OF GLASS-CRYSTALLINE SYSTEMS.

I. PRELIMINARY SINGLE CRYSTAL INVESTIGATION OF AN  
MgO:Al<sub>2</sub>O<sub>3</sub>:3SiO<sub>2</sub> SOLID SOLUTION

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One type of a three-component solid solution of MgO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> has been reported in the literature<sup>1</sup> as a quartz-type structure based on powder x-ray diffraction patterns only. Recently, single crystals of such solid solutions up to 4 mm long have been grown in this laboratory. Single-crystal x-ray patterns of selected crystals indicated previously unreported superstructures. The unit cell was found to be eight times as large as that of high quartz, whereas both the *a* and *c* axes were double the length of those of high quartz. Three-dimensional data were collected on a manually-operated diffractometer, assuming hexagonal symmetry. A check of the equivalent reflections among the zero, first, fourth and fifth levels showed deviations among the equivalent reflections which were not compatible with hexagonal symmetry. However, these intensity deviations can be explained in terms of an orthorhombic unit cell which is twice as large as that of the hexagonal cell or sixteen times that of the high-quartz cell.

The preliminary results of the structure analysis of this crystal are discussed.

## STABILIZATION OF ARAGONITE BY MAGNESIUM ION

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Rates of recrystallization of the unstable forms of calcium carbonate (vaterite, aragonite) into calcite have been studied in the presence of H<sub>2</sub>O+CO<sub>2</sub> (in equilibrium with the atmosphere) solutions, with and without the presence of other ions in solution.

Data presented show that the presence of Mg<sup>2+</sup> and other ions of similar size and charge greatly decreases the transformation rate for both vaterite and aragonite. At 35° C. and in the presence of 0.1f Mg<sup>2+</sup>, vaterite recrystallizes to aragonite rather than calcite, and aragonite does not change over periods ranging up to greater than 100 days. In the absence of magnesium-type ions, conversion to calcite was complete in about 1 day, in the case of vaterite, and in about 50 days in the case of aragonite.

<sup>1</sup> SCHREYER, W. AND J. F. SCHAIRER (1961) *Zeit. Krist.* **116**, 60-82 (1961).



Significance and possible implications of the results of these experiments to diagenesis of carbonates and to the formation of dolomite are discussed.

THE CRYSTAL STRUCTURES OF LAUEITE AND METASTRENGITE  
AND A CRYSTALLOCHEMICAL CLASSIFICATION OF Fe-Mn  
ORTHOPHOSPHATE HYDRATES<sup>1</sup>

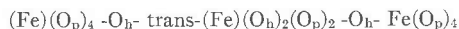
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The crystal structures of laueite and metastrengite were determined by means of vector interpretations of Patterson projections; Fourier projections, and three-dimensional refinements. The intensities were gathered on film, using Zr-filtered MoK $\alpha$  radiation, and corrected for the standard geometric factors as well as crystal shape. 637 independent intensities were collected for laueite and 678 for metastrengite. The final R-factors are .122 and .157 respectively.

Laueite,



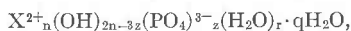
$a = 5.28$ ,  $b = 10.66$ ,  $c = 7.14 \text{ \AA}$ ,  $\alpha = 107^\circ 55'$ ,  $\beta = 110^\circ 59'$ ,  $\gamma = 71^\circ 07'$ , has Mn at 000, Fe at  $0\frac{1}{2}0$  and  $0\frac{1}{2}\frac{1}{2}$ ; 1 P and 9 O in general positions in an asymmetric unit of structure. The structure consists of infinite vertex-linked chains of Fe-centered oxygen octahedra and isolated Mn-centered oxygen octahedra. With  $O_p$  representing oxygen associated with the  $\text{PO}_4^{3-}$  tetrahedral tetradentate group, and  $O_h$  as either watermolecule or hydroxyl oxygen, the chains can be specified as



The isolated octahedron is trans-Mn( $O_h$ ) $_4$ ( $O_p$ ) $_2$ . Possible structures for the stewartite and strunzite polymorphs are suggested.

Metastrengite,  $\text{Fe}^{3+}(\text{H}_2\text{O})_2(\text{PO}_4)$ ,  $P2/n$ ,  $a = 5.30$ ,  $b = 9.77$ ,  $c = 8.73 \text{ \AA}$ ,  $\beta = 90^\circ 36'$ , has 1 Fe, 1 P, and 6 O, all in general positions, in an asymmetric unit of structure. The octahedral asymmetric unit is cis-Fe( $O_p$ ) $_4$ ( $O_h$ ) $_2$ .

Structure classification is based on the general formula (here, for metals of +2 charge):



where X is metal,  $\text{OH}^-$ ,  $\text{PO}_4^{3-}$ ,  $(\text{H}_2\text{O})_z$  are ligands. The formula  $nP$ , where  $P = r + 2n + z$  relates cell stoichiometry to type of octahedral linkage.

