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Abstracts

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The Crystal Structure of Bikitaite[1]

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The basic outline of the crystal structure of bikitaite was reported by Appleman (1960), but neither positional parameters of the atoms nor details of the structure were given. Bikitaite $LiAlSi_2O_6 \cdot H_2O$ (crystals from Bikita, South Rhodesia, kindly provided by the Royal Ontario Museum, Toronto): $a = 8.613$, $b = 4.962$, $c = 7.600$ Å, $\beta = 114.45°$, space group $P2_1$ offered a good example for direct structural determination and for the study of Al and Si ordering. The structure was solved by direct methods from 3-dimensional $MoK\alpha$ data collected on a Picker diffractometer. After selection of starting phases, using 181 E's ≥ 1.4 and application of tangent formula, a set of refined phases with $R_{\text{Karle}} = 13$ percent gave an E-map which revealed the whole structure. The structure was refined by full-matrix least squares, using anisotropic temperature factors to an unweighted R-value of 3.7 percent for 824 observed reflections. Both hydrogens on the water molecule were located from difference Fourier map. There are 3 basic tetrahedral sites in the asymmetric unit of bikitaite, two of them occupied by 0.5 Al + 0.5 Si, the third one occupied by Si. The average T_{Al+Si}–O_4 bond lengths are 1.681; the Si–O_4 tetrahedron gives average bond length of 1.610 Å. These bond lengths are in very good agreement with Jones (1968). The average bond length of Li–(O_3H_2O) tetrahedron is 1.972 Å.[2] Except H_2O, all oxygens in the structure are bridging, forming zig-zag chains running parallel to [010]. These chains form an intricate 3-dimensional network with one large channel containing Li and H_2O and six small empty channels. The present study confirmed the previous work (Appleman, 1960). Details of the structure with explanation of the Al–Si ordering and hydrogen bonding will be given.

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[1] Research supported by grant from National Research Council of Canada.

[2] Bond lengths from original abstract corrected by author.

Tetrahedral Sizes of Orthopyroxenes and Silicon-Aluminum Ordering[1]

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The structure of an aluminan orthopyroxene (TS) from Takasima, Japan (Takeda, 1971) revealed preference of Al into Si(B) tetrahedra over Si(A). Since the sizes of tetrahedra might be affected by substitution of other cations, refinements have been carried out on two more orthopyroxenes; aluminan bronzite (WA1) from Walcha, New South Wales, Australia (supplied by R. A. Binns) and bronzite

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[1] Research was accomplished under National Research Council Associateship.

[2] On leave from the Mineralogical Institute, University of Tokyo, Hongo, Tokyo, Japan.

(BI) from Bonin Island, Japan (supplied by I. Kushiro). Their chemical and cell data are:

	Al	Fe^{2+}	Mg	Ca	Other
WA1	0.15	0.21	1.51	0.07	0.05
BI	0.00	0.27	1.64	0.07	0.03

	Si	Al	O	*a*	*b*	*c*
WA1	1.83	0.17	6	18.257(3)	8.790(2)	5.201(1)Å
BI	1.96	0.04	6	18.272(3)	8.848(2)	5.204(1)

Both crystals show no exsolution of augite. An aluminan subcalcic augite ($\beta = 106°33'$) co-existing with WA1 exsolves large amounts of Mg-rich pigeonite ($\beta = 108°45'$). The structures have been refined in space group *Pbca* to final *R* values of 0.027(WA1) and 0.027(BI) for 1294 and 1391 observable reflections, respectively, which were measured by a Picker FACS-1 system with Mo$K\alpha$ radiation. The mean non-bridging (nbrg) (Si,Al)–O distances, which are useful in estimating Al contents, are given below (standard deviation ± 0.001Å).

Al/(Al + Si)	0.085(WAl)	0.075(TS)	0.019(BI)
Si(A)–O(nbrg)	1.605 Å	1.604 Å	1.602 Å
(Si, Al)(B)–O(nbrg)	1.621	1.615	1.605

The above results confirm the site preference of Al into the Si(B) tetrahedron that is originally larger and more puckered than the Si(A) one. The comparison of the above distances with those of Fe-rich orthopyroxenes (Burnham *et al*, 1971) shows that the sizes of Si(A) tetrahedra are almost identical regardless of the Si–Al or Mg–Fe substitution.

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The Crystal Structure of Scawtite

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Scawtite from Crestmore, California, has $2[Ca_6Si_6O_{18}2H_2O{:}CaCO_3]$, *a* 10.118(3), *b* 15.187(4), *c* 6.626(1) Å, β 100° 40(1) "minutes", and *I*2/*m*(?).

Intensity data from a Picker automated diffractometer, using phases derived from a Patterson synthesis, yielded $R = 0.117$ after Fourier and least-squares refinement.

The idealized structure contains layers of octahedrally-coordinated Ca atoms. Isolated Si_6O_{18} (inner Si–O 1.64, outer 1.60) rings share six apical oxygens with octahedral layers above and below. CO_3 triangles also lie between octahedral layers causing major distortion from ideality.

The CO_3 group formally lies at a center of symmetry in *I*2/*m* and actually must be disordered. Alternatively the space group symmetry is lower, but the zero-moment test was inconclusive.

The H_2O molecule forms part of the octahedral layer, bonding directly to Ca and possibly hydrogen-bonding to O–1, O–4, O–5, O–8. The positional ($\times 10^4$) and thermal parameters are:

	Ca-1	Ca-2	Ca-3	Si-1	Si-2	O-1	O-2
x	2121	5000	5000	7729	0000	9025	0880
y	1402	2495	5000	3959	3232	3932	2686
z	1997	0000	0000	2057	0000	0893	1838
B	1.00	0.66	1.39	0.45	0.46	1.13	0.89

	O-3	O-4	O-5	H_2O	C	O-7	O-8
x	6444	6975	7413	3440	0000	0114	0648
y	3756	1620	0000	0000	0000	0736	0000
z	0322	0911	2277	2015	0000	0961	1783
B	0.84	0.74	0.83	1.66	1.46	4.04	1.47

The Crystal Structure of a Titaniferous Clinohumite[1]

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The humite minerals have recently been the subject of detailed study by Gibbs, Ribbe, and co-workers[2] and the structural analogies of the humites with the olivine group have been amply demonstrated. The humite minerals may be represented by the formula $n[M_2SiO_4]\cdot[M_{1-x}\,Ti_x\,(F,OH)_{2-2x}\,O_{2x}]$ where *n* takes integral values from 1 to 4 for norbergite, chondrondite, humite, and clinohumite; and *M* is predominantly Mg with lesser Fe. A rather unusual occurrence of clinohumite was recorded from a carbonatite complex at Cargill Lake, Ontario, and since it contained TiO_2 varying between 3 and

