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RECENT DISCUSSIONS OF PYROXENES AND AMPHIBOLES

I. AMPHIBOLE SEMINAR

University of Massachusetts, Amherst, Massachusetts,
March 25–26, 1968

An informal seminar on the crystal chemistry, natural occurrence, and conditions of formation of amphiboles. Forty minute talks by twelve invited speakers were each followed by fifteen minutes of discussion. The topics and speakers are given below. Where the substance of the talk has been published subsequently elsewhere, reference to the published work is given in lieu of an abstract.

GEOMETRICAL POSSIBILITIES FOR AMPHIBOLE STRUCTURES: MODEL BIOPYRIBOLES

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As a first approximation, the structure of an amphibole may be regarded as made up of tabular units, parallel to (010), that may be taken apart so that alternate units can be reassembled to form a pyroxene and a trioctahedral mica, or mica-like crystal, respectively. Thus tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$, may be regarded as alternating layers that in their local configuration are diopside, $Ca_2Mg_2Si_4O_{12}$, and talc, $Mg_3Si_4O_{10}(OH)_2$, respectively. Similarly glaucophane may be thought of as jadeite+talc, anthophyllite as enstatite+talc, edenite as diopside+"Na-biotite", and so forth. Each occupied site in an amphibole may be thought of as a pyroxene-like or a mica-like site. This concept has significant consequences both in the interpretation of natural assemblages and in experimental studies of complex systems involving these mineral phases.

These three groups of minerals may *also* be regarded as made of alternating octahedral and tetrahedral layers parallel to (100) in amphiboles or pyroxenes, as conventionally oriented, or to (001) in micas. Models can be made with regular polyhedra corresponding to the octahedral $M(1)$, $M(2)$, and $M(3)$ sites and to the tetrahedral $T(1)$ and $T(2)$ sites, of a simple amphibole. With plastic polyhedra, now available commercially, having a ratio of the octahedral to the tetrahedral edge of $2:\sqrt{3}$, one may construct the conventional, idealized, extended structures. Models may also be constructed, however, with polyhedra having ratios as low as 1:1 or even less though this may be unrealistic. This may be accomplished by simply rotating the tetrahedra about axes normal to the octahedral-tetrahedral layers. These axes pass through the oxygens linking the tetrahedral layers to the octahedral ones. Two senses of rotation are possible: (1) *S-rotation,* in which a tetrahedron rotates so that the triangular face normal to the rotation axis turns toward the *same* orientation as that of the nearest parallel faces of the three octahedra to which the tetrahedron is linked by the oxygen lying on the rotation axis; and (2) rotation in the *opposite* sense which may be called an *O-rotation.* Rotation of 30° in either sense brings the oxygen atoms into a geometric array that is truly close-packed. Upon 30° rotation the amphibole A and $M(4)$ sites, otherwise not regular polyhedra, become regular octahedra identical in size to the other octahedra. S-rotation leads, for both A and $M(4)$ sites, to shared edges with adjacent tetrahedra, whereas O-rotation does not. O-rotation should thus be preferred in real crystals, other things being equal, and seems to be the dominant type in them.

No symmetry operation can transform an O-rotated octahedral-tetrahedral junction into an S-rotated one. Thus symmetry elements present in extended models may be de-

TABLE 1.

Extended structures	Rotated structures		Ratio of O- to S-junctions	Remarks
	Amphiboles	Pyroxenes		
Tremolite $C2/m$	$C2/m$	$C2/c$	all O	Not true derivatives, space group unaffected.
or	$C2/m$	$C2/c$	all S	
Diopside $C2/c$	$P2_1/m$	$P2_1/c$	1:1	Primitive clinoamphibole, pigeonite.
Protoamphibole $Pnmn$ or	$P2_1mn$	$P2_1cn$	1:1	Inversion would preserve external form.
Protopyroxene $Pbcn$	$P2/m$	$P2/c$	1:1	Inversion would destroy external form.
	$P2_1ma$	$P2_1ca$	3:1	Most likely inversion form.
	$P2_1ma$	$P2_1ca$	1:3	
Anthophyllite $Pnma$	$P2_1/m$	$P2_1/c$	1:1	Different O-S schemes, one has $\beta=90°$.
or	$P2_1/m$	$P2_1/c$	1:1	
Enstatite $Pbca$	$P2_1/m$	$P2_1/c$	3:1	Different O-S schemes, 3:1 a possible growth form.
	$P2_1/m$	$P2_1/c$	1:3	
	Pm	Pc	1:1	

stroyed by certain schemes of rotations yielding thereby derivative structures of lower symmetry. The possibilities of such derivative structures, however, are limited by a parity rule affecting both amphibole and pyroxene models. This rule derives from the regularity of the polyhedra and affects the nature of the rotations of adjacent tetrahedral strips in a given tetrahedral layer. If two such tetrahedral strips are both rotated in the same sense then the two octahedral strips (one above and one below the tetrahedral layer) to which they are joined across (100) must both have a "tilt" or "skew" of the same sense. If the rotations are in opposite senses then the tilts must be in opposite senses. If we restrict our attention to derivatives that do not increase the content of the unit cell then the simple extended structures rotate to yield, for the models here considered, only the ones tabulated below. For each the axial ratios, β-angles, and cleavage angles may be calculated by simple formulas as functions of the rotation angle, θ, taken as positive for O-rotation and negative for S-rotation. The values obtained for $0° < |\theta| < 30°$ bracket those found in natural pyroxenes and amphiboles of corresponding space group. Some of the expected structures have already been observed. We may anticipate others, particularly those whose models have a high ratio of O- to S-junctions. It is perhaps significant that many of those that might seem likely, but that have not yet been recognized, belong to non-centrosymmetric space groups. It is conceivable that rotation, in a given crystal, might vary with temperature or pressure, hence that certain displacive transformations involving derivative structures may be explained in this way.

Although the tremolite and diopside structures may rotate without loss of symmetry the β-angles *are* affected by θ. The derivative $P2_1/m$ and $P2_1/c$ structures, however, undergo a lesser change in β for a given degree of rotation, hence would probably be favored as inversion polymorphs, particularly if the crystal were confined. $C2/m$ or $C2/c$ pyriboles, with only O-rotations, should be more likely as growth forms.

STRUCTURE AND CATION ORDERING OF CLINOAMPHIBOLES

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See *Mineral. Soc. Amer. Spec. Pap.* **2,** 117–136 (1969).

EXSOLUTION AND RECRYSTALLIZATION TEXTURES IN AMPHIBOLES

MALCOLM ROSS, *U. S. Geological Survey, Washington, D.C., 20242.*

See *Mineral. Soc. Amer. Spec. Pap.* **2,** 275–300 (1969).

EXSOLUTION LAMELLAE AND OPTICAL PROPERTIES OF CLINOAMPHIBOLES

HOWARD W. JAFFE, *Department of Geology, University of Massachusetts, Amherst, Mass. 01002.*

See *Science,* **160,** 776–778 (1968).

CATION DISTRIBUTION IN AMPHIBOLES: RESULTS OF SPECTRAL STUDIES

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See abstr., *Geol. Soc. Amer., Meet.*; *Mexico City,* p. 110–111, (1968); and *Mineral. Soc. Amer. Spec. Pap.* **2,** 51–58 (1969).

STRUCTURE AND CATION ORDERING IN ANTHOPHYLLITE

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See abstract in Section III, below.

