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SELECTED ABSTRACTS

Semseyite ($Pb_9Sb_8S_{21}$) and the Crystal Chemistry of the Plagionite Group, $Pb_{3+2n}Sb_8S_{15+2n}$[1]

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The plagionite group consists of four minerals, fülöppite ($Pb_3Sb_8S_{15}$), plagionite ($Pb_5Sb_8S_{17}$), heteromorphite ($Pb_7Sb_8S_{19}$), and semseyite ($Pb_9Sb_8S_{21}$), which form an homologous series. Two lattice constants remain essentially invariant throughout the series, while the third increases uniformly as the Pb content increases.

Semseyite is monoclinic, space group $C2/c$ with $a = 13.603(3)$, $b = 11.936(8)$, $c = 24.435(7)$ Å, $\beta = 106.047(10)°$, $D_m = 6.03$ and $D_x = 6.12$ g cm^{-3} for $Z = 4$. The structure was solved with the symbolic addition procedure and refined by least squares techniques to $R = 10.0$ percent for 1827 observable reflections. The asymmetric unit contains 20 atoms. Two Pb atoms are coordinated by six S atoms, one Pb atom by five S atoms, and one Pb atom by seven S atoms in octahedral-like coordination. A fifth Pb atom has an irregular 8-fold coordination which may be described as a square antiprism. Three of the four independent Sb atoms have square pyramidal coordination; a fourth forms a trigonal, pyramidal group. Of the eleven independent S atoms, five have octahedral-like configuration, five tetrahedral, and one square pyramidal. The structure is composed of slabs of PbS-like structure which run parallel to (112) and $(\bar{1}1\bar{2})$ alternately along c and extend indefinitely along $[\bar{1}10]$ and [110] respectively.

From the study of the structures of plagionite and semseyite, a model is created which could predict the structures of fülöppite and heteromorphite in projection. The model involves two types of addition of Pb at a previously Sb site. The interaxial angle β is correctly predicted as well as the change in $c \sin \beta$ and the density.

Zeolite "Rho" and the Sigma Transformation[2]

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A tetrahedral framework model suggested as a possible zeolite framework structure by W. Meier in 1967[5] is constructed from "*A* cages" (the larger cages in the Linde *A* structure) by linking such cages together with oxygen bridges at the "8-rings," much as Linde *A* and faujasite frameworks are constructed by linking truncated octahedra ("sodalite units") together at 4-rings and 6-rings respectively. The resulting body-centered cubic structure has two interpenetrating three-dimensional systems of *A* cages interconnected with 8–8 double rings, but the two systems do not interconnect by anything larger than a 6-ring. Synthetic zeolite "RHO", possessing this framework structure, was obtained by replacing part of the sodium in a conventional faujasite synthesis by cesium. For the "as crystallized" zeolite,

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[1] Research sponsored by the National Science Foundation.

[2] Work done at Esso Research Laboratories or sponsored by ERL at MIT and OSU.

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[5] 1967 London Zeolite Conference, *Soc. Chem. Ind.*, p. 18.

$Cs_3Na_9Al_{12}Si_{36}O_{96} \cdot xH_2O$, $a_0 = 14.6$ Å; for the "hydrogen form" (ammonium exchanged and calcined), $H_{12}Al_{12}Si_{36}O_{96}$, $a_0 = 15.0$ Å. Refinement on $Im3m$ with visual intensity data from 50 powder lines gave $R_1 = 0.12$ and satisfactory distances, but there is evidence that the true symmetry is lower. The RHO structure is the end member of a series of twelve real and hypothetical zeolite framework structures starting from the non-zeolite sodalite structure, derived with repetitions of what we call the SIGMA transformation. This transformation takes place on planes or other suitable surfaces containing only (Si,Al) atoms, which must have two oxygen bridges lying in and two lying out of the surface, and constitutes "fission" of the (Si,Al) atom and creation of a new oxygen bridge connecting the pair generated. The transformation also relates sodalite to faujasite, and through offretite to chabazite, and relates cancrinite to gmelinite, cristobalite to gismondine, and tridymite to paracelsian to phillipsite, in most cases with new hypothetical structures along the way.

Chalcanthite Morphology[6]

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P	C
$*b\ 010$	$c\ 001$
$*a\ 100$	$**m\ 110$
$c\ 001$	$*b\ 020$
$**m\ 110$	$**\omega\ \bar{1}\bar{1}1$
$q\ 0\bar{1}1$	$**\underline{M}\ 1\bar{1}0$
$k\ 011$	$o\ \bar{1}11$
$\phi\ \bar{1}01$	$*t\ 0\bar{2}1$
$**\omega\ \bar{1}\bar{1}1$	$*\tau\ 021$
$**M\ 1\bar{1}0$	$p\ 111$
$\lambda\ 120$	$1\bar{1}1$
$o\ \bar{1}11$	$*\pi\ 130$
$*t\ 0\bar{2}1$	$\zeta\ \bar{1}\bar{3}1$
$\xi\ \bar{1}\bar{2}1$	$x\ \bar{1}\bar{1}2$
$*\tau\ 021$	$\rho\ \bar{2}01$
101	$*a\ 200$
$\ell\ 1\bar{2}0$	$\bar{2}\bar{2}1$
$p\ 111$	$1\bar{3}0$
$1\bar{1}1$	$\bar{1}12$
$*\pi\ 130$	$\psi\ 131$
$\sigma\ \bar{1}21$	$q\ 0\bar{2}2$
$\zeta\ \bar{1}\bar{3}1$	$\bar{1}31$
$0\bar{3}1$	$0\bar{4}1$
$e\ 121$	$\bar{1}\bar{3}2$
$\bar{2}\bar{1}1$	$k\ 022$
$\nu\ 210$	$1\bar{3}1$
$x\ \bar{1}\bar{1}2$	$\phi\ \bar{2}02$