PROOF OF THE FORMULA OF SHATTUCKITE,  $\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2$

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A chemical analysis of a shattuckite concentrate from Ajo, Arizona, established its formula as  $\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2$ . The concentrate contained several per cent of quartz as tiny inclusions, which appeared as an insoluble residue in the analytical procedure. Electron-probe analyses of 4 single crystals used for x-ray studies gave an atomic ratio of Cu/Si = 5:4, thus confirming the analytical procedures used. An infra-red absorption band at  $3.15 \mu$  revealed the presence of (OH) groups, and absence of the  $6\mu$  band showed that water molecules were not present.

Shattuckite crystals are prismatic, elongated [001]; nine prism forms and seven general forms were identified by goniometry; cleavages (010) and (100), perfect and easy. Color dark blue, streak pale blue; hardness  $\sim 3\frac{1}{2}$ . Indices of refraction, close to previously re-

<sup>1</sup> Research supported by NSF.

ported values, are:  $\alpha=1.752$ ,  $\beta=1.782$ ,  $\gamma=1.815$  (all  $\pm 0.002$ ),  $2V$  large. Pleochroism:  $X=b$ , very pale blue;  $Y=a$ , pale blue;  $Z=c$ , deep blue. Space group  $Pcab$ :  $a=9.876 \pm 0.001$  Å,  $b=19.812 \pm 0.003$  Å;  $c=5.381 \pm 0.001$  Å;  $Z=4$ ; cell volume  $1052.86$  Å<sup>3</sup>;  $D_0=4.138$  g cm<sup>-3</sup>,  $D_m=4.11$  g cm<sup>-3</sup>.

The formula  $4 [Cu_5(SiO_3)_4(OH)_2]$ , which differs from those formerly proposed, fulfills the requirement of the space group symmetry that atoms in the structure be present in multiples of 4, contains only hydroxyl groups, and gives close agreement between measured and calculated specific gravity. Application of the Gladstone-Dale relation to this formula, using the specific refractive energy value of  $k_{CuO}=0.173$  (*Am. Mineral.* **50**, 288, 1963) and the calculated specific gravity 4.138, gives a mean calculated  $n$  of 1.786, in excellent agreement with the mean measured  $n$  of 1.783.

THE STRUCTURE OF TSUMEBITE<sup>1</sup>

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Three dimensional single crystal data has been used to determine the crystal structure of tsumebite. The crystal used was from the Morenci, Arizona locality. Due to the extreme tendency of tsumebite to occur as intimately intergrown crystals, considerable difficulty was encountered in obtaining a suitable, single crystal.

The unit cell is monoclinic with  $a=8.70$ ,  $b=5.80$ ,  $c=7.85$  Å,  $\beta=111.5^\circ$  and two formula units per unit cell. The space group is  $P2_1/m$ . Lead and copper coordinates were determined from a Patterson synthesis. The remaining atoms were found using least-square and Fourier methods. The structure determination has indicated that the previous formula  $(Pb_2Cu)(PO_4)(OH)_3 \cdot 3H_2O$  is incorrect. Subsequent fluorescence analysis has shown that the formula is most likely  $Pb_2Cu(PO_4)(SO_4)OH$ .

THE CRYSTAL STRUCTURE OF MIZZONITE, A CALCIUM AND CARBONATE RICH SCAPOLITE

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The crystal structure of a 70.1% meionite scapolite from Grenville, Quebec, with  $a=12.169 \pm .004$ ,  $c=7.569 \pm .003$  Å, and space group  $I4/m$  has been refined using three-dimensional x-ray intensities collected by integrated Weissenberg film techniques. Starting with positional parameters from a refined marialite scapolite structure (Papike and Zoltai, 1965, *Am. Mineral.* **50**, 290) the model was completed by Fourier methods and refined by least squares. The refined structure is basically the same as that of marialite with the interesting differences concerning the aluminum distribution in the tetrahedral framework and the crystal chemical role of carbonate.

	x	y	z
(Ca,Na,K)	.1428 ± .0003	.2170 ± .0003	0
(Si,Al)-1	.3391 ± .0003	.4084 ± .0003	0
(Si,Al)-2	.3393 ± .0002	.0866 ± .0002	.2069 ± .0004
O-1	.4581 ± .0007	.3480 ± .0007	0
O-2	.3120 ± .0008	.1280 ± .0008	0
O-3	.0510 ± .0005	.3489 ± .0005	.2081 ± .0010
O-4	.2332 ± .0005	.1354 ± .0005	.3263 ± .0011
(C,S)	0	0	0

<sup>1</sup> Work performed under the auspices of the U. S. Atomic Energy Commission.

The average T-O distances are  $1.648 \pm .008 \text{ \AA}$  in the T-1 tetrahedron and  $1.680 \pm .006 \text{ \AA}$  in the T-2 tetrahedron. A determinative curve for aluminum tetrahedral occupancy based on scapolite data indicates the following assignments: T-1 (29% Al, 71% Si); T-2 (52% Al, 48% Si).

The results concerning the structural role of carbonate are not conclusive but do indicate that the group is disordered in the (001) plane, the disorder consisting of an averaging over four possible positions for the group rather than a free-rotational disorder.