5 percent it was considered a suitable candidate for this study. The crystal structure of titaniferous clinohumite from Cargill Lake, Ontario—$Mg_{7.34}$ $Fe_{1.45}$ $Ti_{0.26}$ $(SiO_4)_4$ (OH,F,O), $a = 4.753$, $b = 10.269$, $c = 13.724$ Å, $\alpha = 100.90°$, space group $P\ 2_1/b$, $Z = 2$—has been refined by full matrix anisotropic least squares calculations to a residual $R = 3.6$ percent for 1644 observed reflections using Mo$K\alpha$ counter data collected up to $\sin \theta/\lambda = 0.70$. Starting coordinates of clinohumite given by Taylor and West[3] were used in the refinement. There are five distinct types of octahedra in this mineral: $M(1)O_6$ [two types] and $M(2)O_6$, similar to those of the same nomenclature in olivine, and $M(2)O_5$ (OH,F) and $M(3)O_4(OH,F)_2$ like those in chondrondite and humite. The cation distribution refinement [Finger's (1969) least squares program] suggests that Ti is exclusively concentrated in $M(3)$ sites in which Fe is almost completely absent, and there is significant enrichment of Mg in the $M(2)O_5$(OH,F) octahedron. The Fe occupancies in M sites are as follows: $M(1)_A$ 0.194, $M(1)_B$ 0.197, $M(2)_5$ 0.160, $M(2)_6$ 0.241 Fe, $M(3)$ octahedron contains 0.060 Fe and 0.13 Ti. Details of the structure will be given.

References and Notes

[1] Research supported by grant from National Research Council of Canada.

[2] *Amer. Mineral.* **54,** 391–411; **54,** 376–390; **55,** 1182–1194; **56,** 1155–1173.

[3] Taylor and West (1928) *Proc. Roy. Soc.* **117,** 517–532.

The Crystal Structure of Gladite, $PbCuBi_5S_9$[1]

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Gladite is orthorhombic, space group *Pbnm*, with $a = 33.531(6)$, $b = 11.486(2)$, $c = 4.003(2)$ Å, and $D_m = 6.96$, $D_x = 6.91$ g/cm³ for $Z = 4$. Gladite is one of three known phases (Welin, 1966) intermediate between bismuthinite, Bi_2S_3 and aikinite, $PbCuBiS_3$, and which constitute examples of an extensive series of hypothetical bismuthinite superstructures (Moore, 1967). Intensities were recorded photographically using graphite-monochromated Ag$K\alpha$, and a precession camera equipped with a masked film casette, and were measured with an automatic photoscanner. Refinement was carried to $R = 14.6$ percent.

The structure is a superstructure based upon Bi_2S_3, in which 1/6 of the Bi are replaced by Pb, and 1/3 of a set of available tetrahedral interstices are occupied by Cu. In spite of the close similarity between the stibnite-type ribbons in bismuthinite and aikinite (Kohatsu and Wuensch, 1971), gladite surprisingly contains a $[Bi_4S_6]$ and two $[PbCuBi_3S_6]$ slabs alternating along [100] rather than a combination of aikinite and bismuthinite units—*i.e.,* the Pb orders among the maximum possible number of chains. The sulfur atom arrays in gladite, aikinite, and bismuthinite are remarkably similar in spite of the substituted metal atoms. The heavy metal atom positions are similar in the three structures when the site is occupied by the same species, but there is significant displacement of the locations of a Pb (or Bi) in gladite relative to Bi (or Pb) in aikinite or bismuthinite. The magnitude of the Pb displacement in gladite (0.50 Å) is greater than that in aikinite (0.27 Å) because of absence of Cu in one of the adjacent tetrahedral sites.

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[1] Research supported by the National Science Foundation and an IBM Fellowship.

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Borate Framework of Boracite and Its Relationship to the Ferroelectric Effects

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New crystal-structure refinements of $Pca2_1$ boracite, $Mg_3ClB_7O_{13}$, and $R3c$ ericaite, $Fe_{2.4}Mg_{0.6}ClB_7O_{13}$, largely confirm the structure proposed by Ito, Morimoto, and Sadanaga (1951), but the borate "pyra-

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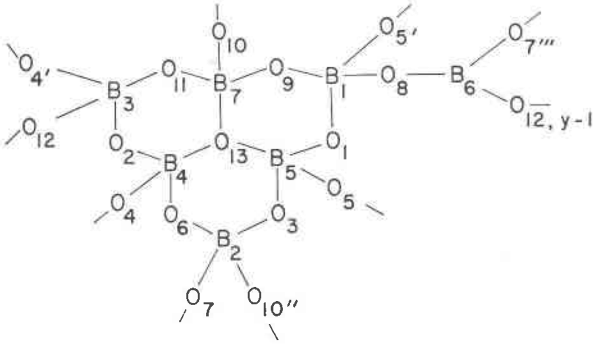
mid" originally postulated by analogy to the cubic form is not found. The asymmetric part of the borate framework we find is shown schematically in the figure, numbered as for the orthorhombic form. Three boroxol rings formed by corner-sharing among tetrahedra are linked at a common oxygen atom, a feature known in only a few other borate structures. This ring system is in turn cross-linked to other symmetry-related units through the B_6 triangle. The distances and angles are all normal for borates. The arrangement in space is such that the triangle boron is at about 2.2 Å from the O_{13} oxygen in a nearby unit. In the various polarity changes, a bond from one of the three tetrahedral boron atoms linked to O_{13} shifts to a nearby B_6, interchanging the coordination accordingly. The atomic displacements involved in these shifts range up to 0.6 Å. Thus the boron and oxygen atoms are involved in the "ferro" transitions as much as are the metal and halogen atoms.



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An Automated Mineralogical Laboratory

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A modular X-ray and electron beam system has been constructed to accomplish most types of mineralogical X-ray analysis automatically. The system includes a vertical powder diffractometer, a vacuum spectrograph, a four-axis single-crystal diffractometer, and an electron microprobe with four spectrometers. The system is controlled by a single computer with auxiliary drum storage. The powder diffractometer has automatic goniometer drive, automatic sample changing with computer cataloguing of samples, and automatic variable divergence slit. The X-ray spectrograph is a standard unit with added 100 Kv capability, automated goniometer drive, eight or 32 position sample changer, six-analyzing-crystal changer, collimator changer, and detector changer. All functions including sample number cataloguing are computer controlled. The four-axis single crystal diffractometer has all functions computer controlled and includes peak search option. The electron microprobe/scanning electron microscope has all spectrometers, *x*, *y*, *z*, stage motions, and sample changer controlled by computer. X-ray channels and current are automatically read-out. Control of probe functions and correction of mechanical errors in stage operation are aided by a digital beam scanner with a light pen. The software is modular. All instruments operate simultaneously in a time-sharing mode. The operating system drives all X-ray hardware, fetches programs and data from the drum, allocates storage, queues final results for printing, and performs other functions. Qualitative analysis spectra for each instrument collected automatically in several modes and stored on the drum, references. A.S.T.M. diffraction, spectrographic and special files maintained on the drum. Quantitative analysis is executed automatically using a version of "MAGIC" on the electron microprobe and a linear regression method and "CORSET" for the spectrograph.