Synthetic crystals of chalcanthite, $CuSO_4 \cdot 5H_2O$, prepared by Mr. Marc Trudeau, gave Mr. Eric Hoffman (private communication) the following cell dimensions, refined from diffractometer data: $a:b:c = 6.1094:10.7008:5.9576 = 0.57093:1:0.55674$, α 97°39′, β 107°18′, γ 77°20′, confirming values obtained by Ievinsh and Ozol (1954), also on synthetic material, *viz* 6.1130:10.7121:5.9576 = 0.57066:1:0.55616, 97°38′, 107°18′, 77°26′. The P lattice so defined is the structural lattice (Beevers and Lipson, 1934; $P\bar{1}$; $Z = 2$), but it does not express the morphology according to the law of Bravais, as can be seen from list P, which gives the forms in order of decreasing interplanar distances $d(HKL)$, H,K,L coprime integers. The Dana letters designate observed chalcanthite forms; asterisks indicate relative predominance (frequency and size). The C centering yields a better morphological lattice: list C, where H,K,L are the smallest integers that satisfy "$(H + K)$ even", brings out the habits, elongated [001] or tabular $(\bar{1}\bar{1}1)$, explains the predominance of m ω M, accounts for the facts that t is more common than q, τ than k, and π than λ. Some anomalies persist, however: c, a rather uncommon form, comes first; b is too high; a is possibly too low. The law of Bravais does not account for all the details of morphology, and chalcanthite is another example of G. Friedel's *double période*. Albeit the C lattice tells us that sites $\cdot 000 \cdot$ and $\cdot \frac{1}{2}\frac{1}{2}0 \cdot$, though crystallographically distinct, should be equivalent from the bond-structure point of view and be the termini of Hartman-Perdok's bond-chain periods. Indeed they are occupied by the Cu atoms (Beevers and Lipson). Bond-valence summations essentially check the Beevers and Lipson hydrogen-bond assignment and indicate strong bond chains along [001], $\frac{1}{2}$ $[\bar{1}10]$, [101], [011], no two of which lie in $c(001)$, whose rarity despite top rank is thus explained. The structure is now being refined by Mr. Hoffman at McGill University.

Prediction of the Trioctahedral Mica Structure at High Temperature[7]

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A computer simulation of structural changes due to thermal expansion of cation octahedra has been

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[7] Supported in part by the U. S. Atomic Energy Commission.

carried out by employing an improved geometrical model on the structure of trioctahedral mica (Takeda, 1971). The input data are cell dimensions of fluorphlogopite, $KMg_3(Si_3Al)O_{10}F_2$ (crystal supplied by M. Ross), measured over the temperature interval 24–800°C, the 2.075 Å Mg–O and the 1.649 Å (Si_3Al)–O separations as well as the 0.984 ratio of the basal to lateral oxygen separations of the tetrahedra determined by our 24°C data refinement, and the 1.21×10^{-5} mean thermal expansion coefficient (MTEC) of the $M(1,3)$–O separation determined in tremolite (Sueno *et al*, 1973).

The results show that (1) the angle α, the rotation of the tetrahedral groups around c^* (Takeda and Donnay, 1966), decreases linearly from 6.5° at 24° to 1.8° at 900°C and may become 0° above 1200°C, (2) the MTEC of the K–O separation (5×10^{-5}) is much larger than that of the Mg–O separation and (3) the Mg octahedra begins to more rapidly elongate perpendicular to the layer at about 400°C. At this temperature, the linear thermal expansivities along the cell directions change; between 24–350°C, values ($\times 10^5$) along a, b, and c are 0.98, 0.93 and 1.73, respectively, while between 400–800°C, values are 0.62, 0.48, and 1.70, respectively. The above results are in good agreement with the refined structures using intensity data measured at 24° and 700°C. The observed structural parameters are:

	Si,Al-O (Å)	Mg-O (Å)	K-O (in)	α (°)	Ψ(Mg) (°)	Ψ(K) (°)
24°C	1.649	2.075	2.990	6.4	58.3	56.1
700°C	1.645	2.092	3.083	4.0	57.7	56.1

The angle ψ defines the flattening of the octahedra based on O–O separations.