## HIGH DISPERSION AND HIGH INTENSITY POWDER DIFFRACTOMETRY<sup>1</sup>

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One of the major difficulties in the analysis and indexing of complex powder patterns is caused by overlapping reflections. Increasing the wavelength increases the dispersion and makes it possible to greatly reduce the overlapping. The use of  $\text{CrK}\alpha$  has been limited mainly because the intensities were so much lower than those of  $\text{CuK}\alpha$ . This paper reports the results of recent developments of a fine focus, high brilliance and high loading Cr target  $x$ -ray tube, modifications of the diffractometer geometry, and a vacuum chamber to reduce air absorption and scattering, which give about 25 times higher intensity as well as higher resolution. The focal line of the  $x$ -ray tube, 0.4 by 10 mm has a specific loading of  $375 \text{ w/mm}^2$  and is viewed at  $10^\circ$  to  $14^\circ$  to reduce self-absorption. The receiving slit and detector are lengthened in the axial plane to increase intensity with no loss of resolution. Specimens with a fixed curvature virtually eliminate the flat specimen aberration over a large angular range. The vacuum chamber reduces the air path from 335 mm to 89 mm. The  $x$ -ray tube, divergence and receiving slit assemblies and detector remain in air to achieve a simplified chamber design and convenient operation. The vacuum is pulled by a mechanical pump through the rear of an enlarged goniometer shaft to a pressure of less than 0.1 mm in about 10 sec. Stationary or rotating specimens may be used and access is by means of a 4 in. diameter cover on the side of the chamber. With the present chamber, equipped with 0.001 in. Mylar windows, transmission (and thus the intensity) of  $\text{CuK}\alpha$  is increased from 71% to 87%, and of  $\text{CrK}\alpha$  from 23% to 58%, with no change of line profile or specimen surface position. The results will be illustrated by data for topaz, a number of other silicate minerals and steroids.

## COMPOSITION AND DISTRIBUTION OF FELDSPARS IN THE MUSKOX INTRUSION, N.W.T.

G. POULIOT, *Geological Survey of Canada.*

The Muskox intrusion is a large stratiform body of ultramafic, gabbroic and granophyric rocks differentiated from a tholeiitic basalt magma. This investigation deals with the composition and petrographic association of its constituent feldspars. Determinative curves for plagioclase in the range  $\text{An}_{60-90}$  based on the parameter  $[2\theta (131) + 2\theta (220) - 4\theta (1\bar{3}1)]$  and for alkali feldspars in the range  $\text{Or}_{80-100}$  based on the variation of  $d (400)$ , have been constructed from analyzed materials from the intrusion. The composition of plagioclase more sodic than  $\text{An}_{60}$  was determined by standard optical methods and the composition of

<sup>1</sup> This research was supported in part by Advanced Research Projects Agency and was technically monitored by Air Force Office of Scientific Research under Contract No. AF49 (638)-1234.

alkali feldspars more sodic than Or<sub>50</sub> by Orville's modification of Bowen and Tuttle's method.

The compositional range of plagioclase in the intrusion is An<sub>10</sub>-An<sub>90</sub>. The most calcic plagioclase occurs in the olivine gabbro layer which is the lowest layer in which plagioclase occurs as a settled or cumulus phase. Interstitial plagioclase is generally more sodic. The most sodic composition occur in the granophyre-rich rocks and pegmatitic segregations near the roof of the intrusion.

The alkali feldspar ranges from Or<sub>25</sub>-Or<sub>100</sub>. It is most sodic when it occurs as an interstitial phase in certain pyroxenitic and gabbroic rocks and becomes more potassic as the rock differentiation series develops toward granophyre. The normative feldspar of the granophyre is approximately Or<sub>90</sub>Ab<sub>8</sub>An<sub>2</sub>. It would appear that the compositional characteristics of the feldspars have developed because of a relatively high content of K<sub>2</sub>O in the original magma.

#### FOURIER TECHNIQUE FOR THE ANALYSIS OF ZEEMAN NQR ZERO CROSSING DATA

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NQR Zeeman studies of single crystals are valuable in unraveling the nature of chemical binding in solids. One particularly useful experimental technique is to search for and analyze the zero crossing ellipses. Such analysis is usually done by graphical means which are not only inaccurate, but are very tedious. To alleviate these difficulties a least squares procedure based upon Fourier analysis of the zero crossing data was investigated. This smoothing in the large method has the advantage of being readily programmed for digital computers and also allows estimates of the random errors to be made. The method is applicable to locating the major axis system of the field gradient tensor and to the evaluation of field gradient asymmetry parameters. It has been applied to both simulated and actual experimental data with some success. The technique appears to be particularly useful in cases where the asymmetry parameter is close to zero.

#### CRYSTAL STRUCTURE OF LARSENITE, PbZnSiO<sub>4</sub>

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AND

A. PREISINGER, *Mineralogisches Institut, Universität Wien, Vienna, Austria.*

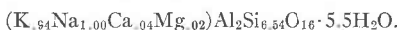
Larsenite is a rare mineral reported from Franklin, New Jersey, U.S.A. It is orthorhombic with  $a=8.244$ ,  $b=18.963$ ,  $c=5.06$  Å,  $Z=8$ , space group  $Pna2_1$ , and is piezoelectric. The structure, determined using three-dimensional diffractometer data, is not similar to that of olivine as was previously thought; nor is it closely related to the structure of esperite (calcium larsenite) which has recently been determined. Instead, it is an entirely new type composed of a network of corner-linked zinc and silicon tetrahedra and "three-sided" and distorted "four-sided" lead pyramids, respectively. The structure has been refined by least squares to an  $R$  of 0.055 for all reflections.