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Silver Radiation Data Used to Reduce μ_l in Refining the Structure of Dyscrasite (Ag_3Sb)

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The structure proposed for dyscrasite by Peacock (1940) has been confirmed in the space group $C^1_{2v} - Pmm2$ with $a = 3.008(1)$, $b = 4.828(1)$, $c = 5.214(3)$ Å. Use of Ag$K\alpha$ rather than Cu$K\alpha$ radiation to collect Weissenberg film packs reduced μ_l to 138 from 2264 cm^{-1} and allowed for a meaningful absorption correction. The structure was refined anisotropically to $R = 0.071$ using 69 independent reflections (4 reflections per parameter). The three silver atoms form an essentially perfect hexagonally close-packed array, but the antimony atom at 0, 0, −0.0254(2) is significantly displaced from the corners of the orthohexagonal cell. For all atoms except Ag_2, which is essentially spherical, thermal motion is greatest parallel to *a*, the direction contrary to hexagonal "ordering." The shortest interatomic distances are Sb-Sb = 3.008(2), Ag_1-Sb = 2.989(8), and Ag_2-Ag_3 = 2.947(4) Å.

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The Crystal Structure of Wittichenite, Cu_3BiS_3

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Wittichenite, Cu_3BiS_3, from the type locality in Wittichen, West Germany, is orthorhombic, $a = 7.723(10)$, $b = 10.395(10)$, $c = 6.716(5)$ Å; [$D_{\text{meas}} = 6.01$, $D_{\text{calc}} = 6.11$;][1] $Z = 4$; space group $P2_12_12_1$. The structure was solved by the heavy atom method from 695 observed symmetry-independent reflections $(F_o^2) \geq 2\sigma(F_o^2)$ collected on a Picker four-circle FACS-1 diffractometer using Zr filtered Mo$K\alpha$ [($\lambda = 0.71069$ Å)] radiation. Spherical absorption corrections were applied to the data ($\mu R = 10.5$), and the structure was refined by full matrix least squares using anisotropic temperature factors to an *R* value of 4.9 percent ($R_w = 6.7$ percent). [The structure consists of infinite $BiCu_3S_3$ chains parallel to [001] which are linked by Cu–S bonds to form continuous sheets normal to [010]. Adjacent sheets are related by the 2_1 axes parallel to [100] and are linked by Cu–S and Bi–S bonds.][1] Cu is in nearly trigonal planar coordination with S (Cu–S distances 2.255 to 2.348 Å; S–Cu–S angles 110.8 to 131.8°). The packing of CuS_3 polyhedra in the structure yields short Cu–Cu contacts ranging from 2.61 to 2.94 Å. Bi is trigonally coordinated by S (Bi–S distances 2.569 to 2.608 Å; S–Bi–S angles 94.2 to 98.7°). S is tetrahedrally coordinated by 3Cu and 1Bi. Wuensch (1964) has reported similar, less distorted coordination in tetrahedrite, $Cu_{12}Sb_4S_{13}$.

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Anionic Bond-Valence Sums in Borates[1]

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Empirical relations between bond length and bond valence (also called bond order and bond strength) have been given by Pauling (1947), Zachariasen (for B–O and O–H ··· O exclusively, 1963), Don-

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[1] Estimated standard deviations of cell edges and bracketed information provided by the author after presentation of the paper.

nay and Allmann (1970), and Brown and Shannon (1972). The results of Zachariasen in the case of β–HBO_2 are compared with those of the other three methods. After the anionic valence sums are corrected for hydrogen bonding (by the Lippincott-Schroeder relation, in Pauling's case), the mean absolute deviation $\overline{|\Delta v|}$ from the anionic formal charge (2 for O^{2-}, 1 for OH^-, 0 for H_2O) and the maximum absolute deviation $|\Delta v|_{\max}$ have the following values: 0.19, 0.32 (Plg); 0.06, 0.10 (Zach.); 0.07, 0.17 (D–A); 0.23, 0.47 (B–S). Although Zachariasen gave both O–H and O–H ··· O *vs* bond length curves, he used the latter. Donnay and Allmann have applied their procedure to structures for which the hydrogen positions are well known and find that using O–O approach as the basis for estimating valence transfer due to hydrogen bonding always gives better results than relying on the O–H distance. Although Lippincott and Schroeder assumed a linear H bond, in the potential function they used, to obtain the energy associated with the two halves of a hydrogen bond, their data are applicable regardless of the degree of non-linearity of the bond. The Donnay-Allmann curves are then applied to gowerite, $CaB_6O_8(OH)_4 \cdot 3H_2O$ (Konnert, Clark, and Christ, 1972), $K_2B_5O_8OH \cdot 2H_2O$ (Marezio, 1969), and kernite, $Na_2B_4O_6(OH)_2 \cdot 3H_2O$ (Cooper, Larsen, Coppens, and Giese, in press[2]), with the following results. For gowerite: 0.07, 0.13; the hydrogen bond reported as donated by $H_2O(2)$ to $H_2O(3)$ turns out to be donated by $H_2O(3)$ to $H_2O(2)$. For $K_2B_5O_8OH \cdot 2H_2O$: 0.03, 0.10. For kernite: 0.05, 0.14; here the hydrogen positions have been determined experimentally so that it was possible to check that all the predicted hydrogen bonds and donor-acceptor assignments were correct.

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Cell and Pseudo-Cell Transformations in Calcite

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Cells and pseudo-cells of calcite, after early fumbling finally got unravelled and have been repeatedly discussed in the literature. The last paper on the subject, by Winchell (1956), stresses two structural cells (i and iv, below) but not the pseudo-cells. A pseudo-cell for the structure may well be a true cell of the bond assemblage that controls the morphology. G. Friedel (1926, reprinted 1964) has shown that at least two cells must be considered to account for the morphological development of calcite crystals ("la double période"). X-ray data on calcite have referred to various cells, in both rhombohedral and hexagonal descriptions. Coordinate transformations are tedious. For all these reasons, we decided to offer the following synoptic tabulation, to facilitate the comparison of calcite cells. Note that all the cell edges mentioned here can be determined on a single $(010)^*_0$ precession pattern.