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Crystal Structure of Ferrous Orthophosphate, $Fe_3(PO_4)_2$[8]

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$Fe_3(PO_4)_2$ crystallizes in the space group $P2_1/c$ with $a = 8.881(2)$, $b = 11.169(2)$, $c = 6.145(1)$ Å, $\beta = 99.36(3)°$ and ρ(X-ray) = 3.948 g/cm³ for $Z = 4$. A full three-dimensional least-squares refinement was made to $R = 0.048$ using 1766 independent reflections (counter data) with a data-to-parameter ratio of 14.8. $Fe_3(PO_4)_2$ is isotypic with the mineral graftonite, $(Fe,Mn,Ca)_3(PO_4)_2$ [C. Calvo, *Am. Mineral.* **53,** 742 (1968)], with ferrous ions in three distinct coordination polyhedra. The interesting differences in the metal ion coordination polyhedra in the several compounds crystallizing in this structure type will be discussed.

The Crystal Structure of Paratacamite—$Cu_2(OH)_3Cl$

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A single crystal diffractometer study on material from Sierra Gorda, Chile, has confirmed that paratacamite has a variant of the β-$Co_2(OH)_3Cl$ structure. The substructure, with $a = 6.827(3)$ Å $c = 14.041(6)$ Å, space group $R\bar{3}m$ (D^5_{3d}), $Z = 6$, has been refined to a conventional R value of 0.023 assuming disordered O atoms. The Cu atoms in the $9e$ position are coordinated to four O at 1.95 Å to 2.00 Å and two Cl at 2.78 Å, consistent with one of the two Cu coordinations in atacamite. Cu atoms in the $3b$ position are coordinated to four O at 2.02 Å and two O at 2.29 Å. However, attempts to rationalize the weakly developed superstructure by ordered arrangements of the O atoms have been unsuccessful. The O–Cu–O and O–Cu–Cl bond angles

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[8] Supported by the University of Connecticut Research Foundation.

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associated with shared coordination edges are all significantly less than 90°, suggesting that the filled t_{2g} orbitals on the Cu atoms projecting toward the shared edges do not screen the atomic charges very effectively in these directions. The approximate positions of the H atoms, as indicated by difference synthesis, suggest O–H···Cl associations, three hydrogen bonds being directed to each Cl. Analogous hydrogen bonding schemes are predicted for the other two $Cu_2(OH)_3Cl$ polymorphs, atacamite and botallackite.

Stereochemistry of Copper (II) and Iodine (V) in Bellingerite, $Cu_3(IO_3)_6 \cdot 2H_2O$

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Bellingerite, $Cu_3(IO_3)_6 \cdot 2H_2O$ is triclinic, space group $P\bar{1}$, with $a = 7.256(2)$, $b = 7.950(2)$, $c = 7.856(2)$ Å, $\alpha = 105.10(2)°$, $\beta = 92.95(2)°$ and $\gamma = 96.95(2)°$, $Z = 1$. The crystal structure was determined by the heavy atom method and refined by the anisotropic least squares to an R-factor of 0.038 for 3156 reflections. The standard error in Cu–O and I–O bond lengths is ±0.005 Å and O–Cu–O and O–I–O angles ±0.02°. The bellingerite structure is a three dimensional framework consisting of corner-sharing tetragonally distorted Cu(1) O_6-octahedron, $[Cu(2)_2O_8(H_2O)_2]$ octahedral dimer, and three independent pyramidal IO_3 groups. Cu(1) at a symmetry center is bonded to 4 oxygens at 1.936(×2) and 1.967 Å(×2) approximately in a square plane, while 2 oxygens at 2.528 Å(×2) complete the octahedron. Cu(2) has 3 oxygens at 1.942, 1.946, and 1.973 Å and a H_2O molecule at 1.950 Å approximately in a square plane, while 1 oxygen at 2.456 Å and a H_2O molecule at 2.483 Å complete the distorted octahedron. Two Cu(2)-octahedra form a dimer by sharing an edge. The pyramidal $I(1)O_3$ group (point symmetry $3m$) has 3 oxygen atoms at 1.815, 1.823, and 1.824 Å from the iodine atoms with O–I–O angles 96.0, 95.7, and 97.3°; I(1) is weakly bonded to three further oxygens at 2.755, 2.676, and 2.796 Å, the $I(1)O_6$ group being a distorted octahedron. Both $I(2)O_3$ and $I(3)O_3$ pyramidal groups approximate point symmetry m. $I(2)$ is bonded to 3 oxygens at 1.817, 1.815, and 1.825 Å, the O–I–O angles being 99.1, 99.4, and 95.1°; four further oxygens form weak bonds at 2.737, 2.957, 3.050, and 3.172 Å. The I(3) is bonded to 3 oxygens at 1.801, 1.823 and 1.795 Å with O–I–O angles 96.7°, 101.0°, and 101.1°. I(3) is weakly bonded to 2 further oxygens at 2.771 and 2.873 Å. The $I(3)O_5$ polyhedron is a distorted trigonal bipyramid. This is the first known occurrence of 5-fold coordination for I(V).