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## K-Na PHILLIPSITE, CROOKED CREEK, OREGON

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An unusually pure K-Na phillipsite occurs in Tertiary lake beds in southeastern Oregon as a uniform 1-2 inch bed over an area of ten square miles. The phillipsite-bearing bed is loosely consolidated, gray to yellow, overlies a mordenite bed and is overlain by an erionite bed. It consists of 80-85% phillipsite, to 20% clinoptilolite, and less than 1% quartz and volcanic glass. Thenardite and hydrated iron oxide are found in variable amounts up to a total of 4% in some outcrops. A chemical analysis of a thenardite-free sample is 58.0 SiO<sub>2</sub>, 13.8 Al<sub>2</sub>O<sub>3</sub>, 2.8 Fe<sub>2</sub>O<sub>3</sub>, 0.2 TiO<sub>2</sub>, 0.6 CaO, 0.2 MgO, 3.8 Na<sub>2</sub>O, 5.8 K<sub>2</sub>O, 14.0 H<sub>2</sub>O. A corrected, calculated formula for the phillipsite is



The phillipsite occurs as euhedral monoclinic crystals up to 80 microns in length. Indices of refraction are  $\alpha$  1.484,  $\beta$  1.486,  $\gamma$  1.487; biaxial (-).

The phillipsite appears to be the result of a replacement process by secondary solutions.

## AN UNUSUAL DOLOMITIC BASAL FACIES OF THE CHATTANOOGA SHALE IN THE FLYNN CREEK STRUCTURE, TENNESSEE

DAVID J. RODDY, *Division of Geological Sciences, California Institute of Technology, Pasadena, California, and U. S. Geological Survey, Flagstaff, Arizona.*

A thin deposit of cross-bedded carbonates and bedded-breccia form a unique and unusual basal facies of Chattanooga Shale within the crater of the intensely deformed Flynn Creek "cryptoexplosion" structure in north-central Tennessee. These units thicken to at least 15 m in the center of the crater and rapidly thin out on the upper flanks of the crater walls. Evidence for a Late Devonian crater has caused speculation that these beds are lake deposits consisting of fresh-water limestones and breccia cemented by fresh-water limestone. However, studies by Conant and Swanson (1961) and Huddle (1963) have described early Late Devonian conodonts in these rocks indicating a marine depositional environment. Mineralogical and chemical studies by the author have shown that limestones occur only as fragments derived from Ordovician limestones in the crater breccia and crater walls. Other breccia fragments consist of dolomites and dolomitic limestones derived from the surrounding contemporaneous erosion surface. Cementing material of this bedded breccia has been identified as dolomite with less than 10% calcite. The cross-bedded, thinly laminated unit overlying the bedded breccia consists almost entirely of dolomite with less than 3% calcite. The total mineralogy of this dolomite strongly suggests as source area the rocks underlying the early Late Devonian surface that surround the crater. Some dolomite grains within the cross-bedded dolomite and bedded-breccia cement are probably detrital grains, whereas other dolomite grains may have undergone recrystallization. Deposition probably in a shallow-water, marine environment preceding the introduction of sediments of the Chattanooga Shale.

## SYSTEMATIC DESCRIPTION AND IDENTIFICATION OF MICA POLYTYPES

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The systematic derivation of unit-cell parameters, stacking sequences, space groups, and "structural presence criteria" has been accomplished for all possible 1-, 2-, 3-, and 4-layer mica polytypes; data for the 1-, 2-, 3-layer forms are given below. A new method of designating polytypes is proposed and is based on vector relationships between adjacent layers.

Stacking Symbol	$a(\text{\AA})$	$b(\text{\AA})$	$d_{001}(\text{\AA})$	$\alpha$	$\beta$	$\gamma$	Space Group	Structural Presence Criteria
1M[0]	5.3	9.2	10.0	90°	100.0°	90°	$C2/m$	—
2M <sub>1</sub> [22̄]	5.3	9.2	20.0	90°	95.1°	90°	$C2/c$	$h3h1:l=2n+h$
2M <sub>2</sub> [11̄]	9.2	5.3	20.0	90°	98.7°	90°	$C2/c$	—
2O[33]	5.3	9.2	20.0	90°	90°	90°	$Ccmm$	—
3T[222]	5.3	—	30.0	90°	90°	120°	$P3_112$	$hh2\bar{h}l:l=3n$
3M <sub>1</sub> [033]	5.3	9.2	30.0	90°	93.4°	90°	$C2/m$	$Ok1:l=3n$
3M <sub>2</sub> [112]	5.3	9.2	30.0	90°	93.4°	90°	$C_2$	—
3Tc <sub>1</sub> [022]	5.3	9.2	30.0	92.9°	95.1°	90°	$C\bar{1}$	$hOl:l=3n$
3Tc <sub>2</sub> [011̄]	5.3	9.2	30.0	98.7°	91.7°	90°	$C\bar{1}$	$Ok1:l=3n$
3Tc <sub>3</sub> [123]	5.3	9.2	30.0	90°	93.4°	90°	$C2$	—