COEXISTING AMPHIBOLES

CORNELIS KLEIN, JR., *Department of Geological Sciences, Harvard University, Cambridge, Mass. 02138*

See *J. Petrology,* **9,** 281–330 (1969); and *Amer. Mineral.,* **54,** 212–237 (1969).

CHEMOGRAPHIC EXPLORATION OF AMPHIBOLE ASSEMBLAGES FROM MASSACHUSETTS AND NEW HAMPSHIRE

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See *Mineral. Soc. Amer. Spec. Pap.* **2,** 251–274.

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TALC-ANTHOPHYLLITE RELATIONS

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No abstract.

STABILITY RELATIONS OF CALCIC AMPHIBOLES

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See W. G. Ernst (1968) *Amphiboles.* Springer-Verlag, New York, p. 50–67.

STABILITY RELATIONS OF SODIC AMPHIBOLES

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See W. G. Ernst (1968) *Amphiboles.* Springer-Verlag, New York, p. 77–101.

AMPHIBOLE-BIOTITE RELATIONS

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Because amphiboles and biotites are the most common hydrous silicates in igneous rocks, knowledge of their stabilities has led to estimates of H_2O fugacities during igneous and metamorphic processes. The presence of biotite or amphibole in any given rock has been usually thought of as the result of bulk composition, rocks with normative diopside usually containing amphibole, and rocks with normative or and hypersthene containing biotite.

However, a number of reactions which conserve water can be written between biotites and amphiboles such as the following:

$$\underset{\text{riebeckite}}{Na_2Fe_2^{3+}Fe_2^{2+}Si_8O_{22}(OH)_2} + \underset{\text{Kspar}}{KAlSi_3O_8} = \underset{\text{annite}}{KFe_3AlSi_3O_{10}(OH)_2} + \underset{\text{acmite}}{2NaFeSi_2O_6} = \underset{\text{qtz}}{4SiO_2}$$

$$\underset{\text{tremolite}}{Ca_2Mg_5Si_8O_{22}(OH)_2} + \underset{\text{Kspar}}{KAlSi_3O_8} = \underset{\text{phlogopite}}{KMg_3AlSi_3O_{10}(OH)_2} + \underset{\text{diopside}}{2CaMgSi_2O_6} + \underset{\text{qtz}}{4SiO_2}$$

$$\underset{\text{edenite}}{NaCa_2Mg_5AlSi_7O_{22}(OH)_2} + \underset{\text{Kspar}}{KAlSi_3O_8} = \underset{\text{phlogopite}}{KMg_3AlSi_3O_{10}(OH)_2} + \underset{\text{albite}}{NaAlSi_3O_8} + \underset{\text{diopside}}{2CaMgSiO_6}$$

$$\underset{\text{paragasite}}{NaCa_2Mg_4AlAl_2Si_6O_{22}(OH)_2} + \underset{\text{Kspar}}{KAlSi_3O_8} = \underset{\text{phlogopite}}{KMg_3AlSi_3O_{10}(OH)_2} + \underset{\text{plagioclase}}{\begin{matrix} NaAlSi_3O_8 \\ CaAl_2Si_2O_8 \end{matrix}}$$

$$+ \underset{\text{monticellite}}{CaMgSiO_4}$$

The available data on amphibole stabilities, when combined with the biotite stability data permit several permutations to be tested, although several important amphiboles have not been studied in enough detail to obtain a complete set of generalizations.

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The tremolite-phlogopite reaction has been partially studied and biotite-diopside-quartz is the high temperature assemblage, and K-spar-tremolite the low temperature assemblage, assuming that the equilibrium water pressure is greater than about 400 bars. Below this H_2O pressure the biotite-diopside-quartz assemblage is metastable. However, in the ferrous system, the assemblage annite-ferrohedenbergite-quartz should always be stable. Such data also permit estimates of the Fe/Mg distributions between biotites and amphiboles. For calcic amphiboles iron is concentrated in the coexisting biotites, but for sodic amphiboles, iron should be concentrated in the amphiboles.

With the exception of ferropargasite and perhaps of hastingsite, the assemblage biotite-pyroxene is more stable than amphibole-Kspar at high temperatures, whereas the reverse is true at low temperatures. This implies that Bowen's reaction series is not strictly valid. An investigation of paragenetic sequences based on inclusions in minerals of granitic rocks indicates that biotite frequently crystallizes earlier than alkali feldspar, amphibole or even plagioclase. This is true for granitic rocks of the Huntington Lake quadrangle, Fresno County, California (Sierra Nevada batholith) and for the alkalic rocks of New England. The Stillwater Complex in Montana contains biotite, not amphibole, in the ultramafic zone.

However, if the K_2O content of a given magma is low, biotite will crystallize late due to the low activity of K_2O. Hence amphibole will precede biotite in the crystallization of magmas of low H_2O and K_2O content.

A question remains as to whether biotite or amphibole is the K_2O and H_2O rich phase in the mantle. For all cases in which the amphibole is not potassic, the biotite-pyroxene assemblage is more dense, so that if there are high K_2O contents in the deep crust or upper mantle, a biotite-pyroxenite might be the typical assemblage rather than amphibolite. Another fact is that lower SiO_2 contents will favor biotite. Potassium rich amphiboles are characterized by either low OH or low Al contents and if the K_2O/Al_2O_3 and K_2O/H^2O ratios are >1, then potassic amphiboles may be present in the deep crust or upper mantle.

II. PYROXENES AND AMPHIBOLES: CRYSTAL CHEMISTRY AND PHASE PETROLOGY

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VIRGINIA POLYTECHNIC INSTITUTE, BLACKSBURG, VIRGINIA, SEPTEMBER 7–11, 1969

ABSTRACTS

MÖSSBAUER SPECTRA OF OMPHACITES

MICHAEL G. BANCROFT, AND PAUL G. L. WILLIAMS, *University Chemical Laboratory, Cambridge, England and* ERIC J. ESSENE, *Department of Geophysics, Australian National University, Canberra, Australia.*

Mössbauer spectra of five omphacites are distinctive and can be used to characterize omphacites having $P2$ symmetry. The spectra have been fitted to Lorentzian line shapes, and consist of 10 lines: eight due to four ferrous doublets, and two due to a ferric doublet. The center shift (C.S.) values for all the Fe^{2+} doublets are about 1.25 mm/sec, while the quadrupole splittings (Q.S.) vary from about 2.8 mm/sec for the outer peaks to about 1.7 mm/sec for the inner peaks. The C.S. and Q.S. for the ferric doublets are about 0.5 and 0.4 mm/sec respectively. We tentatively assign the four Fe^{2+} doublets to Fe^{2+} in the four $M(1)$ positions. The results indicate that appreciable amounts of Fe^{2+} occupy all four of these *M*(1) positions; moreover the intensity of the one well-resolved ferrous peak indicates that the Fe^{2+} ordering varies markedly between these five omphacites. These differences in ordering may well reflect differences in temperature and pressure of formation. The ferrous/ferric ratios calculated from these spectra are not in good agreement with chemical analyses, which generally overestimate the Fe^{3+} content.