	Rhombohedral Cells	
i	ii and iii	iv, v, and vi
	Angle α	
∿46°	∿76°	∿102°
	Structural Symbols	
$\{100\}$ $\{10\bar{1}1\}$	$\{011\}$ $\{\bar{1}012\}$	$\{211\}$ $\{10\bar{1}4\}$
	Morphological Symbols	
$\{3\bar{1}\bar{1}\}$ $\{40\bar{4}1\}$	$\{\bar{1}11\}$ $\{\bar{2}021\}$	$\{100\}$ $\{10\bar{1}1\}$
	Z($CaCO_3$ in rh. cell)	
2(i)	8(ii) and 1(iii)	32(iv), 4(v), 1/2(vi)
	Pseudo-cells	
(i)(ii)(iv) are true cells	(iii)CO_3 ions taken as equivalent	(v)CO_3 ions equivalent (vi) all ions equivalent
	Cell Dimensions	
a_{rh}, α	$a^{ii}_{rh}=2a^{iii}_{rh}$, $\alpha^{ii}=\alpha^{iii}$	$a^{iv}_{rh}=2a^{v}_{rh}=4a^{vi}_{rh}$, $\alpha^{iv}=\alpha^{v}=\alpha^{vi}$
a, c, c/a	$a^{ii}=2a$, $c^{ii}=c$	$a^{iv}=4a$, $a^{v}=2a$, $a^{vi}=a$
	$a^{iii}=a$, $c^{iii}=c/2$	$c^{iv}=c$, $c^{v}=c/2$, $c^{vi}=c/4$
	$c^{ii}/a^{ii}=c^{iii}/a^{iii}=c/2a$	$c^{iv}/a^{iv}=c^{v}/a^{v}=c^{vi}/a^{vi}=c/4a$

Example of transformation. Faivre (1944) gave a'_{rh} 4.039, α' 76°05′. In existing tables (Donnay-Takeda, 1963), we read $a'_{rh}/a' = 0.81138$ and $c'/a' = 1.71027$ (both are functions of α'). From iii above, one division and one multiplication give us $a = a' = 4.978$ and $c' = 8.514$, whence $c = 17.028$. For c/a 3.42054, the same tables give $\alpha = 46°04'$, and for this α yield $a_{rh}/a = 1.27790$, whence $a_{rh} = 6.362$.

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[1] The work was supported by the National Research Council of Canada.

[2] Published, *Amer. Mineral.* **58,** 21–31 (1973).

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Evidence of Carbonate Order-Disorder In $CaCO_3 \cdot H_2O$

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Single crystals of $CaCO_3 \cdot H_2O$, in the form of trigonal bipyramids, were synthesized by a silica gel technique. Precession and Weissenberg photographs indicated one of the two enantimorphic space groups, $P3_121$ or $P3_221$. The lattice parameters of the subcell, a = 6.092(2) Å, and c = 7.529(2) Å, were obtained from precision back-reflection Weissenberg data. There are three formula units in the unit cell. The presence of very weak superstructure-type reflections on overexposed precession photographs indicated that the real structure has a tripled unit cell with $[a,b,c] = [1/3\ 1/3\ 0/-1/3\ 2/3\ 0/0\ 0\ 1]\ [a,b,c]$.

The substructure was solved by successive Patterson map and electron density calculations using only the substructure reflections. Calcium and $O(H_2O)$ are on special positions, two carbonate group oxygens are on general positions, while the remaining carbonate oxygen and carbon are statistically distributed on general positions, very close to special positions. This model, which assumes half occupancy of the aforementioned carbon and oxygen in the general positions, refined to an R factor of 3.4 percent using anisotropic temperature factors. Calcium is surrounded by eight oxygens at distances ranging from 2.42 to 2.49 Å. One extraordinarily long C–O distance in the carbonate group, 1.367 Å compared to the other two of 1.251 and 1.273 Å, suggested that hydrogen was bonded to it forming a HCO_3^- ion as in $NaHCO_3$. Accordingly, a more representative chemical formula might be $CaHCO_3(OH)$, which seems to be substantiated by the IR absorption spectra. The structure is further characterized by disordered CO_3 groups, pointing up and down the c axis, and structurally related by a 2-fold axis which bisects the edge of the CO_3 plane. The superstructure is proposed to result from the ordering of the carbonate groups according to one of two possible models.

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[1] Postdoctorate Fellow, National Research Council.

Crystal Structure of Lemoynite $(Na,K)_2\ Ca\ Zr_2\ Si_{10}\ O_{26} \cdot H_2O$[1]

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Lemoynite is a new mineral species found at Mont St. Hilaire, Province of Quebec.

It is monoclinic, space group $C\ 2/c$, pseudo $C\ 2/m$. The unit cell parameters are: a = 10.384, b = 15.948, c = 18.601 Å, β = 104.59°. It contains 4 formulas per unit cell. The $C\ 2/c$ structure was determined by direct methods and the superstructure by image seeking methods from 4200 independent structure factors. The final residual is 7.9 percent.

Na, K, Ca, and H_2O are in the large tunnels opened in the zirconosilicate frame. The frame, of formula $Zr\ Si_5\ O_{13}$, is made of thick sheets of silicate hexagonal rings bound together by zirconium atoms.

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[1] Research sponsored by the National Research Council of Canada.

Nenadkevichite, $(Na,K)_{2-x}\ (Nb,Ti)_2\ (O,OH)_2\ Si_4O_{12} \cdot 4H_2O$, A New Four-Fold Silica Tetrahedra Ring Structure[1]

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Nenadkevichite crystallizes in space group $Pbam$: a = 7.408(2), b = 14.198(3), and c = 7.148(2) Å. The structure was determined by the symbolic

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[1] Research sponsored by the National Research Council of Canada and by la Direction Générale à la recherche Scientifique et Technique, France.

addition technique and refined by anisotropic full-matrix least-squares to an R value of 0.084 from 3,264 independent observed X-ray reflections. The structure consists of square rings of silica tetrahedra Si_4O_{12} in the (100) direction joined together by chains of NbO_8 octahedra in the [100] direction. Large cavities in this structure accommodate Na^+ and $[H_2O]$.

Patterson Function of Satellite Intensities of a Plagioclase[1]

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The concept of a "generalized atomic scattering factor" and of its Fourier transform is introduced and is used to discuss properties of Fourier transforms of difference reflections.

On this background Patterson functions based on experimentally determined intensities of "e" and "f" satellites of a plagioclase crystal (An55) are discussed in terms of directions and magnitudes of displacements of individual atoms from their average positions.

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[1] Research supported in part by the National Science Foundation, grant number GA-35246.