Electronmicroscopy as a Tool in Geology

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The submicroscopic structure of minerals—intermediate between the atomic structure and characteristics observed in the optical microscope—is analyzed with the transmission electron microscope (TEM). Description of domains, lamellae, and dislocations provide important geological information which cannot be obtained with standard mineralogic and geochemical methods. Of main concern is the history of rocks after the initial crystallization of the minerals and determination of parameters such as rate of cooling in igneous rocks, time and temperature of annealing, and temperature and strain-rate during deformation in metamorphic rocks. Since most electron-microscopists have their training in metallurgy, a team of geologists (formulating geological questions and selecting specimens), crystallographers (aware of structural implications), and electron microscopists has been most successful.

Some geological aspects of TEM are illustrated using the Bergell Alps as an example. A principal problem is to separate metamorphic events and to determine whether deformation preceded or followed recrystallization. Wollastonite, $CaSiO_3$, contains stacking faults parallel to (100), producing a disordered superstructure. This proves that the contact metamorphic mineral has been deformed at a late stage. A TEM study of quartz SiO_2 (with P. Phakey) revealed a gradient in the dislocation structure indicating that quartz has partially recrystallized after deformation. In unmetamorphic quartzites dislocation density is high with tangles and heterogeneous distribution. In greenschist terrain large grains are similar, but in addition small crystallites (0.25–2.0 μm) point to a low-temperature crystallization event. Quartz mylonites in the high-metamorphic zone show good grain-boundaries, nearly in equilibrium, ample dislocation interaction, and networks indicating recovery. Similar results were observed in calcite, $CaCO_3$ (with D. Barber). So far the analysis was restricted to experimentally deformed specimens, but will later be applied to natural rocks of the same Triassic sequence as the quartzites. Anorthites, $CaAl_2Si_2O_8$, in the high-metamorphic calcsilicate rocks, display *c*-antiphase domain boundaries. As shown by a study instigated by this observation (with W. Müller) it indicates that the rock crystallized at high temperature (900°) and cooled slowly. Another candidate for an interesting microstructure is staurolite. A superstructure is typical of high-grade crystals and absent in low grade.

Transmission Electron Microscopy of Deformation Structures in Minerals

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The substructures of deformed mineral crystals and rocks have been studied by conventional and high-voltage transmission electron microscopy in several laboratories over the last decade. The minerals most extensively analyzed are quartz [SiO_2], olivine [$(Mg,Fe)SiO_4$], and pyroxene [$(Mg,Fe,Ca)SiO_3$], all of which have been examined in naturally and experimentally deformed samples. The deformation mechanisms identified in minerals include slip by dislocation motion, mechanical twinning, recovery and related diffusional processes, and recrystallization. The behavior at high temperatures and slow strain-rates in both experimental and natural deformations is qualitatively similar to that observed in metals. At low temperatures and rapid strain-rates, notably in shock deformation, extensive glass production is observed in crystals of some minerals (*e.g.*, quartz), and there is evidence that dislocations do not play a role in the deformation process. Growth of high-pressure crystalline phases has also been observed in shocked materials. Application of these studies to geological problems will be discussed.

TEM of Lunar Minerals and Rocks

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The use of TEM in mineralogy and petrography appears to have been greatly expanded with the return of the Apollo 11 mission in late 1969 and the desire to obtain the maximum amount of information possible from the limited quantity of lunar samples. The versatility of TEM in providing useful geological as well as crystallographic information on diverse lunar problems has been impressive. These range from studies of phase transitions involving change of symmetry and/or composition, to studies of fossil particle tracks by diffraction contrast, to studies of the deformation induced by meteoritic impact, to studies of lithification mechanisms of lunar breccias. These various aspects of lunar electron microscopy will be reviewed in the presentation, with particular emphasis on problems of major crystallographic interest.

Aspects of High Resolution Electron Microscopy of Minerals[10]

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Structure images, obtained at critical operating conditions, of major silicate types show a close correspondence with structures calculated from single crystal X-ray data. Both physical and chemical effects are observed at the unit cell level.

Emphasis is placed on the chain silicates, and particularly the orthorhombic pyroxenes ($MSiO_3$) because they display a number of features that are evident only at high resolution. Both coherent and incoherent defects are common, especially in naturally or artifically strained samples. Microtwinning is the most abundant coherent defect; it occurs in all

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the specimens we have examined. We confirm that periodic microtwinning explains the polymorphic relation between orthorhombic and monoclinic enstatite ($MgSiO_3$). When relatively wide, such zones of microtwinning have been interpreted as simply being stacking faults. Using high resolution microscopy, it is becoming increasingly apparent that antiphase boundaries and domains are relatively common in pyroxenes as well as in other silicate types. Incoherent defects stabilize the ends of the twin planes, and can in some cases be observed to occur in *en echelon* series, stepping across (100) planes. Incipient partings are characterized by zones of strain localized along certain (100) planes. The development of and distinction between parting [$||$(100)] and cleavage [$||$(110)] is clearly evident.