Within the brackets of the stacking symbol are  $n$  numbers where  $n$  is the number of mica layers per unit cell. The  $n$ -th number refers to the vector relationship between the  $n$ -th and  $(n+1)$ -th layer. The number 0,  $\pm 1$ ,  $\pm 2$ , and 3 refer, respectively to 0°,  $\pm 60^\circ$ ,  $\pm 120^\circ$ , and  $180^\circ$  rotations of adjacent layers. Recent studies indicate the following distribution of mica polytypes: biotites—mixture of many polytypes with 0° and  $\pm 120^\circ$  stacking sequences; phlogopites—1M, rarely 2M<sub>1</sub>, 3T; Li-micas—1M, 2M<sub>1</sub>, 2M<sub>2</sub>, 3T, plus more complex forms; muscovite, paragonite—2M<sub>1</sub>, rarely 1M, 3T; authigenic micas—1M, 2M<sub>1</sub>, plus possible disordered 1M<sub>r</sub>- $n(1)$ , 1M<sub>r</sub>- $n(2)$ , 1M<sub>r</sub>- $n(3)$ , and two-dimensional forms, where  $r$ =random and (1), (2) and (3) indicate 60°, 120° and 180°.

### CLINOHUMITE FROM COTOPAXI, COLORADO

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Clinohumite is locally a prominent gangue mineral in a Precambrian Cu-Zn skarn deposit at Cotopaxi, Colorado. It occurs along with gahnite, phlogopite, diopside and minor forsterite within a coarse-grained magnesian actinolite-anthophyllite groundmass. Clinohumite is younger than the amphibolitic matrix, fills fractures in gahnite, and replaces forsterite. Retrograde alteration is extensive, and serpentine is pseudomorphous after clinohumite.

A partial chemical analysis shows:

SiO <sub>2</sub>	37.	MnO	1.8
Al <sub>2</sub> O <sub>3</sub>	0.26	Total H <sub>2</sub> O	1.4
TiO <sub>2</sub>	2.8	F	2.0
Total iron as Fe <sub>2</sub> O <sub>3</sub>	8.7	CaO	0.32
		MgO	major

Individual specimens of Cotopaxi clinohumite exhibit strong variations in their optical properties. Most unaltered hand specimens are reddish-brown; a minor amount is yellow-tan. A summary of the optical properties is as follows:

	reddish-brown	yellow-tan
	$\alpha$ 1.647	1.635
	$\beta$ 1.655	1.652
	$\gamma$ 1.669	1.668
	$\gamma - \alpha$ 0.022	0.033
	$2V = 80^\circ$ (calc) (+)	$88^\circ$ (calc) (-)
Extinction	$18^\circ$	$16^\circ$ (?)
	reddish-brown	yellow-tan
	$\alpha$ yellow-orange	yellow-tan
	$\beta$ yellow-tan	straw yellow
	$\gamma$ pale yellow to colorless	colorless
Dispersion	$r > v$ , weak	$r > v$ , very weak

Single crystal  $x$ -ray photographs show a high degree of pseudosymmetry. Principal rows are not strongly defined and a choice of the unit cell is in part arbitrary. Twinning is not confined to a single twin plane. Using single crystal and powder  $x$ -ray photographs of the same specimen, an attempt has been made to index the clinohumite  $x$ -ray pattern.

#### THE CRYSTAL SUBSTRUCTURE IN $\text{BeO}^1$

D. K. SMITH AND H. W. NEWKIRK, *Lawrence Radiation Laboratory, Livermore, California.*

Single crystals of beryllium oxide grown by flux techniques have been studied by the Berg-Barrett, Lang and divergent beam techniques. Several substructural features have been observed which can be related to the sequence of operations involved in growth. The crystals can be classified into three main groups based on growth direction and habit, which depend on temperature, flux composition and additive. The groups are: 1. Prisms growing in the positive polar direction, 2. Prisms and pyramids growing in the negative polar direction with an axial twin (a core growing in the positive direction), and 3. Plates and truncated pyramids growing perpendicular to the polar axis. Groups 1 and 3 are in general free of growth defects; however, group 2 shows several interesting growth features.

Berg-Barrett and Lang topographs reveal four prominent classes of defects in the group 2 crystals. 1. They are twinned with the core evidently existing from the time of nucleation of the crystal. 2. A single (occasionally multiple) screw dislocation, centrally located in the core, is active throughout the growth of the crystal. 3. Banding, evidently due to inclusion of absorbed impurities, exists parallel to the growth face. 4. A 6-rayed star, observed by viewing along the  $c$ -axis, exists which is also evidently due to precipitation of impurities on the growth surface. None of these features is visible in the optical microscope.

Divergent beam photographs indicate very low values of strain exist at the twin boundaries. This low strain is also evidenced in the Lang photographs where the twin boundaries are usually observed only by discontinuities in the impurity banding.

<sup>1</sup> Work performed under the auspices of the U. S. Atomic Energy Commission.