The Crystal Structure and Site-Chemistry of a Zinc Manganese Cummingtonite by Least-Squares Refinement of X-ray and Mössbauer Data

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The crystal structure of a zinc cummingtonite—$Na_{0.21}Ca_{0.28}Mg_{3.70}Fe^{2+}{}_{0.42}Mn_{1.60}Zn_{0.75}Fe^{3+}{}_{0.07}Al_{0.09}Si_{7.87}O_{22}(OH)_2$, $a = 9.6063(4)$, $b = 18.1262(5)$, $c = 5.3168(2)$, $\beta = 102.632(1)$, space group $C2/m$, $Z = 2$—has been refined by full-matrix least-squares methods to a R—factor of 3.7 percent for 1383 observed reflections measured with $MoK\alpha$ on a Syntex automatic diffractometer. A simple procedure has been developed whereby any least-squares program utilizing linear constraints of the form $\Sigma_i b_i a_{ij} = c_j$ (where a_{ij} is any variable, and b_i and c_j are constants) may be used to refine the site-populations of any number of cation species distributed over any number of non-equivalent sites with complete bulk chemical constraints, provided the differences in species scattering powers are large enough to be resolved by X-rays. This procedure has been used to provide complete site-populations for all cation sites in this structure. Fe^{2+} and Fe^{3+} site-populations were assigned from peak intensity ratios obtained by least-squares refinement of Mössbauer spectra at 273 and 77°K, and the distribution of Mg, Mn and Zn over the three non-equivalent octahedral sites was refined using bulk chemical constraints from the mineral analysis.

Zinc cummingtonite is isostructural with other C-centered cummingtonites, and bond-valence considerations show that the $M(4)$ site must be considered as eight-coordinated in this series, rather than six- or four-coordinated as has been proposed elsewhere.

Key sentence: Complete structural refinement of an amphibole using conventional and Mössbauer derived chemical constraints.

Barium Chloride Silicate with an Open Framework Crystal Structure: Verplanckite

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Verplanckite is one of the few examples of a new series of compounds which can be called barium chloride silicates and which have a porous open framework. Because of the porous open framework verplanckite is a likely candidate for having zeolitic properties. It is hexagonal, space group $P6/mmm$, with $a = 16.40(1)$, $c = 7.200(4)$ Å. The general formula for the contents of the unit cell, deduced from an electron microprobe analysis and from the structural analysis, is $[(Mn,Ti,Fe)_6(OH,O)_2Si_{12}O_{36}]Ba_{12}Cl_9\{(OH,H_2O)_7\}$. The final R is 0.102 for 386 F(obs) collected on a diffractometer. The structure consists of a three dimensional framework composed of four-membered rings of silicate tetrahedra and of triple units of square pyramidal coordination polyhedra which are randomly occupied by Mn, Ti, or Fe. Each triple unit and the adjoining silicate tetrahedra can be visualized as forming a slab of triangular cross-section parallel to the *c*-axis. These triangular slabs are arranged in chinese-checkerboard fashion thus leaving a wide void of hexagonal cross-section between them. This void which extends parallel to the *c*-axis is the most striking feature of this framework structure. The walls of the hexagonal void are lined with Ba atoms which are coordinated by the silicate oxygen atoms and by the Cl atoms located in the void. The effective diameter of the void is 7.2 Å. Part of OH and H_2O included in the general formula must be assumed to occupy the void either statistically over many positions with very small occupancy factors, or freely floating through the framework. A large degree of disorder is also evident in the framework part of the structure. Similar structures are $[(Ca,Mn,Ti)_4(OH,O)_4Si_8O_{24}]Ba_{10}Cl_8(H_2O)_4$, muirite[1], and the synthetic compound $[(Si,Al)_8O_{16}]Ba_3Cl_2(OH,Cl)$.[2]

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[1] Khan and Baur (1971) *Science,* **173,** 916.

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Crystallography of the Heating Products of Gaylussite and Pirssonite

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The double carbonate minerals gaylussite (G), $Na_2Ca(CO_3)_2 \cdot 5H_2O$, and pirssonite (P), $Na_2Ca(CO_3)_2 \cdot 2H_2O$, have been studied with the Guinier-Lenne heating powder camera, in air over a range of 20°–650°C, using Cu$K\alpha$ radiation. G transforms at 98°C (±5°) and P at 156°C to a poorly crystallized, anhydrous double carbonate phase (E), for which 13 out of 14 diffuse lines are indexed satisfactorily on a hexagonal unit cell that has (at 100°C) $a = 10.17(1)$ and $c = 6.58(1)$ Å. E transforms sluggishly (250°–310°C) to a well crystallized double carbonate phase (α–N) which passes through two displacive transitions, at 384°C to β–N, and at 433°C to γ–N. The N transitions are reversible and α–N persists to room temperature. γ–N gives 16 lines which index completely, as shown by Billhardt (1969) in a study of synthetic $Na_2Ca(CO_3)_2$, on a hexagonal unit cell with $a = 5.079(1)$ and $c = 12.755(3)$ Å (450°C). Billhardt also observed the transitions to β–N and α–N but erroneously assumed progressively larger hexagonal unit cells for these phases. β–N is orthorhombic, and 24 out of 27 lines are indexed on a *C*-centered unit cell with $a = 5.034(1)$, $b = 8.865(2)$ and $c = 12.644(3)$ Å (400°C). α–N is also orthorhombic, and has a structure based on a *C*-centered subcell with $a = 5.016(1)$, $b = 8.746(1)$ and $c = 12.234(2)$ Å (25°C). Natural crystals near α–N, the mineral nyerereite, give complex Buerger precession patterns resulting from multiple twinning of the pseudohexagonal lattice, plus a set of satellite reflections which can be indexed according to $h \pm \delta, k, l$ where hkl corresponds to the subcell reflections and $\delta = 0.38$. The satellites presumably represent an ordering of Na and Ca ions with a period that is not rational with the CO_3 packing framework, quite like the situation in the plagioclase feldspars. Nyerereite is found in the unusual "natrocarbonatite lavas" of Oldoinyo Lengai, Tanzania; natural gaylussite, pirssonite, and phase E (pseudomorphous after G and P) were collected at Lake Magadi, Kenya, and Green River, Wyoming.