THE VARIATION OF THE SI-O BOND LENGTHS, SI-O-SI AND O-SI-O ANGLES IN THE CHAIN AND SOROSILICATES

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A study of the variation of individual Si-O bond lengths, Si-O-Si and O-Si-O angles in the amphiboles, pyroxenes and certain sorosilicates has resulted in a number of correlations which are consistent with the *d-p* π-bonding model proposed by Cruickshank (1961): (1) the mean Si-O(br) bond lengths [= $\overline{\text{Si-O}}$(br)] decrease as the Si-O-Si angle widens; (2) the difference between the $\overline{\text{Si-O}}$(br) and $\overline{\text{Si-O}}$(nbr) bond lengths decreases with increasing Si-O-Si angle; (3) the O-Si-O angles decrease in the order O(nbr)-Si-O(nbr) > O(nbr)-Si-O(br) > O(br)-Si-O(br) in agreement with the VSEPR theory of Gillespie (1963). Correlation (3) could not be established for the O-Al-O angle with the small amount of data available, although a linear relationship was found between Al-O and nonbonded O . . . O distances for O-Al-O linkages. The slope of this line is near zero, reflecting a smaller bond pair-bond pair repulsion and less electron density in the Al-O bonds than in the Si-O, P-O or S-O bonds.

Additional correlations are established for four *C*2/*m* amphiboles with vacant A-sites: (4) the Si(1)-O(1), Si(2)-O(2) and Si(2)-O(4) bond lengths increase as the average electronegativity, $\bar{\chi}$, of the non-tetrahedral cations coordinating O(1), O(2) and O(4) increases or as the residual negative charges on O(1), O(2) and O(4) decrease; (5) the O(2)-Si(2)-O (4) angle varies directly with the predicted bond orders of the Si(2)-O(2) and Si(2)-O(4) bonds. Correlation (4) is at variance with Bent's (1961) hypothesis which predicts that the Si-O(nbr) bond lengths should decrease with increasing $\bar{\chi}$. Correlations (4) and (5) could not be established for the recently refined clinopyroxenes.

CORRELATIONS OF MÖSSBAUER AND INFRARED SPECTRAL DATA IN SITE POPULATION STUDIES OF AMPHIBOLES

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Measurements of the Mössbauer spectra of Fe^{2+} and Fe^{3+} ions in amphiboles and the fundamental hydroxyl stretching frequency in the infrared have complemented one another in site population studies of amphiboles. This is illustrated by data for alkali amphiboles. For example, the Mössbauer spectrum of the crocidolite $Na_2Fe^{2+}{}_{2.76}Mg_{0.30}Fe^{3+}{}_{1.93}Si_8O_{22}(OH)_2$ consists of one ferric doublet and two doublets, an outer and an inner pair, originating from absorption by Fe^{2+} ions. The ratio of the peak areas leads to estimates of the proportion of ferrous ions giving rise to each doublet and the percentage of ferrous iron in the amphibole. Thus, in the crocidolite 1.78 Fe^{2+} ions contribute to the outer doublet and 0.98 Fe^{2+} ions to the inner doublet. With Na^+ ions filling the *M*(4) positions, there are six possible distributions of Fe^{2+} ions over the remaining two $M(1)$, two $M(2)$ and one $M(3)$ sites per formula unit contributing to the ferrous doublets. These possibilities are resolved by the infrared measurements which show that Fe^{2+} ions are concentrated in the $M(1)$ and $M(3)$ positions with relative enrichment in the $M(1)$ positions. The results show that the only possible peak assignment in the Mössbauer spectrum is: outer doublet, Fe^{2+} in $M(1)$ positions; inner doublet, Fe^{2+} in $M(3)$ plus $M(2)$ positions. Similar results are obtained for other Fe^{2+} in $M(3)$ plus $M(2)$ positions. Similar results are obtained for other crocidolites and glaucophanes of low temperature-high pressure origins, in which pronounced cation ordering occurs. Trivalent ions are concentrated in $M(2)$ positions of all alkali amphiboles, but the relative enrichment of Fe^{2+} ions varies with composition, being higher in $M(3)$ positions of glaucophanes and $M(1)$ positions of riebeckites.

Measurements of pegmatitic alkali amphiboles of high temperature origins show that cations are more randomly distributed in the crystal structures. An additional ferrous doublet due to Fe^{2+} ions in the $M(2)$ positions may be resolved in the Mössbauer spectra, while the infrared measurements show that appreciable amounts of Fe^{2+} ions occupy $M(1)$ and $M(3)$ positions.

By means of Mössbauer and infrared spectroscopy, it is possible to distinguish between Fe^{2+} and Fe^{3+} ions in a crystal structure and to rapidly obtain accurate and reproducible site population data.

HOW TO RECOGNIZE $O^{=}$, OH^{-} AND H_2O IN CRYSTAL STRUCTURES DETERMINED BY X-RAYS

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A double-entry table of cation-to-anion bond lengths and associated bond valences leads to valence sums for the oxygen anions. These sums are close to two for oxygen ions, close to one for hydroxyl oxygen ions and close to zero for water oxygen ions. The deviation from the integral value gives information about hydrogen bonding and site occupancies. An empirical plot expresses bond valence v in terms of bond length l. It is based on two equations:

$$(1)\ \text{For } l \le \bar{l}, \quad v = v_i\left(\frac{\bar{l}}{l}\right)^n; \qquad (2)\ \text{For } \bar{l} \le l \le l_{\max}, \quad v = v_i\left(\frac{l_{\max} - l}{l_{\max} - \bar{l}}\right),$$

where $\bar{l}$ is the mean bond length of the cation polyhedron found in the structure under consideration, $l_{\max}$ is the largest cation-anion distance that can still be considered a bond. Values of $l_{\max}$ for the common cation-oxygen distances are tabulated. By imposing the condition that the two curve segments have equal slope at their common point $l = \bar{l}$, n is found to be equal to $\bar{l}/(l_{\max} - \bar{l})$. The procedure is applied to sonoraite, grunerite and bultfonteinite.

MÖSSBAUER, INFRARED, X-RAY AND OPTICAL STUDY OF CATION ORDERING AND DEHYDROGENATION IN NATURAL AND HEAT-TREATED SODIC AMPHIBOLES

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Investigation of 12 natural sodic amphiboles, all but one of which crystallized under low-grade metamorphic conditions, confirms the conclusions of earlier workers that refringence and unit cell dimensions increase with increasing iron content. The present study demonstrates that Fe^{3+} is concentrated in the $M(2)$ structural position whereas Fe^{2+} is ordered in $M(1)$ and $M(3)$. Aluminous sodic amphiboles characteristically display a Fe^{2+}/Mg fractionation which enriches $M(3)$ in ferrous iron relative to $M(1)$, whereas the converse relationship holds for iron-rich analogues.

Heat treatment of sodic amphiboles in air at 705±2C° results in rapid loss of hydrogen and concomitant increase in oxidation state. To the extent that Fe^{2+} ions are available in $M(1)$ and $M(3)$ sites, electrons are transferred to adjacent bonded hydroxyls, allowing neutralization and expulsion of hydrogen. Dehydrogenation takes place over a period on the order of one hour under the experimental conditions. Subsequent to loss of all hydrogen, continued oxidation takes place by a much slower process, possibly one involving electron and/or iron diffusion. In addition, significant disordering of cations occurs on experiments of four days' duration. Sodic oxyamphiboles possess shorter *b* axis repeats, higher indices of refraction and birefringence compared to natural starting materials.

Natural glaucophane hydrothermally heated for 15,667 hours at 513±10C°, P_{fluid} of 2000 bars and f_{O_2} of $10_{\ 22}$ bars, was strongly oxidized, completely dehydrogenated, and now displays both unusually large *a* and *b* axis dimensions and elevated refringence. It is tentatively concluded that the octahedrally coordinated cations are virtually completely disordered in this oxyglaucophane.