An Electron Microscopy Study of Augite Exsolution Lamellae in Enstatite

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The composition, structure, and matrix-precipitate boundaries of narrow exsolution lamellae in enstatite, an orthopyroxene, are investigated using several transmission electron microscopy techniques. These lamellae, which are visible optically, are 0.25 μm wide and hundreds of microns long. Analytical TEM demonstrates that the lamellae are substantially richer in Ca and slightly richer in Cr than the matrix. Selected area diffraction patterns from the lamellae are consistent with the monoclinic space group $C2/c$. These compositional and structural results indicate that the lamellae are augite, a clinopyroxene. Bright-field microscopy shows that the matrix-lamellae interfaces are parallel to (100) and that the interfaces contain defects parallel to [010] at 500 Å intervals. In the weak-beam mode, the interface defects are determined to be pairs of edge dislocations spaced 100–200 Å apart. Direct lattice images of the (200) matrix planes, 9.2 Å, and (200) lamellae planes, 4.6 Å, at the interface reveal that a ledge extends between each dislocation pair. These ledges are one or two atomic steps of enstatite which jut into the augite phase. To remove the "salt-and-pepper" noise, the high resolution electron micrographs of direct lattice images are light-optically reconstructed and filtered. This process makes the examination of lattice fringes and, in particular, terminating lattice fringes substantially easier.

Observations on the Dislocation Substructures in a Hedenbergite from Nordmark, Sweden

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X-ray transmission topography (Lang technique) has revealed a variety of substructures in a crystal of hedenbergite, $Ca(Fe,Mg)(SiO_3)_2$ from Nordmark, Sweden. Using 0.1 mm thick sections cut parallel to (100), it is possible to image low angle boundaries and dislocations which may be interpreted through their contrast conditions.

The most obvious features exhibited by this crystal are the many subgrains which range in size from 0.2 to 5 mm^2. Some boundaries show variable constrast with minimum intensity observed with ($hk0$) type reflections.

Within the subgrains are sets of straight bands and a background showing a mottled appearance. One band, which is parallel to [010], shows maximum contrast in ($h0l$) reflections and minimum contrast in ($hk0$) reflections indicating Burgers vector of [001]. Other lines parallel to [010] are sharper and show the contrast indicating [010] Burgers vectors. The differences in behavior of these two sets is in qualitative agreement with that which would be predicted considering the elastic behavior (Alekssandrov *et al*, 1964) of $C2/c$ pyroxenes. This evidence shows that (100) is an active slip plane in these pyroxenes.

Reference

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Exsolution Phenomena in Feldspars: An Overview

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The first application of transmission electron microscopy to mineralogical problems was undertaken in 1962 at Cambridge University. The electron optical resolution and S.A.D. identification of two plagioclases An_0 and An_{25} as the lamellar exsolved components of peristerite, the iridescent feldspar of pegmatitic occurrence, led to an understanding of the iridescence as an interference phenomenon. Moonstone—cryptoperthitic exsolved albite and orthoclase—was likewise investigated by TEM, resulting in a visual confirmation of the prior careful X-ray work of F. Laves, J. V. Smith, and W. S. MacKenzie. Later studies of labradorite and its remarkable interference colors were undertaken by groups of investigators at Monash University and at the E.T.H. in Zürich, suggesting peristerite-like exsolution which has been directly proven only in the past year by EMMA analyses of individual alternating lamellae of $An_{\sim 40}$ and $An_{\sim 60}$ composition (Nissen *et al*, 1973). Recently H.-U. Nissen and G. L. Nord have described a third plagioclase "solvus" in the composition range $An_{\sim 67}$–$An_{\sim 90}$. A number of independent studies of spinodal decomposition and anti-phase phenomena have greatly increased both our understanding of and amazement at the enormous structural complexity of the chemically simple feldspars of the $KAlSi_3O_8$–$NaAlSi_3O_8$–$CaAl_2Si_2O_8$ ternary. [Excellent coverage of recent progress in TEM studies of feldspars may be found in *The Feldspars*, a book containing 32 major papers from a 1972 NATO Advanced Study Institute (W. S. MacKenzie and J. Zussman, Eds., Manchester University Press, 1974, 717 p.)].

Reference

NISSEN, H.-U., P. E. CHAMPNESS, G. CLIFF, G. W. LORIMER (1973) Chemical evidence for exsolution in a labradorite. *Nature Phys. Sci.* **245**, 135–137.

Transmission Electron Microscope Investigation of Ternary Feldspars

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A study is in progress of the exsolution and twinning of a number of ternary feldspars $Ab_xOr_yAn_z$ which occur as phenocrysts in lavas. Specimens with mole percent compositions $Ab_{80\pm2}Or_{\sim10}An_{\sim10}$ show exsolution lamellae approximately parallel to $(60\bar{1})$. Since this is the characteristic plane of exsolution in alkali feldspars, it implies that the exsolved phases differ essentially in the Na and K contents. This is observed even in a specimen with $y = 9.0$ and $z = 10.5$. In most specimens the exsolution is in the form of a quasi-sinusoidal lamellar-substructure with a period of about 200 Å. This type of substructure has been observed in a number of alkali and plagioclase feldspars and has been interpreted as spinodal decomposition. However, in specimens from one locality, the exsolution is in the form of thin lenticular regions of orthoclase in a twinned matrix of albite (cryptoperthite). Since these two types of exsolution substructure do not appear to correlate with the measured differences in composition, it must be assumed provisionally that the different exsolution substructures imply differences in cooling histories.