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Symmetry and Twinning of Phillipsite and Harmotome[1]

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Phillipsite $Ca(K_{1-x}Na_x)Si_5Al_3O_{16}\cdot 6H_2O$ and harmotome $BaSi_6Al_2O_{16}\cdot 6H_2O$, which form complete solid solutions, should be isostructural. Yet the structure of phillipsite was reported as orthorhombic (Steinfink, 1962) and that of harmotome as monoclinic (Sadanaga *et al*, 1961). The resulting confusion is well illustrated by the page heading "Phillipsite Harmotome, monoclinic (or orthorhombic)" found in Deer, Howie, and Zussman (Vol. 4, 1963, p. 386). Our specimens come from a new locality, Cupra Mine[2], Stratford Centre, Quebec. Electron-probe analysis gives the formula

$$Ba_2(\square_{1.31}K_{0.40}Ba_{0.22}Na_{0.06}Sr_{0.01})\cdot(Si_{11.08}Al_{4.92})O_{32}\cdot 8H_2O.$$

$D_m = 2.38 g/cm^3$. All the specimens are the familiar twins [2] with 90°-cruciform cross-section. A fragment of one of the arms [1] of the cross gave orthorhombic diffraction symmetry ($a' = 9.822$, $b = 14.134$, $c'' = 14.217$Å, $B^{**}b$), in agreement with Steinfink's findings, but proved monoclinic and twinned on the optical analyzer. An optically homogeneous fragment, hand-picked under the polarizing microscope, turned out to be monocrystalline. Its X-ray patterns, from which the pseudo-orthorhombic symmetry of intensities has disappeared, yield Laue class $2/m$ and space group $P2_1$ (pyroelectric). Our reduced cell ($a = 8.640(2)$, $b = 14.134(4)$, $c = 8.640(2)$Å, $\beta = 110°43'$; $D_x = 2.37 g/cm^3$), which confirmed the identification, can be derived from the "orthorhombic" cell by matrix $\frac{1}{2}0\bar{\frac{1}{2}}/010/\frac{1}{2}0\frac{1}{2}$ and from monoclinic cell $a'bc'$ with $\beta \sim 125°$ (in the literature since 1846) by $001/010/\bar{1}0\bar{1}$. The first fragment was a twin of the known morvenite type [1], with twin planes $(10\bar{1})$ and (101), index 1, obliquity ~ 0, and twin symmetry $2'/m'\ 2/m\ 2'/m'$, presumably superimposed on twinning by hemihedry $(2/m')$. The fact that 723 reflections, obtained from such a twin mistaken for a single crystal, could lead to a plausible orthorhombic crystal structure, with $R = 0.14$, is cause for concern. A pseudo-cubic 8-fold cell predicts another well-known twin [3]. Figures[3] modified after G. Friedel (1926).

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[1] Supported by the National Research Council of Canada.

[2] Published with permission of Sullivan Mining Group.

[3] The figures, referred to by numbers between brackets, can be found in *Amer. Crystallogr. Assoc. Progr. Abstr., Ser. 2,* **1,** 168 (1973).

Structure and Properties of Super Ionic Conductors: Neutron Diffraction Investigation of Relation of Ion Transport to Structure of β''-Alumina[1]

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β''-alumina is a sodium aluminate that has the highest room temperature conductivity for sodium ions of any presently identified ionic solid. A three-dimensional neutron diffraction analysis has been carried out (1) to establish the composition and stoichiometry of the phase, (2) to learn why magnesium stabilizes the rhombohedral β'' structure, and (3) to obtain structural and thermal parameters to elucidate the mechanism of ion transport. Position, occupation, and thermal parameters have been refined by least squares to $R(F^2) = 4.4$ percent and the location of magnesium atoms in the structure established by difference Fourier sections. β'' crystallizes in $R\bar{3}m$ with $a = 5.623$ Å, $c = 33.591$ Å, $Z = 3$. The structure is built of spinel-like blocks joined by loosely packed planes of sodium and oxygen atoms. The composition

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of the crystal, determined completely from the neutron data, is $Na_{4.7}Al_{30.4}Mg_{2.6}O_{51.0}$. Magnesium was found to substitute selectively for aluminum in one set of four crystallographic cation sites in the spinel block. This site is tetrahedrally coordinated and characterized by abnormally short cation-oxygen distances in β-alumina which does not contain magnesium. Stabilization of β'' is probably due to reduction of local strain at this site since the exchange of magnesium for aluminum is accompanied by an increase in the interatomic distance toward normal ionic values. Electric current in β'' is carried by two dimensional diffusion of sodium between two sets of partially occupied sites lying approximately in a plane between adjacent spinel blocks. The sodium thermal parameters are anomalously large and anisotropic. Fourier sections indicate the thermal vibrations may be strongly anharmonic, even at room temperature.

A Lunar Pigeonite: Crystal Structure of Primitive-Cell Domains

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Least-squares refinements of a lunar pigeonite, $Ca_{0.06}Fe_{0.26}Mg_{0.68}SiO_3$, from a rock 15476 have been carried out separately for data set 1 [all reflections] and data set 2 [b-type ($h + k =$ odd) reflections]. The results from the data set 2 are considered to represent the structure of domains, whereas those from the data set 1 give an average structure of domains and boundary regions (Clark *et al*, 1971). Employing a constant-precision data collection procedure (Finger, 1973), more than 700 above-minimum ($I_o > 2\sigma_F$) b-reflections were collected and used for anisotropic temperature factor refinement. The refinement of the data set 2 shows: (1) a lower residual index [R (wt.) = 3.2 percent for 710 observed reflections] than that for data set 1 [R (wt.) = 4.2 percent for 1532 observed reflections]; (2) a slightly smaller $M2$ polyhedron (ave. $M2$–O = 2.203 Å), indicating essentially no Ca in the site, than that for data set 1 (ave. $M2$–O = 2.216 Å); and (3) smaller thermal vibration ellipsoids than the corresponding ellipsoids for data set 1. About 87 percent of the crystal, estimated from refined scale factors, contributes to b-reflections and thus is considered to be the domains having $P2_1/c$ symmetry. The Fe–Mg distribution is found highly ordered (K_D = Fe ($M1$)·Mg ($M2$)/[Fe ($M2$)·Mg ($M1$)] = .072 for data set 1 and .006 for data set 2). Existence of augite exsolution was not observed on X-ray precession photographs. The b-reflections are significantly more diffuse than the a-reflections ($h + k =$ even).

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The Crystal Structure of $CaCO_3$(II), A Metastable High Pressure Phase of Calcium Carbonate[1]

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The crystal structure of $CaCO_3$(II), metastable high pressure phase of calcium carbonate, has been investigated. *In situ* intensity measurements were carried out using a new miniature gasketed diamond anvil pressure cell in which the sample crystal is immersed in a hydrostatic medium. The pressure cell is mounted on a standard eucentric goniometer which may be attached interchangeably to various single crystal diffraction devices. The principal advantage of this new cell is its capability of combining single crystal counting techniques with the precession method in X-ray studies at high pressure.

Calcium carbonate which crystallizes in the calcite structure at atmospheric pressure and room temperature transforms to $CaCO_3$(II) at 15 kbar and room temperature. The transformation can be detected visually under the polarizing microscope by a Becke line which moves across the face of a cleavage rhomb. The single crystal state of the sample is preserved in the calcite-$CaCO_3$(II) phase transformation. The unit cell of $CaCO_3$(II) is monoclinic, and the systematic absences are consistent with space group symmetry $P2_1/c$. There are four molecules per

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[1] Research supported by the National Science Foundation.