THE STRUCTURE REFINEMENT AND CATION ORDERING OF AN ANTHOPHYLLITE

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An anthophyllite from the Dillon Complex, Montana (Rabbitt, 1948), was selected for structural analysis ($a=18.560$, $b=18.013$, $c=5.2818$ Å, $V=1765.8$ Å^3, $Mg_{5.53}Fe^{2+}{}_{1.47}Si_8O_{22}(OH)_2$). Refinement of 2656 counter-measured reflections in space group *Pnma* converged to a conventional residual of 6.3%. The residual for the 2063 data with intensities greater than the minimum observable was 4.4%.

The M-site cation occupancies were refined with the occupancies constrained to agree with the formula. The following fractional occupancies for magnesium were obtained: $M(1)$ 0.960(3), $M(2)$ 0.973(3), $M(3)$ 0.966(4), and $M(4)$ 0.349(4). The extremely high degree of fractionation of iron into $M(4)$ probably indicates a relatively low temperature of formation or annealing. However, unlike the cummingtonite structure, this material contains an appreciable amount of Mg in $M(4)$. The orthorhombic structure has two symmetrically distinct double chains and one of these is distorted such that two rather than one of its chain-linking oxygens must be considered bonded to $M(4)$ which thus has seven nearest neighbors rather than the six such neighbors in the cummingtonite structure.

SYNTHESIS AND SODIUM-POTASSIUM EXCHANGE IN THE RICHTERITE SERIES

$(K,Na)NaCa\text{-}Mgi_5Si_8(OH)^2$

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Compositions in the series $(K,Na)NaCaMg_5Si_8O_{22}(OH)_2$ have been synthesized at 730–850°C and $P_{H_2O} = 1$ kbar Unit-cell parameters (at STP) of intermediate compositions do not deviate significantly from a linear relationship between the parameters of end-member compositions: potassic richterite *a* 10.049 (2), *b* 17.988 (3), *c* 5.272 (1) Å, *β* 104°48.1 (0.5)′, *V* 921.4 (0.4) Å^3; and sodic richterite 9.907 (2), 17.979 (4), 5.268 (1) Å, 104°15.1 (0.9)′, 909.6 (0.4) Å^3. (The numbers in parentheses are the standard deviations of five determinations and refer to the least significant digit.) This is the first reported synthesis of a potassic amphibole, and yields the largest cell volume of any known monoclinic magnesian amphibole. Homogenization experiments demonstrate the absence of a two-phase region at the above conditions.

Potassium is coordinated by eight oxygen neighbors within 3 Å in potassic richterite. The coordination of potassium is tighter in clinoamphiboles than in mica, which has only six neighbor oxygens within 3 Å. By analogy with the K-Na richterite series, the molar volume of K-edenite can be estimated to be 275 cm^3/mole, which is less than the molar volume of the compositionally equivalent assemblage phlogopite+diopside, 281.9 cm^3. Similarly, the estimated volume of K-pargasite, 276 cm^3/mole, is less than phlogopite+(diopside−lime Tschermak's molecule solid solution), 279 cm^3. Consequently, at high pressures characteristic of the lower crust or upper mantle, potassium may be present in amphibole structures rather than mica structures, for appropriate bulk compositions.

The *A*-site cation can be reversibly and completely exchanged by equilibration with slightly hydrous NaCl or KCl melts at 850°C and 1 kbar. End member richterites formed in this way have cell dimensions identical to those for richterites formed by synthesis in a chloride-free environment, indicating that Cl^- does not enter the structure (F^-, which proxies for hydroxyl, does cause considerable change in *a* and *β* and *V*). Reversed equilibration experiments with intermediate (K,Na)Cl melts demonstrate that the mole fraction ratio of potassium to sodium in the amphibole A-site is greater than in the melt. At the termination of an experiment, two discrete amphiboles are commonly noted: unreacted starting material, and exchanged product. Exchange of amphibole, when it occurs, results directly in a product in equilibrium with the melt. The duration of an experiment affects the relative proportions of the two amphiboles, but not their compositions. The success of the exchange experiments demonstrates a useful technique for studying the phase relationships of alkali-bearing amphiboles. The rapidity of the exchange process in the laboratory suggests that the K/Na ratios of natural amphiboles may have changed with time.

AMPHIBOLES OF THE IRISHMAN CREEK SILL, BRITISH COLUMBIA, CANADA

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Numerous, intrustive, amphibole-rich sills occur within the Proterozoic formations of the Purcell Mountains, British Columbia. The sills are probably the intrusive equivalents of the altered Purcell tholeiitic basalts.

The Irishman Creek Sill, about 25 feet thick, is classified as quartz diabase and is dominantly composed of amphibole, plagioclase, and quartz. The contacts of the sill are well exposed. In this section biotite has replaced the hornblende of the lower contact rock found below the sill. Within the lower margin of the sill biotite has replaced some of the earlier-formed amphibole. These secondary biotites of the contact rock and the sill gave K-Ar ages of 844 million years and 835 million years respectively. This suggests the occurrence of a metamorphic event about 800 million years ago and is called the East Kootenay Orogeny (Hunt, 1962).

A date of 1580 million years of the amphibole found well within the sill may indicate that the metamorphic grade of the East Kootenay Orogeny was not above the biotite facies at this locality and the amphibole was able to retain its argon.

If the amphibole of the Purcell Sills is secondary, why is there such meagre evidence of this transformation? No pyroxene or pyroxene relicts were recognized in the sills. If the Irishman Creek Sill was emplaced contemporaneously with the Purcell basalt, the sill would have intruded sediments about 26,000 feet stratigraphically below its extrusive equivalent. The incorporation of OH groups in the amphibole structure is favored by crystallization under pressure (Mason). Petrographic evidence suggests a primary-deuteric interpretation for the origin of the green and fibrous amphibole in the Purcell sills.

AUGITES AND HORNBLENDES FROM CALC-ALKALINE VOLCANIC ROCKS, PUERTO RICO

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Twenty-eight augites and five hornblenders from calc-alkaline basalts, andesites, and dacites from the Puerto Rican orogen have been analyzed for nine elements with an electron probe microanalyzer. The range for augites in weight per cent is: SiO_2-49.7 to 53.7; Al_2O_3-1.5 to 5.5; total Fe as FeO-4.3 to 13.9; MgO-11.2 to 17.1; CaO-17.3 to 22.0; Na_2O-0.1 to 0.4; K_2O-<0.01 to 0.02; TiO_2-0.2 to 0.9; MnO-0.2 to 0.7. In general, the augites are characterized by high Al and Ca. Augites from basalts contain more Al and Ca, less Si, and slightly less Fe than those from andesites and dacites. Zoning in most augites is slight to moderate. Continuous scanning across several augites from basalts show that Mg and Al increase, Fe and Si decrease, and Ca and Ti remain essentially constant from core to margin. The values for hornblendes in weight per cent are: SiO_2-39.8 to 42.2; Al_2O_3-12.4 to 17.2; total Fe as FeO-9.2 to 14.2; MgO-12.3 to 14.4; CaO-10.0 to 11.9; Na_2O-1.5 to 1.8; K_2O-0.02 to 0.03; TiO_2-1.2 to 2.9; MnO-0.3 to 0.5. Zoning in these tschermakitic hornblendes results in an outward increase in Si, Ca, and Mg and a decrease in Al and Fe. These minerals and the coexisitng plagioclases, hypersthenes, and magnetites demonstrate the complexity of fractional crystallization in producing the calcalkaline series in Puerto Rico.