## MICROPROBE CORRECTION FACTORS

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Measurements have been made for a variety of wavelengths and kilovoltages on samples of known chemical composition to test various correction formulae suggested for  $x$ -ray emission analysis. The Philbert atomic number correction  $(1+h)$  is too small by several per cent for iron oxides and sulfides referred to iron metal. The Reed and Long atomic number correction is also too small but gives a closer fit. Starting from the Reed and Long formula, a new factor has been proposed which fits present data to about 2% except when  $V$  is close to  $V_K$ . The factor is

$$(4.7 + 0.9 \log_e (V - V_K) - \log_e \bar{Z}) \cdot \left( \frac{\bar{Z}}{A} \right) \cdot \frac{1}{R}$$

( $V$  beam voltage;  $V_K$  excitation voltage;  $Z$  atomic number;  $A$  atomic weight,  $R$  back-scatter coefficient of Green).

Using this atomic number correction, and Reed and Long's fluorescence correction, tests of the absorption correction have been made by comparing  $x$ -ray emission for Mg, Al and Si. Mass absorption coefficients evaluated by Heinrich have been used to obtain plots of  $F(X)$  vs.  $X$ . There is strong disagreement between the experimental curves and theoretical formulae, and until the theory is more highly developed, empirical corrections based on the experimental curves for  $F(X)$  are being used. It is concluded that at the present time accurate results for light elements can only be obtained by interpolation between large suites of standards.

## THE IMPERFECT STRUCTURE OF EXCESS NITROGEN TiN

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The titanium nitride was obtained from the Union Carbide Co. and was analyzed by 3 methods. As an average a composition of  $Ti_{0.936}N$  was calculated which agreed well with  $Ti_{0.926}N$  obtained directly from lattice parameter and density determinations. There were 2 kinds of N in the compound: about 2 to 4% by weight could be vacuum extracted at elevated temperatures or could be collected upon dissolution of the compound in HF in presence of  $KMnO_4$ ; the other part of N could be quantitatively transferred into  $NH_3$  upon dissolution. Thus it was assumed that  $N^0$  atoms and  $N^{3-}$  are in equilibrium with the  $Ti^{3+}$  of the structure held together by homopolar but for the most part by ionic forces. of the introduction of  $N^0$  atoms into the structure, vacant sites must also be present there. As the number of  $Ti_{0.936}N$  molecules,  $n^1$ , per unit cell was 3.9665 (the exp. density at 25° C. was  $5.0833 \text{ g cm}^{-3}$ ) the number of monovacancies could be calculated: about 7.2% of the cationic and 0.84% of the anionic sites were empty and there were 0.254 atoms of  $N^0$  per unit cell on regular positions. The  $a_{25}$  of  $Ti_{0.936}N$  was  $4.23986 \pm 0.00007 \text{ \AA}$ , the expansion coefficient was  $5.71 \times 10^{-6} \text{ C}^{-1}$ .

<sup>1</sup> W. J. JAMES AND M. E. STRAUMANIS (1964) *Acta Cryst.* **12**, 739.



THE  $RMn_{12}$  ( $ThMn_{12}$ -type) COMPOUNDS BETWEEN LANTHANIDE  
SERIES ELEMENTS AND MANGANESE; THE CRYSTAL  
STRUCTURE OF  $LuMn_6$

F. E. WANG AND J. V. GILFRICH, *U. S. Naval Ordnance Laboratory,  
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The compounds of  $R_6Mn_{23}$  ( $Th_6Mn_{23}$ -type) series between rare earth elements and manganese have been reported previously.<sup>1</sup> Based on the "Enveloping Effect," a geometrical consideration, the absence of  $Eu_6Mn_{23}$ ,  $Yb_6Mn_{23}$  and  $Ba_6Li_{23}$  has been explained.<sup>2</sup> The magnetic properties of these compounds have been found to be unique from  $RMn_{12}$  (Laves phase) series and a qualitative mechanism of magnetic interaction has been offered.<sup>3</sup>

The present work, based on the combination of single crystal and powder diffraction methods, shows  $RMn_{12}$  ( $ThMn_{12}$ -type) compounds to exist in the following systems: Gd-Mn, Tb-Mn, Dy-Mn, Ho-Mn, Er-Mn and Tm-Mn. This confirms the earlier suggestion of the existence of  $GdMn_{12}$  and  $DyMn_{12}$  by Moriarty and Baenziger.<sup>4</sup>

Through single crystal diffraction study, a hitherto unknown compound  $LuMn_6$  is characterized in the Lu-Mn system in which no  $LuMn_{12}$  is found. Unlike  $RMn_{12}$ -type ( $I4/mmm$ ),  $LuMn_6$  crystallizes in space group  $P6_3/mmc$  with the lattice constants of  $a = 5.13$  and  $c = 8.05$  Å. The atomic arrangement characteristic in  $LuMn_6$  is similar to that of  $RMn_{12}$ -type ( $I4/mmm$ ), though their crystal structures are different.