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unit cell with all atoms in general positions 4(*e*). The crystal lattice parameters are $a = 6.334 \pm 0.020$, $b = 4.948 \pm 0.015$, $c = 8.033 \pm 0.025$ Å, and $\beta = 107.9 \pm 1.0°$.

The intensities of 115 independent reflections (164 total reflections) were collected and used in the refinement of the positional and thermal parameters. A least squares residual, $R = 10.6$ percent, was obtained in the final cycle of refinement. The $CaCO_3$ (II) crystal structure closely resembles calcite. The transition is displacive in nature and involves both the rotation of carbonate groups by 12° and a small displacement of adjacent planes of calcium atoms in opposite directions parallel to the calcite $(1\ 0\ \bar{1}\ 4)$ crystallographic plane. In this model there are five atoms in the asymmetric unit. The average bond and interatomic distances are C-O = 1.274, O-O = 2.20, and Ca-O = 3.335 Å.

The Crystal Structure of Argentian Pentlandite, $(Fe,Ni)_8AgS_8$

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A single crystal structure analysis of argentian pentlandite has been performed using multiple sets of 3-dimensional intensity data. The occurrence of this mineral at the Bird River deposits, Manitoba, is to be described shortly by Scott and Gasparrini.[1] Crystal data are: space group $Fm3m$, $a = 10.521(2)$ Å, $Z = 4$. The composition was determined (D. C. Harris, personal communication) using a electron probe to be $Fe_{4.83}Ni_{3.17}Ag_{0.99}S_{8.00}$.

Intensity data were collected on a Picker 4-circle diffractometer using Mo$K\alpha$ radiation and a graphite monochromator. Generalized Gaussian absorption corrections were applied and the atomic parameters refined using full-matrix least-squares procedures. Final R-values are 0.111 (all data) and 0.041 (obs. data only). The structure is similar to that of pentlandite $(Ni,Fe)_9S_8$[2] but with the octahedrally-coordinated 4*b* sites occupied almost exclusively by Ag atoms. The resulting interatomic distances are Ag–S = 2.679(2); (Fe,Ni)–S = 2.263(2), 2.243(2) and (Fe,Ni)–(Fe,Ni) = 2.670(2) Å.

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Special Search Indexes for the Powder Diffraction File—the Mineral Subfile[1]

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The Powder Diffraction File (PDF), published by the Joint Committee on Powder Diffraction Standards (JCPDS), currently contains more than 25,000 X-ray powder patterns of inorganic and organic compounds. Present indexes permit search of the inorganic or organic sections separately. New patterns are added to the PDF at a rate of 2000 per year, and the increasing number of patterns in the File has complicated its main function—identification by pattern matching. In order to facilitate identification, special subfiles based on specific categories of compounds are being evaluated.

The PDF contains some 2700 mineral patterns. A subcommittee of the JCPDS is developing a Mineral Subfile (MSF) using these patterns. The MSF is composed principally of an alphabetic list of mineral names, an alphabetic list of chemical formulae, and a three-entry Hanawalt search index under one cover and PDF card images under a second cover. The MSF will be available December 1973 and will include all patterns from PDF Sets 1–23 which are minerals or synthetic counterparts of minerals.

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[1] This work is sponsored by JCPDS, 1601 Park Lane, Swarthmore, Pennsylvania 19081.

In defining which compounds to include in the MSF, compendia by M. Fleischer, H. Strunz, and M. H. Hey, as well as the extensive mineral files of the U.S. Geological Survey, have been used. Names used correspond to the accepted North American usage, but common nonaccepted names are cross-listed with the accepted name. Thus a user can be directed to proper terminology. Phases not known in nature are excluded even though they may be known by mineral-like names.

The MSF is one of several subfiles being considered and was developed first because it is a definable subgroup with many potential users. The success of the MSF will help the JCPDS evaluate the usefulness of other subfiles.

Interatomic Distances in Sulfides: the Structure of Millerite (α-NiS)

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Many important sulfide minerals containing the ransition elements Fe, Co, and Ni exhibit unusual solid solution characteristics because of variable oxidation and spin states of these cations. As with oxides, interatomic distances are helpful in determining the nature of these states in given structures, but the situation is more complicated in sulfides, partly because of the greater importance of anion-anion repulsion and extensive metal-metal bonding. The availability of good structural data from as many different structures as possible is essential for understanding transition-metal sulfide chemistry but, until recently, not many reliable refinements have been published. The structure of millerite (α–NiS) appears to be unique in that Ni is in square-pyramidal coordination with S and takes only small amounts of Fe and Co in solid solution. The structure of a single crystal of millerite from Quebec, Canada, with $a = 9.619$ Å and $c = 3.150$ Å, space group $R3m$, $Z = 9$, and composition $Ni_{1.02}Fe_{0.02}S$ has been refined using intensity data collected on a four-circle diffractometer, resulting in an R factor of 0.014. The Ni and S atoms are in fivefold coordination (tetragonal pyramidal) with each other; the new interatomic distances are Ni–S = 2.261 Å, 2.261 Å (×2), and 2.383 Å (×2), Ni–Ni = 2.534 Å. The average Ni–S distance is consistent with a divalent Ni in fivefold coordination. It is suggested that the metal-metal bonding and the formation of a trinuclear metal cluster parallel to the basal plane are significant in stabilizing the millerite structure.

Crystallographic Modifications of Manganese Dioxide

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The current literature indicates considerable discrepancies in what is accepted as standard powder diffraction patterns for MnO_2 and its modifications. The Joint Committee on Powder Diffraction Standards (JCPDS) file lists over fifteen patterns for MnO_2, several of which are for natural minerals with undetermined purity. X-ray powder diffraction patterns have been calculated for α–MnO_2, β–MnO_2, and ramsdellite using the program of D. K. Smith (1967). These patterns are free of the effects due to particle size, poor crystallinity, impurities, and mixed phases, and represent ideal patterns against which experimental patterns can be compared.

Diffraction patterns have been calculated for γ–MnO_2 based on an ordered arrangement of ramsdellite and pyrolusite units distorted to fit into a single triclinic unit cell. Different cases distorting both the ramsdellite and pyrolusite and conforming to and violating octahedral coordination for the manganese were used. This over-simplified model approximates the more probable state of γ–MnO_2 as a random distribution of distorted pyrolusite in a ramsdellite matrix as suggested by de Wolff (1959). The calculated patterns account for the broad features of the published patterns for γ–MnO_2 while predicting some unobserved reflections which probably result from the over simplified model.