A REFINEMENT OF THE STRUCTURE OF ACTINOLITE

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The crystal structure of an actinolite [$a=9.8906$ (3), $b=18.1995$ (3), $c=5.3058$ (5) Å, $\beta=104.639$ (4)°, $C2/m$, $Z=2$; $\rho=3.271$] of composition $(Ca_{0.875}Na_{0.04}Mn_{0.08})_2(Fe^{+2}{}_{0.506}Fe^{+3}{}_{0.06}Mg_{0.372}Mn_{0.044}Al_{0.014}Ti_{0.002}Cr_{0.002})_5(Si_{0.955}Al_{0.045})_8O_{22}(F_{0.03}OH_{1.97})_2$ was refined by least-squares and Fourier methods using 672 intensities recorded with a counter-diffractomoter.

The mean $T(2)$-O distance (1.633) in actinolite is statistically identical with that (1.632) reported for tremolite (Papike *et al.*, 1969) wheres its mean $T(1)$-O distance (1.630) is ~0.01 Å longer, perhaps because 10 percent of the available $T(1)$ sites in actinolite contain Al. However, the $T(1)$-O(1) distance in actinolite is about 0.02 Å longer than the corresponding distance in tremolite. This longer bond length may reflect a partial covalency of the bonds between the *M*-cations (Fe,Mn) and O(1) in actinolite. Contrary to this suggestion, however, the *T*(2)-O(2) bond lengths are statically identical in tremolite (1.616) and actinolite (1.616) as are the *T*(2)-O(4) bond distances (tremolite, 1.586; actinolite, 1.589 Å).

The mean *M*-O distances for *M*(3), *M*(1) and *M*(2), respectively 2.097, 2.104 and 2.095 Å compared with those for tremolite, respectively, 2.066, 2.075 and 2.077 Å suggest an ordering of Fe^{2+} and Al^{3+} into the *M*(2) site. Difference map calculations and isotropic temperature factors indicate the following site populations: *M*(3), 0.42 Mg+0.58 Fe^{2+}; *M*(1), 0.37 Mg+0.63 Fe^{2+}; *M*(2), 0.45 Fe^{2+}+0.16 Fe^{3+}+0.35 Mg+0.04 Al; *M*(4), 0.88 Ca+0.08 Mn+0.04 Na.

PRELIMINARY CHEMICAL DATA ON THE AUGITE SERIES OF THE KIGLAPAIT LAYERED INTRUSION

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The Kiglapait cumulus augite series begins at the Lower Zone/Upper Zone boundary at about 84% solidified (by volume), and continues throughout the remainder of the exposed layered series, presumably to 100% solidified. The range in eleven analyzed samples is from $Wo_{39}En_{44}Fs_{17}$ to $Wo_{42}En_{4}Fs_{54}$, comparable to the range shown by the Skaergaard intrusion. In contrast to the latter, there appears to be no central dip in Ca content. Data points are scarce in the critical region, but if the approximately straight trend holds up with further analyses, it will be no surprise, since primary Ca-poor pyroxenes are lacking and the augites therefore lie off the solvus at liquidus temperatures. They do, however, intersect the solvus at subsolidus temperatures, as shown by abundant but very fine pigeonite lamellae in (001); these occur to compositions at least as iron-rich as $Wo_{42}En_{17}Fs_{41}$.

The Al_2O_3 content of Kiglapait augites falls rapidly up stratigraphy from 2.5 to less than 1%; TiO_2 is nearly constant near 1%, and Fe_2O_3 is nearly constant near 2%. In comparison to the Skaergaard augite series, Al_2O_3 is slightly lower, TiO_2 is virtually identical, and Fe_2O_3 is slightly higher in Kiglapait augites.

Standard pyroxene molecules calculated after the manner of Kushiro (1962) show progressive changes in abundance with increasing stratigraphic height. $CaFe^{3+}AlSiO_6$ drops very rapidly from about 3.5 mole % to zero; $CaTiAl_2O_6$ drops moderately from about 3 to 1.5%; and $CaFe^{3+}Fe^{3+}SiO_6$ (with minor $CaTiFe_2O_6$) rises smoothly from zero to 2.5 mole %. This systematic behavior suggests partitioning with magma, rather than subsolidus redox reactions, as the dominant control on the titanium and ferric pyroxene molecules.

Kiglapait augites are charged with thin, elongate opaque plates lying parallel to *a* and *c* in (010). Their thickness is submicroscopic ($\sim 10^2$ Å?), and their length and breadth reach 500×50 microns. These plates are, at least in part, ulvöspinel-rich magnetite in which the cloth-textured exsolution pattern may be seen in reflected light. The plates are commonly more abundant in inner portions of augite grains and depleted near the margins, perhaps suggesting collectively the outline of the original cumulus grain. Their origin appears to be one of exsolution from an initially homogeneous pyroxene during very slow cooling. A cooling rate difference might explain their absence or scarcity in augites of equivalent composition from the smaller, higher-level Skaergaard. The magnetite components, with metal: oxygen of 3:4, represent excess metal relative to pyroxene (2:3). An origin of opaque plates by intergranular reaction would involve either gain of metal or loss of oxygen, and appears doubtful. An intragranular, closed-system origin appears more likely. Such an exsolution origin would imply a pyroxene which, at the liquidus, was oxygen deficient relative to low-temperature pyroxene stoichiometry, but in which the anion positions were statistically satisified by thermal motion. The indicated oxygen deficiency is approximately 1 ion to 600.

GEDRITES; CRYSTAL STRUCTURES AND INTRACRYSTALLINE CATION DISTRIBUTIONS

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The crystal structures of two aluminous and sodic orthoamphiboles (gedrites) have been refined. Gedrite-001 is from metamorphosed ultramafic rocks, Mason Mountain, North Carolina and gedrite-002 is from metamorphosed volcanic rocks Richmond, N. H. Gedrite-001 has $a = 18.531 \pm 0.004$, $b = 17.741 \pm 0.004$, $c = 5.249 \pm 0.005$ Å, space group *Pnma*, and its chemical analysis can be expressed as:

$$(\square_{0.55}Na_{0.45})(Na_{0.02}Ca_{0.03}Mg_{4.52}Al_{1.21}Fe_{1.14}Ti_{0.06}Mn_{0.02})_{\Sigma=7} \cdot (Si_{6.25}Al_{1.75})_{\Sigma=8}O_{22}(OH)_2.$$

Gedrite-002 has $a = 18.601 \pm 0.004$, $b = 17.839 \pm 0.003$, $c = 5.284 \pm 0.002$ Å, space group *Pnma*, and its chemical analysis can be expressed as:

$$(\square_{0.47}Na_{0.53})(Na_{0.02}Ca_{0.04}Li_{0.02}Mg_{3.01}Al_{1.36}\overset{2+}{Fe}_{2.36}\overset{3+}{Fe}_{0.13}Ti_{0.03}Mn_{0.03})_{\Sigma=7} \cdot (Si_{5.95}Al_{2.05})_{\Sigma=8}O_{22}(OH)_2.$$

Sodium mainly occupies the *A*-site, and is tightly coordinated by six oxygens (G-001; 2.66, 2.66, 2.64, 2.64, 2.41, 2.30 Å, G-002; 2.65, 2.65, 2.62, 2.62, 2.41, 2.36 Å) and shows little positional disorder. This contrasts with sodium in the *A*-site of