OBSERVATIONS ON THE MORPHOLOGY AND GROWTH OF  
COLLOIDAL CRYSTALS OF HYDRATED TUNGSTEN OXIDE  
BY ELECTRON MICROSCOPY OF  
THEIR ULTRATHIN SECTIONS

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Tactoid-forming colloidal crystals of  $WO_3$  from slowly hydrolyzing  $NaWO_4$  solutions are studied by bright and dark field electron microscopy and by selected area electron diffraction (SAD), and the results compared for unsectioned and ultrathin sectioned crystals. SAD indicates an identical single-crystal nature for every crystalline particle regardless of the "age" of the solution, size of the particle, or its exterior shape. The same patterns were produced from both the smallest, elliptical "nuclei" crystals, after only hours of formation in the gel, as from large, regularly-shaped crystals which had been grown for years in aqueous suspension. The SAD pattern of sectioned crystals demonstrated a greater incidence of double, or poly-spots. In both sectioned and unsectioned crystals, by bright and dark field, there was a wide variety of characteristic moire and extinction contours, with some rotational moire. In micrographs the contours were more sharply visible in the sections, as if the knife acted to distort the crystal lattice, to introduce distortions otherwise, or to bend the crystals without disruption. The maxima areas in dark field had a spotted appearance, supporting the conclusion that there is a substructure within the crystals. A layered structure (10 Å) was visible within cross sections of single crystals, the layers lying parallel to the broad flat surfaces. Dimensional ratios of the single crystals

<sup>1</sup> F. E. WANG, ACA Annual Meeting, Bozeman, Montana, 1964.

<sup>2</sup> F. E. WANG AND J. R. HOLDEN, *Trans. Met. Soc. AIME*, April 1965.

<sup>3</sup> B. F. DESAVAGE, R. M. BOZORTH, F. E. WANG AND E. R. CALLEN, *Jour. Appl. Phys.*, **36**, 992, 1965.

<sup>4</sup> J. MORIARTY AND N. BAENZIGER, Rare Earth Symp. ASM Meeting, Chicago, 1959.

could be measured with good accuracy by use of the thin sectioning technique. The cross sections are rectangular with no obvious center thickening.

### DETERMINATION OF PROTON POSITIONS IN CRYSTALS BY INFRARED SPECTROSCOPY

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The hydroxyl ion absorbs strongly in the 3-micron region of the infrared spectrum due to the vibration of the proton against the oxygen. When the proton links to an adjacent oxygen through hydrogen bonding, the vibrational frequency decreases. Since the strength of the hydrogen bonding is a sensitive function of oxygen-oxygen distance, measurement of the frequency shift is a good method of characterizing essential hydroxyls in a structure and for locating impurity hydroxyl ions in non-hydroxylated structures where the oxygen-oxygen distances are known. A critical survey of available literature data (mainly organic compounds) has been combined with measurements of the infrared spectra of some 20 metal hydroxides, mainly with the brucite structure, to provide a new and greatly improved curve relating frequency shift to O-H—O distance. The data can be fitted to a curve obtained from a quantum mechanically derived potential function. The curve is nearly linear and fits with less scatter in the region of weak hydrogen bonds such as occur in most crystals and is thus more valuable for crystal structure interpretation than for the organic compounds for which the method was originally derived. The complex spectra which are usually obtained in hydroxyl region can be assigned to O-H fundamental vibrations arising from OH groups on non-equivalent sites, and a set of bands resulting from combinations of OH fundamental with various lattice vibrations. The fundamental can usually be recognized by its intensity and only the fundamental is necessary to determine the O-H—O distance. In the case of very dilute impurity hydroxyls, only the fundamentals usually appear.

### OPTICAL ABSORPTION SPECTRA OF IRON IN THE ROCK-FORMING SILICATES

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Optical absorption spectra have been obtained at 300° K. and at 78° K. on polished single crystals of a suite of low iron-content olivine, pyroxene, amphibole and epidote family minerals. The spectra cover the range of 0.4 to 3.5 microns. The single most characteristic feature is a strong band at  $\sim 1.0$  microns due to  $\text{Fe}^{2+}$  in 6-fold coordination. This band varies in shape and intensity depending on the actual symmetry of the 6-fold site. The crystal field splitting parameter ( $D_q$ ) varies from 950–990  $\text{cm}^{-1}$  depending on the iron-oxygen distance. In diopside a band occurs at 2.26 microns ( $D_q = 442 \text{ cm}^{-1}$ ) which appears to be due to  $\text{Fe}^{2+}$  in 4-fold coordination and suggests that a small amount of the ferrous iron is on the 4-fold sites. In the range of 1.5 to 3.5 microns are a complex group of very sharp bands arising from both essential and impurity  $\text{OH}^-$  groups in the silicate structure.

COMPARISON OF THE CRYSTAL STRUCTURES OF BINNITE,  $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ,  
AND TETRAHEDRITE,  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ 

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Tetrahedrite and binnite are isostructural and have a curious superstructure based on a distorted sphalerite-like arrangement of atoms. The structure was proposed by Pauling and Neuman in 1934 on the basis of a limited number of reflections. The two structures have been refined to confirm this arrangement, to compare the nature of the distortions in the As and Sb phases, and to compare the results of refinement of photographically recorded data with those obtained by counter techniques.