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Inorganic Structure Studies

The [Regular] Phosphate Tetrahedron is a Mythical Beast

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The shapes of 210 PO_4^{3-} tetrahedra were studied. Their dimensions are known accurately from published X-ray and neutron diffraction investigations: Results: (1) The site symmetry of the *P*-atoms was found in 85 percent of the cases to be 1. Other observed symmetries are *m*, 2, 3, 4, *mm*, and 222, while $\bar{4}3m$ was not found. (2) The deviations from ideal symmetry, $\bar{4}3m$, are pronounced. The distortions can be measured by defining for every PO_4^{3-} group three distortion indices: $DI(TO) = \sum|TO_i - TO_m|/4TO_m$, $DI(OTO) = \sum|OTO_i - OTO_m|/6OTO_m$, and $DI(OO) = \sum|OO_i - OO_m|/6OO_m$, where TO is the distance P–O, OTO the angle O–P–O, OO the distance O–O, *m* is the mean, and *i* an individual value. The average distortion indices for all groups are: DI(TO) = 0.021, DI(OTO) = 0.028, DI(OO) = 0.012. This means that distortions are more pronounced in the P–O distances than in O–O and thus PO_4^{3-} can be viewed, to a first approximation, as a rigid regular arrangement of O-atoms, with the P-atoms displaced from their centroid. (3) The *mean* P–O distances of PO_4^{3-} vary from 1.506 to 1.572 Å. These variations are correlated with DI(TO) and with the average coordination number of the oxygen atoms. (4) The *individual* P–O distances are correlated with the bond strengths received by the individual oxygen atoms (Baur, 1970). (5) The individual O–P–O angles are strongly correlated with the average of the P–O distances on the sides of the angle, and slightly less strongly with the opposite O–O distance. The regression equation based on the whole sample—$\log(\sin \text{O–P–O}/2) = 0.166 - 1.37 \log(\text{P–O})$—can be used to predict individual angles in the phosphate groups (with a mean deviation of 1.8°). Since the individual bond lengths in turn can be predicted from the bond strengths (see 4), the complete shape of a near-tetrahedral PO_4^{3-} group can be calculated for any given bond strength distribution. The correlations are affected by the presence of shared edges in the phosphate groups and differ for various subpopulations of the sample (ortho-, di-, poly-, acid, or organic phosphates). A PO_4^{3-} group of ideal tetrahedral shape does not seem to exist in crystalline solids. However, the observed distorted shapes can be rationalized on the basis of the bond strength distributions to the individual O-atoms. The calculated shapes can be used as input to computer simulation of crystal structures.

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Empirical Relationships for Predicting the Detailed Stereochemistry of Polysulfate and Hydrogen Sulfate Ions

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The observed angles in polysulfate and hydrogen sulfate ions vary from 97°–128°. These angles can be predicted to within 1.5° using two empirical relations, one depending on the bond lengths, the other depending on the configuration around the bridging oxygen atom. The former can be calculated equally well by assuming that the O_4 tetrahedron remains regular and the sulfur atom goes off center, or by a linear relation between angle and bond strength (Brown and Shannon, 1973). The latter effect consists of a displacement of all the oxygen atoms towards the pseudo $\bar{4}$ axis of the tetrahedron that lies in the plane of the two bridging oxygen bonds. In the case of the $S_2O_7^{2-}$ ion, these relationships, together with the bond strength–bond length relationships of Brown and Shannon, allow an *a priori* prediction of the bond lengths and angles of the ion to within 0.013 Å and 0.8°.

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Symmetry and Its Applications

Combinatorial Structures: Nature as a Degenerate Roulette Wheel[1]

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Combinatorial topology, network topology, graph theory, and bracelet theory provide rich ore for the prospector in structure systematics and structure type retrieval. Backed up by myriads of known crystal structures of oxysalts (including 24 solved in this laboratory within the past year), the following problems have been tackled:

1. Systematics of X_2TO_4 structures (alkali sulfates, calcium nesosilicates, *etc*). By utilizing a simple combinatorial technique, the glaserite, room temperature K_2SO_4, bredigite, larnite, and merwinite structures have been rationalized. Some 150 compounds belong to this group.
2. The $1/\infty$ $[M\sigma_5]$ octahedral corner-chain structures. Many basic phosphates and sulfates of Al^{3+} and Fe^{3+} belong here (over 50 structure types). All possible chain configurations and their lattices have been worked out. Several unknown structures were predicted this way, and subsequently retrieved by structure analysis.
3. Octahedral edge-sharing clusters. A device utilizing graph theory provides rational classifications of all $M_r\sigma_s$ octahedral edge-sharing clusters in three-dimensions. Topological and geometrical isomers can be retrieved. The point symmetries, stoichiometries, and electrostatic valence balances for the 144 "first enclosure" clusters are now known and provide a basis for retrieving the iso- and heteropolyanion and polycation clusters.

Is Nature a roulette wheel? Yes, but She selects those arrangements among the myriad isomers with highest *maximal* point symmetry (hence, highest degeneracy).

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Graphically Assisted Presentations

The Crystal Structure of Haycockite, $Cu_4Fe_5S_8$

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Haycockite (hc) is a recently characterized Cu-Fe-S mineral (Cabri and Hall, 1972) that is closely related to chalcopyrite (cp), $CuFeS_2$. A single-crystal structure analysis of haycockite has been performed. Crystal data are: orthorhombic, probable space group $P222$, $a = 10.705(5)$, $b = 10.734(5)$, $c = 31.63(2)$ Å, $Z = 12$.

The intensity data were collected on a Picker 4-circle diffractometer using Mo$K\alpha$ data and a graphite monochromator. The super-lattice nature of the large cell results in a very low proportion of measurable intensities at high angles. To facilitate practical data collection, maximum 2θ values were limited according to the class of reflection. In this way 2890 reflections were measured, of which 801 could be considered observed to the 10 percent significance level, *i.e.*, $I_{\text{net}} > 1.65\ (I)$. The presence of twinning (twin plane $= \{103\}$) required that the data be adjusted for the two major twin components which represented 50 percent and 45 percent of the crystal. Generalized Gaussian absorption corrections were applied. For the full-matrix least-squares refinement unmeasured reflections, out to a 2θ limit of 50°, were given a random value between specified limits. The total data set then consisted of 4126 reflections.

The basic structure may be described as being 12 chalcopyrite-like cells with $a_{\text{hc}} \simeq b_{\text{hc}} \simeq 2a_{\text{cp}}$ and $c_{\text{hc}} \simeq 3c_{\text{cp}}$, and additional metals at interstitial sites. The locations of these interstitial sites, and the assignment of metal types, is complicated by a space group ambiguity and a poor data-to-variable ratio. The atomic parameters determined, although consistent with the data, cannot be considered unequivocal. To assist in determining these parameters a reduced cell, with all cell dimensions halved, was used to refine a low-resolution structural model to an R of 0.17 (all data).

References

CABRI, L. J., AND S. R. HALL (1972) *Am. Mineral.* **57,** 689–708.