TABLE 1. PRELIMINARY *M* AND *S* SITE OCCUPANCIES IN GEDRITES

		Gedrite-001		Gedrite-002	
Site	Atom	Mole fraction	Atoms per formula unit	Mole fraction	Atoms per formula unit
M(1)	Mg	0.88	1.76	0.67	1.34
	Fe[a]	0.12	0.24	0.33	0.66
M(2)	Al	0.60	1.20	0.68	1.36
	Mg	0.36	0.72	0.23	0.46
	Fe[a]	0.04	0.08	0.09	0.18
M(3)	Mg	0.90	0.90	0.61	0.61
	Fe[a]	0.10	0.10	0.39	0.39
M(4)	Mg	0.55	1.10	0.32	0.64
	Fe[a]	0.42	0.84	0.65	1.30
	Ca	0.02	0.04	0.02	0.04
	Na	0.01	0.02	0.01	0.02
A	Na	0.34	0.34	0.52	0.52
	Vacant	0.66	0.66	0.48	0.48

[a] Fe = Fe + Mn + Ti

clinoamphiboles where sodium shows a high degree of positional disorder and irregular coordination. The significant difference in *A*-site coordination between clinoamphiboles and orthoamphiboles results from differences in stacking of the tetrahedral chains around the site. A chain direction can be defined in terms of the trigonal aspect of the six-membered rings of tetrahedra. In clinoamphiboles the chains point in opposite directions above and below the site ($+c$, $-c$) whereas in these orthoamphiboles both chains are identically directed ($+c$, $+c$ or $-c$, $-c$).

Tetrahedral aluminum is disordered over three of the four independent tetrahedral sites in these gedrites. The fourth is occupied mainly by silicon. In clinoamphiboles the distribution of tetrahedral aluminum is more restricted and these differences between clinoamphiboles and orthoamphiboles can be explained largely by charge balance requirements.

Preliminary site occupancies for the *M* and *A* sites are given in Table 1. The predicted *A*-site occupancy from the chemical analysis is 0.45 and 0.53 Na for gedrite-001 and gedrite-002, respectively.

Intracrystalline distribution coefficients calculated from these data and consideration of distribution isotherms for orthopyroxenes indicate gedrite-002 reflects a higher temperature equilibration than gedrite-001.

A GENERAL METHOD FOR CONSTRUCTING THE SET OF ALL END MEMBERS OF A MINERAL GROUP

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The chemical composition space of any mineral group can be represented as a convex polyhedron in some *m*-dimensional space. For most silicate groups of geologic interest, *m* is conveniently taken as the number of oxides in terms of which the chemistry of those groups can be described. The geometry of such a polyhedron is defined by its extreme points, *i.e.* those points which cannot be represented as a convex combination of any other two points of the polyhedron. Physically, the extreme points are the true end members of the mineral group. As such they represent the limits of certain ionic substitutional schemes, subject to the constraints imposed by the mineral group structural formula.

In the present paper, it is shown that it is possible, with the aid of a single linear transformation and a simple theorem from linear programming, to construct the unique set of all extreme points for a given mineral group provided that the structural formula of that group is known. The approach described is illustrated using the amphiboles and pyroxenes. A number of the extreme points generated for the amphiboles and pyroxenes have not been previously described, but appear to be necessary for the complete representation of chemical analyses from these groups in higher (*i.e.* greater than three) dimensional spaces.

CUMMINGTONITE: A REVERSIBLE, NONQUENCHABLE, TRANSITION FROM $P2_1/m$ to $C2/m$ SYMMETRY

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Cummingtonite from the Gouverneur, New York, talc district (sample no. 115046) with the composition $(Ca_{0.36}Na_{0.06}Mn_{0.96}Mg_{0.57})$ $Mg_5Si_8O_{22}(OH)_2$, unit cell parameters $a=9.550\pm.001$, $b=18.007\pm.003$, $c=5.298\pm.001$ Å, $\beta=102°39' \pm 1'$, and space group $P2_1/m$, has been used in a high-temperature, single crystal, X-ray diffraction study. At room temperature the crystals give diffraction patterns showing numberous hkl reflections with $h+k=2n+1$, indicating space group $P2_1/m$ rather than the usual clinoamphibole space group $C2/m$. When diffraction patterns are taken of the crystals heated in a sealed silica capillary to 45°C or higher, these reflections disappear, indicating a transition to $C2/m$ symmetry. If the crystals are agains cooled to temperatures below 35°C, the resultant patterns are identical to the initial ones. This transition remains even if the crystals are heated as high as 500°C before cooling. Using the results of a previous refinement of the $P2_1/m$ structure, the observed transition can be attributed to change in coordination of the cations in the $M(4)$ sites. At room temperature the tetrahedral chains kink to produce a more regular coordination for the $M(4)$ cations, especially Mg, and the resultant atomic displacements give rise to the $P2_1/m$ symmetry. At slightly higher temperatures ($\simeq$40°C and up) the thermal vibrations of the $M(4)$ cations effectively allow them to occupy a larger $M(4)$ site without requiring extreme kinking of the tetrahedral chains. Thus the normal $C2/m$ symmetry is maintained. The transition appears to be analogous to the $P2_1/c$ to $C2/c$ transition between 700° and 800°C recently discovered by Smyth (1969) in $(Mg_{.30}Fe_{.70})SiO_3$ clinopyroxene.

The above observations together with previous studies of exsolution in amphiboles suggest the following cooling sequence: a $C2/m$ cummingtonite with a high concentration of Ca and Mg in the $M(4)$ site, which is stable with respect to anthophyllite, on cooling unmixes sufficient calcic clinoamphibole to place its composition in the stability field of anthophyllite. Recrystallization to anthophyllite should occur but since this would require a complete reconstitution of the crystal structure inversion is prevented and a displacive transformation to $P2_1/m$ cummingtonite proceeds.

In addition to the cummingtonite transition, we have also found a transition in pigeonite at higher temperatures. Morimoto and Tokonami (1969) and Smith (1969) predicted that a transition from $P2_1/c$ to $C2/c$ symmetry would occur in pigeonite at high temperatures and this has now been confirmed. This transition occurs in this pigeonite (Gunflint Iron Formation, $(Ca_{0.04}Fe_{0.78}Mg_{0.18})SiO_3$) at or slightly higher than 668°C and definitely below 675°C. This is a significantly lower temperature than was found by Smyth (1969) for the Ca-poor clinopyroxene.

APPLICATION OF MÖSSBAUER DETERMINATION OF CATION ORDERING IN A CROSSITE TO GEOTHERMOMETRY

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The crossite chosen for this work conformed to the alkali amphibole formula: $Na/Al_{2-x}Fe_x^{3+})(Mg_{3-y}Fe_y^{2+})Si_8O_{22}(OH)_2$ with $x=0.87$ and $y=1.35$. Assuming the recoil-free fractions to be the same in all sites, the Mössbauer spectra showed the Fe^{2+} to be distributed between (2) $M(1)$ and (1) $M(3)$ positions in the ratios 0.378:0.594. Within the sensitivity of the method, there was neither Fe^{2+} in M2 nor Fe^{3+} in $M(1)$ or $M(3)$. The ordering scheme agrees with that obtained by Papike and Clark.

Because of the short diffusion paths (measured in Ångstroms rather than meters), the cation distributions between sites within crystals are frozen in at a much lower temperature than the distributions between different crystals, so that intersite distributions are suitable for geothermometry only in minerals formed below about 750°K. The $M(1):M(3)$ distribution in glaucophanes formed near 550°K is thus a potentially useful geothermometer.