Tetrahedrite has been refined to  $R=3.9\%$  using counter data. The structure contains two sorts of Cu atoms. A first type is coordinated by four S atoms at 2.342 Å which form a nearly regular tetrahedron. A second type of Cu is in triangular coordination, being bonded only to one S atom at 2.234 Å and two at 2.272 Å. This group is planar and the Cu atom has a highly anisotropic thermal motion. The Sb atom is bonded to three S at 2.446 Å which form bond angles of  $95^\circ 8'$  and is also in van der Waals contact with six second-nearest S neighbors. The absolute configuration of the structure was established.

Binnite has been refined to  $R=7.2\%$  using photographic data. Corresponding bond lengths in the coordination polyhedra are 2.337 Å for the tetrahedrally coordinated Cu, 2.204 and 2.258 Å for the triangularly coordinated Cu, and 2.246 Å and  $98^\circ 22'$  for the bond length and bond angle in the  $\text{AsS}_3$  pyramid. The As atom is not in van der Waals contact with its second-nearest S neighbors. Some Sb had substituted for As in the binnite studied. The occupancy of this site was also refined, and a value in excellent agreement with a chemical analysis was obtained.

The nature of the distortion of the  $\text{CuS}_4$  tetrahedron differs in the two structures. This may be explained in terms of a slightly different mode of S packing. It is found that the results of the two refinements were quite comparable. With the photographic data, however, a larger fraction of the diffracted intensities are unobservable, and the standard deviations of the parameters of the structure, the bond lengths, and the bond angles are roughly 50% higher.

## THE CRYSTAL STRUCTURE OF COPPER(II) SULFATE TRIHYDRATE

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Crystals of  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  (bonattite) are monoclinic, space group  $Cc$ , with  $a=5.59$ ,  $b=13.03$ ,  $c=7.34$  Å,  $\beta=97.1^\circ$ ,  $Z=4$ ,  $D_x=2.68$  g.  $\text{cm}^{-3}$ . Three dimensional data were collected on a Buerger precession camera with  $\text{Mo-K}\alpha$  radiation. The structure was solved from a three dimensional Patterson synthesis and refined by least squares techniques to  $R=0.069$  for 936  $F_{hkl}$  with  $\sin\theta/\lambda < 0.8$  Å $^{-1}$ . The coordination polyhedra around the  $\text{Cu}^{2+}$  ions do not share any edges or corners with each other; they are connected by hydrogen bonds and via linking sulfate groups. The square planar coordination around the copper ion consists of three water oxygen atoms and one sulfate oxygen atom at an average distance of 1.96 Å. Two more sulfate oxygen atoms at 2.39 and 2.45 Å complete the distorted octahedral coordination. The average S-O bond length in the sulfate tetrahedron is 1.472 Å. Each water oxygen atom forms two hydrogen bonds. One of the sulfate oxygen atoms accepts two hydrogen bonds: it is the only oxygen atom in the structure which does not belong to the octahedral coordination around the copper ion. The average hydrogen bond length is 2.74 Å. The study was aided by a grant from the Office of Saline Water.

X-RAY DIFFRACTION STUDIES ON THE PROBLEM OF CARBONATE  
SUBSTITUTION IN THE APATITE STRUCTURE

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The role of carbonate in the apatite structure (especially in the apatite of teeth and bone) remains a controversial issue. It still remains unresolved whether (1) carbonate is merely adsorbed on the surface of the crystallites, or (2) it is an integral part of the apatite structure. Among those who agree that carbonate is in the structure, a disagreement exists as to the mode of substitution: whether (1)  $\text{CO}_3$  substitutes for  $\text{PO}_4$  or (2)  $\text{CO}_3$  substitutes for OH. A convenient method of synthesizing carbonate-apatites and carbonate-F apatites have been developed. The method consists of the drop-by-drop addition of 0.02M  $\text{Ca}(\text{Ac})_2$  (250 ml) to a continuously stirred 750 ml solution which is 0.016M with respect to  $\text{Na}_2\text{HPO}_4$  and from 0 to 0.54M with respect to  $\text{NaHCO}_3$ . Precipitates containing 0.4 to 24 wt. %  $\text{CO}_3$  are obtained by varying the carbonate concentration in the solution. These precipitates give a very well crystallized x-ray diffraction pattern of carbonate apatite whose *a*-axis shortening is linearly related to the carbonate content. No other phase (under conditions where 0.5% by weight of calcite or aragonite is detectable) was observed. These precipitates exhibit an *a*-axis lengths which range from 9.43<sub>3</sub> to 9.29<sub>9</sub> Å and *c*-axis of 6.87<sub>7</sub> to 6.93<sub>2</sub> Å.

Ignition of the synthetic carbonate-OH-apatites at 400° C. resulted in a slight shortening of the *a*-axis. Ignition at higher temperatures caused a loss of carbonate (as  $\text{CO}_2$ ) and an expansion of the *a*-axes. As more and more carbonate is expelled, the *a*-axis of the precipitate reverts back to the *a*-axis of the OH-apatite.

Results of this study support the mechanism of carbonate for phosphate substitution in the apatite structure, originally proposed by McConnell almost 30 years ago.