Albite and pericline twins are observed as well as planar features parallel to these twin composition planes. Examination of the diffraction contrast and associated diffraction patterns shows that these features do not exhibit the correct twin relationships. They are, therefore, interpreted tentatively as partially annealed-out twins. Specimens with compositions near $Ab_{70}Or_{25}An_5$ show the cryptoperthitic exsolution substructure. Albite and pericline twin superlattices are observed. The nature of the associated diffraction pattern depends upon the relative magnitudes of the superlattice period and the coherence area of the electron beam. Experimental work is in progress to determine the thermal conditions to produce the different exsolution and twin substructures for various compositions.

A TEM Study of Labradorite-Anorthite Intergrowths in Metamorphic Plagioclase Feldspars[11]

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A 100 kV TEM was used to study plagioclases from a sillimanite grade calc-silicate rock. Two-phase intergrowths present in labradorites (An_{65}) have lamellae widths of 1 micron. Electron microprobe

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analyses of one of the lamellar sets indicate a composition as calcic as An_{85}. Two directions of exsolution are present, one parallel to $(03\bar{1})$ and one parallel to an undetermined $(h0l)$ plane, possibly $(\bar{1}01)$ (Nord *et al,* 1973). Although electron diffraction patterns of the lamellar intergrowths show only one reciprocal lattice, tilting experiments in dark field show that two phases are present, each with a characteristic lattice geometry and with slightly different crystallographic orientations. The reciprocal lattice of the exsolved calcium-rich phase is that of transitional anorthite with type "a" and "b" reflections as well as weak, diffuse type "c" reflections. The labradorite host has diffraction symmetry similar to that of an intermediate plagioclase containing type "a" reflections and "e" and "f" satellites. Dark field observations using type "b" reflections of the calcic lamellae phase reveal the presence of "b" antiphase domains, while similar observations using "e" reflections of the labradorite host show strain contrast about a set of planar features oriented perpendicular to $\bar{s}$ (as defined by Bown and Gay, 1958). The features are parallel to planes having non-integral indices that approach $(01\bar{1})$ orientation when viewed on [100]. Growth of the calcic lamellae is related to these features.

References

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Factors Affecting the Symmetry of SAD Patterns from Micas

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SAD patterns of the same mica may display different symmetries. The major factors affecting these patterns are: specimen thickness, lattice properties of the crystal, and objective lens properties. The effect of the finite thickness of the crystals requires an exact evaluation of crystal shape transform. This has been done in a general form which is independent of any real or reciprocal cell parameters. The observed intensity variations of (hk) spots indicate that the focusing conditions of the objective lens may be critical for the symmetry of SAD patterns. As an inherent lattice property of micas, symmetry related (hk) spots may have different "excitation errors" and therefore they may not have equal intensities on SAD pattern. When the above factors are critically evaluated, the discrepancies between the 'apparent' SAD symmetry and the real crystal symmetry may be explained.

Deformation Mechanisms in Peridotites: A Review of Transmission Electron Microscopy Studies

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The near simultaneity of the plate-tectonic revolution in geology and the introduction of the tool of transmission electron microscopy to the science has resulted in a concentrated effort by several laboratories to characterize the deformation substructure of peridotites to better understand upper mantle processes. These studies, on both experimentally and naturally deformed material, have confirmed and expanded earlier work based on optical microscopy. Deformation in olivine at lower temperatures and higher strain-rates proceeds by propagation of unit dislocations dominantly of the $\{110\}$ [001] system; diffusion-controlled dynamic recovery processes are inhibited, but grain-boundary recrystallization is observed. At higher temperatures and lower strain-rates glide of unit dislocations on $\{0kl\}$ [100] become predominant, simultaneous recovery effects become pronounced, and syntectonic recrystallization is extensive. Experimental deformation of orthopyroxene below $\sim$1000°C is complicated by extensive (martensitic) transformation to clinoenstatite, while above $\sim$1300°C deformation is dominantly by slip of partial dislocations on (100) [001]. The clinoenstatite transformation is quite rare in natural deformation; (100)[001] slip ($b = \frac{1}{4}[001]$) is the most common mechanism. Recovery kinetics in orthopyroxene are much slower than in olivine; static annealing studies to simulate transportation of xenoliths to the surface in a magma show appreciable effects in olivine if residence time in the magma exceeds a few days, but no discernible substructural change in orthopyroxene. The identity of major deformation mechanisms in nature and in high temperature experiments provides strong support for extrapolation of flow laws measured in the laboratory to conditions of flow in the mantle. Such extrapolation argues against the Newtonian-viscous behavior usually assumed in geophysical models of mantle convection.