Observed site preference energies agree well with those calculated by Wood and Strens [abst. *Amer. Mineral.* **55,** 315 (1970)], and inspection of the calculated distribution isotherms suggests that the temperature of formation of a glaucophane could be found to be +25°C using site populations derived from Mössbauer spectra. The distribution coefficient is relatively insensitive to pressure and composition.

A REFINEMENT OF THE CRYSTAL STRUCTURE OF PARGASITE

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The crystal structure of pargasite ($a=9.910$ (1), $b=18.022$ (1), $c=5.312$ (1) Å; $\beta=105.78(1)°$; $C2/m$; Z=2; $\rho=3.209$ g/cc.) from Pargas, Finland, has been refined by three-dimensional Fourier and least-squares methods, using 974 intensities recorded with a single crystal x-ray counter-diffractometer and weighted to give constant $\overline{w\Delta^2}$ for groups of increasing F_{obs}'s. The formula unit $Na_{0.626}K_{0.302})(Ca_{0.996})_{2.0}(Mg_{0.651}Fe_{0.215}Al_{0.107}Ti_{0.018}Mn_{0.002})_{5.0}(Si_{0.767}Al_{0.233})_{8.0}O_{23.16-x}(OH)_{2x}F_{0.841}$ was obtained by normalizing an electron microprobe analysis to the density and the unit cell volume of the crystal.

The mean $T(1)$-O bond length of 1.677 Å compared to the mean $T(2)$-O bond length of 1.634 Å suggests a segregation of Al into the T (1) site, as might be expected with a nearly filled A site. Preliminary results indicate the following occupancies of the M-sites: M (1): Mg∼0.8, Fe∼0.2; M (2): Mg∼0.5, Al∼0.3, Fe∼0.2; M (3): Mg∼0.7, Fe∼0.3; M (4): Ca∼1.0.

Mean metal-anion distances of $M(1)$-(O, OH, F) = 2.089, $M(2)$-O = 2.036, $M(3)$-(O, OH, F) = 2.080 Å suggest that the $M(2)$ site contains Fe^{3+} in addition to Al^{3+}. The Ca ion in the $M(4)$ site is coordinated by eight oxygen ions with a range of Ca-O distances of less than 0.3 Å and mean Ca-O = 2.491 Å.

THE COMPOSITION FIELD OF ANTHOPHYLLITE AND THE ANTHOPHYLLITE MISCIBILITY GAP

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The limits of the composition field of anthophyllite under given metamorphic conditions are controlled both by crystal chemistry, and the compositions and relative free energies of competing phases. Wet chemical analyses of six orthorhombic amphiboles from metamophosed volcanic and related rocks from southwestern New Hampshire and adjacent Massachusetts demonstrate a solid solution series between anthophyllite, $R_2{}^{2+}R_5{}^{2+}Si_8O_{22}(OH)_2$, and gedrite, $Na_xR_2{}^{2+}(R_{5-y}{}^{2+}R_y{}^{3+})(Al_{x+y}Si_{8-x-y})O_{22}(OH)_2$, where Na occupies the otherwise vacant A site, $R_2{}^{+}=Mg+Fe^{2+}+Mn+Ca$, and $R^{3+}=Al+Fe^{3+}+(R^{2+}Ti^{3+})_{1/2}$. The relationship between the substitutions x (A site Na + K) and y (octahedral R^{3+}), the sum

SUBSTITUTIONS IN AMPHIBOLES

	(1) x	(2) y	(3) $x + y$	(4) $\overset{IV}{Al}$	(5) $(x + y) - \overset{IV}{Al}$	(6) $x/\overset{IV}{Al}$	(7) $x/(x + y)$
134I	.53	1.55	2.08	2.05	+.03	.26	.25
134JX	.32	1.37	1.69	1.60	+.09	.20	.19
138DX	.33	1.22	1.55	1.44	+.11	.23	.21
W95JX	.27	1.11	1.37	1.32	+.05	.20	.20
N30X	.18	.65	.83	.82	+.01	.22	.22
6A9X	.14	.64	.78	.68	+.10	.21	.18

of $x + y$, and tetrahedral Al is given in Table 1 calculated on the basis of 23 oxygens per formula unit exclusive of H_2O, F.

The residual value in column (5) indicates the extent to which the analysis deviates from the idealized formula. A positive residual could indicate an additional glaucophane-like or richterite-like substitution, analytical errors, or errors in the mode of calculation. Probably a negative residual can be due only to errors. For amphiboles that agree with the formula there could be great differences in the proportions of x and y, but columns (6) and (7) show a very limited range for the analyzed amphiboles and a ratio between A site occupancy and tetrahedral Al of 1/4 to 1/5. Based on crystal chemical reasoning, Papike, Ross and Clark (1969) predict that the maximum amount of Al that can substitute for Si in an amphibole structure is approximately two out of eight atoms per formula unit. If true, then sample 1341 is possibly an end member gedrite with the approximate formula:

$$Na_{0.5}R_2^{2+}(R_{3.5}^{2+}R_{1.5}^{3+})(Al_{2.0}Si_{6.0})O_{22}(OH)_2.$$

Reasonable published or recalculated structural formulae from 21 wet analyses of orthorhombic amphiboles and 12 partial electron probe analyses from the area under study, all with tetrahedral Al between 0.3 and 1.98, were evaluated as in the above table. Thirty-one have a residual in column (5) between +0.20 and −0.20. These show a mean in column (6) of 0.21 with 20 values between 0.28 and 0.18, and a mean in column (7) of 0.21 with 19 values between 0.28 and 0.17, again demonstrating a strong tendency toward a ratio of 1/4 or 1/4 or 1/5 between A site occupancy and tetrahedral Al with the charge deficiency of the tetrahedral Al compensated by octahedral Al, Fe^{3+}, and Ti^{4+}. Thus the single value for tetrahedral Al (or Si) gives a good indication of both x and y substitutions in anthophyllites, an apparent example of coupled substitutions. Analyses of 323 hornblendes treated in the same way give nearly identical results and suggest an end member composition $Na_{0.6}Ca_2(R_{3.6}^{2+}R_{1.4}^{3+})(Al_{2.0}Si_{5.0})O_{22}(OH)_2$.

In the New Hampshire and Massachusetts sillimanite zone rocks being studied anthophyllites with tetrahedral Al of 0.36 to 0.98 coexist with hornblende, cummingtonite, or both depending on the Fe/Mg ratio. Anthophyllites with tetrahedral Al of 1.32 to 2.05 coexist with cordierite, kyanite, sillimanite, staurolite, or garnet depending on the Fe/Mg ratio. Anthophyllites with intermediate values of tetrahedral Al would be expected in the middle of the anthophyllite field in assemblages lacking the other phases. The tetrahedral Al of 0.78 in

TABLE 2. CHARACTERISTICS OF INTERGROWN GEDRITE AND ANTHOPHYLLITE

	Tetrahedral Al	X-ray estimate % gedrite	Gedrite *b* in Å	Anthophyllite *b* in Å	Visible (010) lamellae
I34I	2.05	100	17.84		None
I34JX	1.60	100	17.81		Trace
I38DX	1.44	80	17.87	18.11	Pervasive
W95JX	1.32	80	17.76	17.89	Pervasive
N30X	0.82	50	17.84	18.04	Trace
6A9X	0.68	30	17.88	18.05	None
QB27C-2B	0.47[a]	20	17.81	18.00	None

[a] Electron probe analysis.

anthophyllite coexisting with cordierite at Orijarvi, Finland, shows the control exercised on the high Al limit of the anthophyllite field by the relative free energy of a competing phase.