Phase Transformations in the Pyroxenes $(Ca,Mg,Fe)_2Si_2O_6$

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100 and 100 kV electron microscopy have been used to study the mechanism of exsolution in natural pyroxenes from different geological environments. In monoclinic volcanic specimens fine-scale "tweed" structures and corresponding diffraction patterns in which a single reciprocal lattice is convoluted with satellites indicate that the mechanism is spinodal decomposition. Later stages show a coarsened structure where two phases co-exist with a diffuse, coherent interface. Pyroxenes from plutonic rocks exsolve by heterogeneous nucleation and growth, and thickening of the lamellae takes place by the propagation of ledges across coherent interface. In a hypabyssal rock (from the Whin Sill) a Ca-rich pigeonite was found to contain both heterogeneously- and (apparently) homogeneously-nucleated augite. The reasons for the variation in behavior with cooling rate will be discussed. In the system orthopyroxene-clinopyroxene metastable, intermediate precipitates (G. P. zones) were found between the heterogeneously-nucleated precipitates when the matrix was Ca-poor, but not when it was Ca-rich. A precipitate-free zone of the G. P. zones, a result of lower solute concentration, occurred adjacent to the equilibrium precipitates.

In pigeonites precipitated from augites in plutonic rocks the transformation to orthopyroxene occurs by propagation of a twin fault on (100) which nucleates at a growth ledge or at the planar (001) interface. As a result inverted pigeonite contains mistakes in the sequence of (100) planes which can be observed by direct lattice resolution.

HVTEM Studies of Deformed Carbonate Rocks and Crystals

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Transmission electron microscopy (TEM) on rocks and mineral aggregates has only become possible with the advent of the sputter-etching method of making thin foils, but it is already established as a powerful technique for investigating deformation, the nature of exsolution processes, phase transformations, *etc.* With carbonate minerals high voltage TEM is essential because the regions of the foils which are transparent to 100 keV electrons are almost completely amorphized by the sputter-etching process. Another difficulty is that carbonates are susceptible to radiation damage by the electron beam, the form of damage varying with sample composition and history. Observations on deformed limestones and dolomites, Iceland Spar, and aragonite will be presented, and the general effects of strain rate and temperature on deformation mechanisms, dislocation densities, and recovery will be illustrated. Specific effects such as the creation of geometrical voids at intersecting twins, microcleavages, the generation of intense deformation bands, non-stoichiometry, *etc,* will also be discussed. Where possible the observations will be presented with reference to the extensive optical and X-ray data already published by other workers.

The Submicroscopic Structure of Wenkite

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Wenkite—$Ba_4(Ca_{9.1}\square_{0.9})_6(Al_{0.4}Si_{0.6})_{20}O_{39}(OH)_2(SO_4)_3$, $a_o = 13.515$ Å, $c_o = 7.465$ Å—is an interrupted framework silicate with six- and eight-fold Al/Si tetrahedral ring channels (such as occur in gmelinite or cancrinite) linked by lone Al/Si tetrahedra that have either $+\bar{c}$ or $-\bar{c}$ orientations. A structure refinement (Wenk, 1973) of wenkite that

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showed partial occupancy of certain lattice sites suggested the occurrence of domains. Examination by transmission electron microscopy confirmed their occurrence with antiphase domain boundaries ($\bar{R} = 1/2[111]$) and lamellar twinning. This examination also revealed a superstructure ($2a_o \times 2c_o$) that can be credited to a unique orientation of the linking Al/Si tetrahedra.

Reference

WENK, H. R. (1973) The structure of wenkite. *Z. Kristallogr.* **137,** 113–126.

Investigation of the Steps of Apatite Formation—$CaHPO_4 \rightarrow Ca_2P_2O_7 \rightarrow Ca_5(PO_4)_3F$—by Electronmicroscopic Methods

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High voltage electronmicroscopy, electron diffraction, and scanning electronmicroscopy are demonstrated to be very useful and complementary tools, in the investigation of the structure of synthetic apatites. Separate crystallites of 3-10 μm size prepared on carbon film substrates were selected for these investigations. In this paper the structure of the starting material—$CaHPO_4$, that of the intermediate product—$Ca_2P_2O_7$, and that of the calcium fluorapatite—$Ca_{10}(PO_4)_6F_2$, will be discussed. It has been stated that during the transformation of $CaHPO_4 \rightarrow Ca_2P_2O_7$ the basic monocrystal decomposes to an agglomerate of microcrystallites whereas the habit of the particles remains unchanged. In the apatite formation process an inner recrystallization occurs resulting in particles containing only a few number of crystal blocks. Cavities arranged parallel to given crystallographic directions can be detected inside the apatite particles and on the surface as well.

Transmission Electron Microscopy in Ceramics and Mineralogy

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The rapidly increasing interest in applying transmission electron microscopy to studying the microstructures of ceramics and minerals has come about mainly as a result of three factors: (a) development of reliable thinning techniques for preparing specimens which are transparent to electrons, (b) the commercial availability of high voltage (650–1000 kV) electron microscopes which allows thicker samples to be used, and (c) the interest and funding available for studies of the lunar samples resulting from Apollo missions.

This review paper will summarize the techniques and analyses for interpreting microstructural features such as faults, antiphase domains, dislocations, and precipitates. A discussion of artifacts arising from radiation damage and effects associated with the environment of the specimen will also be presented.

Examples will be given of applications to the studies of defects and phase transformations in spinels and anorthite feldspars. Attention will be drawn to current needs such as more theoretical work on contrast from defects.

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On the Use of Photo-Emission Electron Microscopy (PEEM) on Decomposition Features in Minerals and Other Materials

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If decomposition processes (unmixing or exsolution) take place on a submicroscopic scale, valuable information on the texture and the chemical composition of such products can be gained by the application of PEEM, which may even sometimes prove to be an easier method than TEM or SEM as preparation is concerned. In addition, some information can be gained by PEEM that cannot be gained at all by TEM or SEM. The reason for this is that practically only the *surface* of a polished (first mechanically outside a PEEM instrument and then inside it with an argon beam) specimen contributes to the electron-microscopically magnified image because the imaging electrons (emitted by ultraviolet irradiation) are produced at or very near the specimen surface. Different phases behave differently with respect to different image intensities.

Feldspars [$(K,Na)AlSi_3O_8$ and $(Na,Ca)(Al,Si)_4O_8$] investigated with PEEM will be discussed as illustrations of the method and as examples of feldspar decompositions.

The PEEM instrument used was the so-called "Metioskop" manufactured by Balzers, Liechtenstein, designed by Dr. L. Wegmann.

Analytical Electron Microscopy of Minerals

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The technique of Analytical Electron Microscopy enables quantitative chemical analyses to be carried out from areas less than 0.1 μm in diameter. The possibility of obtaining, within the same instrument, a high-resolution image exhibiting diffraction contrast, diffraction patterns from areas less than 1 μm in diameter, and chemical information from volumes of approximately 10^{-15} cm^3 is a major advance over conventional electron microprobe analysis which is restricted to optical microscopy, can give only limited —if any—diffraction information, and provides chemical information from a volume of approximately 10^{-12} cm^3.

Examples will be given of the application of analytical electron microscopy to the following problems: (a) chemical analysis of small crystals of separated roggianite; (b) correlation of microstructure and chemical composition of a bytownite feldspar; and (c) analysis of an exsolved pyroxene and the correlation of the chemical composition with the distribution of phases.

Precipitation in Non-Stoichiometric Magnesium Aluminate Spinel

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Precipitation in non-stoichiometric magnesium aluminate spinel ($MgO{:}3.5\ Al_2O_3$) single crystals was studied by transmission electron microscopy. For crystals annealed at 850°C for various times, the following three-stage sequence of precipitation was confirmed:

	Supersaturated Solid Solution	
Stage I	Pre-precipitate I (Guinier-Preston zones?)	and Pre-precipitate II (G.-P. precipitates?)
Stage II	Intermediate Phases, Type I and Type II	
Stage III	Equilibrium $\alpha - Al_2O_3$ Phase	

The phases forming in stages I, II, and III are believed to be coherent, semi-coherent, and incoherent, respectively. The mechanical properties of crystals aged to Stage I or II are much better than the supersaturated single phase crystals or the over-aged crystals represented by Stage III.

Work Hardening and Solid Solution Hardening of Sapphire (α–Al_2O_3)

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The flow stress curves of pure sapphire (Al_2O_3) deformed at 1200-1500°C in compression exhibit a significant initial work hardening rate, *e.g.* $\sim\mu/400$ at 1400°C (where μ is the shear modulus), which eventually decreases with increasing strain until a region of zero work hardening is obtained. Using transmission electron microscopy, long edge dipoles were found to form by edge-trapping; screw portions of the dislocations annihilate by cross-slip. Work hardening is attributed to the accumulation of dislocation dipoles. As deformation proceeds the dipoles break-up into smaller loops by climb, causing recovery. The steady state region of zero work harden-

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ing is reached when the rate of accumulation of dipoles by edge-trapping is equal to their rate of annihilation by climb.

To assess the effectiveness of solid solution hardening as a strengthening mechanism in sapphire, a study was performed on "alloys" containing Cr and Ti. Examining a range of compositions in the metastable continuous solid solution Al_2O_3–Cr_2O_3, the hardening rate was found to be of the order of $\sim\mu/25$ and was attributed to an elastic interaction between glide dislocations and solute. However, when sapphire was alloyed with Ti, the yield stresses were found to be a function of the valence of Ti. Specimens with Ti primarily in the trivalent state had lower yield stresses than oxidized specimens in which Ti was tetravalent. This difference in mechanical properties was attributed to the asymmetric distortion of Ti^{4+} and its association charge compensating defect being a more potent hardener than the symmetric distortion produced by Ti^{3+}.