Single crystal X-ray photographs of seven analyzed anthophyllites from New Hampshire and Massachusetts show that two appear to be homogeneous. The remaining five consist of fine to submicroscopic intergrowths of anthophyllite and gedrite that differ in their *b* crystallographic dimensions. Visual estimates of relative intensities of the two sets of X-ray reflections give an indication of the percent of exsolved gedrite as shown in Table 2. Some of the specimens contain visible lamellae parallel to (010). Specimen 138DX contains alternate lamellae about 0.2 μm thick and about 0.8 μm thick. The 0.2 μm lamellae have a slightly lower index of refraction and are probably anthophyllite in a higher index gedrite host. The size of the lamellae could be related to the ease of Al ordering in tetrahedral positions that is related to the amount of Al present.

The *b* dimension cannot be used directly to determine tetrahedral Al in the lamellae because it is strongly dependent on variable Fe content. Furthermore, the fractionation of iron between the two sets of lamellae is unknown. Assuming that all of these specimens underwent equilibrium exsolution under the same *P-T* conditions (five were collected within 3,000 feet of each other), a liner regression on the last six numbers in the first two columns gives approximate tetrahedral Al contents of the lamellae, 0.20 for the anthophyllite and 1.62 for the gedrite. These tetrahedral Al contents lie close to or even outside the limits of the anthophyllite field under conditions of coarse crystallization.

Recently Stout (1969) has reported two coexisting coarse orthorhombic amphiboles from Norway that must have crystallized at a temperature lower than the primary crystallization of the New Hampshire and Massachusetts anthophyllites and lower than the crest ~~of the~~ anthophyllite solvus. Their approximate tetrahedral Al contents of 0.3 and 1.4 suggest they crystallized at a higher temperature than the exsolution temperature of the New Hampshire and Massachusetts specimens and may suggest an asymmetrical solvus, steeper on the anthophyllite side than on the gedrite side.

If the anthophyllite solvus is mainly temperature dependent and the relative stability of competing phases such as cordierite is mainly pressure dependent, then the mutual interference of these two kinds of relations will produce an interesting array of topological facies types.

STRENGTH AND DEFORMATION BEHAVIOR OF HORNBLENDE

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Little experimental information exists on mechanical properties and deformation behavior of amphibole minerals. In a series of over 300 tests we surveyed the strength of amphibolite and single-crystal hornblende in Bridgeman-type opposed anvil equipment and in Griggs-type constant strain-rate apparatus at pressures to 70 kbar and temperatures to 1200°C.

In the range 400°–600°C, 10–15 kbar confining pressure, and at a strain rate of 10^{-5} sec^{-1}, strength of hornblende compressed parallel to "*c*" is 17 to 22 kbar. However, at 20 kbar, hornblende strength drops 40%. A second strength anomaly exists in tests near 800°C, at any confining pressure. Amphibolite is generally 30 to 100% weaker.

In room-temperature shear tests, deformation bands and lamellar twins are produced. Deformation twinning persists to higher temperature, possibly changing from a composition plane on (100) to (001) or ($\bar{1}01$). Well-developed kink bands are also present, the geometry of which suggests slip on (100). Deformation lamellae with characteristics identical to those in quartz or olivine have not yet been produced. However, complex lamellar features suggestive of glide on several subparallel planes appear in tests near the hornblende dehydration point.

CHEMICAL REACTIONS IN PYROXENE CRYSTALS

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The following generalizations concerning inclusions in pyroxenes are based on references from the literature and personal observations. The (001) lamellae in $C2/c$ Ca-rich clinopyroxenes such as augite are always uninverted $P2_1/c$ pigeonite. The failure of (001) pigeonite lamellae to invert to orthopyroxene is an anomaly in light or our present understanding of pyroxene phase relations. The (100) lamellae in $C2/c$ Ca-rich clinopyroxenes are usually orthopyroxene rather than pigeonite. Offset kinking of the (001) pigeonite lamellae where intersected by (100) orthopyroxene lamellae indicates that pigeonite was exsolved from the augite host prior to the exsolution of orthopyroxene. Pyroxene lamellae in an orthopyroxene host are always $C2/c$ Ca-rich clinopyroxene (100) lamellae. Blebby $C2/c$ Ca-rich clinopyroxene inclusions in "inverted pigeonite" generally are not crystallographically oriented with the host. Ilmenite and spinels of various compositions are common inclusions in clinopyroxenes and spinel inclusions are often observed within (100) orthopyroxene and (001) pigeonite lamellae in the $C2/c$ Ca-rich clinopyroxene host, suggesting a simultaneous unmixing of spinel and pyroxene phases. Inclusions of biotite and amphibole in clinopyroxenes appear to be quite common.

During cooling of crystals such as augites homogeneous equilibrium is generally maintained through redistribution of ions on various crystallographic sites to temperatures much lower than the temperature of crystallization, perhaps as low as 400–500°C (Virgo and Hafner, 1969). Also, generally, crystals as chemically complex as augites must also change in composition with falling temperatures in order to maintain internal equilibrium. If the crystal grains become essentially closed systems soon after crystallization and as such only *intra*granular reactions can take place then it is reasonable to expect the crystals to unmix other phases as well as to readjust site occupancies. In other words the augites become multiphase rocks through solid-state recrystallization and a new system of heterogeneous equilibria is set up. In the more general case a crystal grain may remain open to certain whole rock components such as H_2O, O_2 and K^+ and then react to form inclusions such as amphibole, oxides, or biotite.

STABILITY RELATIONS OF THE AMPHIBOLE MAGNESIOHASTINGSITE

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The high-temperature stability limit and the breakdown assemblages of magnesiohastingsite, $NaCa_2Mg_4Fe^{3+}Si_6Al_2O_{22}(OH)_2$, have been studied as a function of temperature, fluid (H_2O) pressure and oxygen fugacity, by hydrothermal and solid buffer techniques. Augite, olivine and nepheline are the major phases of the breakdown assemblage. Gehlenite (+melilite?) and magnetite are minor additional phases at respectively low (IQF buffer), and high (higher than NNO) oxygen fugacities. Substitution of octahedrally coordinated Fe^{3+} for Al in pargasite increases the maximum temperature at which the amphibole decomposes, making magnesiohastingsite the most refractory hydroxyl amphibole yet studied experimentally:

Buffer	P_f:	300 bars	500 bars	1000 bars
IQF		—	780° ± 15°C	>930°C
FMQ		860°C ± 7°	938° ± 5°C	—
HM		950°C ± 15°	(1020°C)	—
CuO—Cu_2O		>980°C	—	—
Paragasite		875°C	960°C	

Iron partitioning between olivine and augite varies with oxygen fugacity. Cell parameters, refractive indices, and Mossbauer absorption spectra of the breakdown products are consistent with the following compositional variation over the range 920–950°C, 250–700 bars:

Buffer	Augite (approx.)	Olivine
IQF	$Ca_{0.66}Na_{0.15}Mg_{0.99}Fe^{2+}_{0.10}Al_{0.10}Si_{1.75}Al_{0.25}O_6$	$Fo_{70}Fa_{30}$
FMQ	$Ca_{0.80}Na_{0.05}Mg_{0.90}Fe^{2+}_{0.05}Fe^{3+}_{0.05}Al_{0.15}Si_{1.65}Al_{0.32}Fe^{3+}_{0.03}O_6$	$Fo_{74}Fa_{26}$
HM	$Ca_{0.80}Na_{0.10}Mg_{0.80}Fe^{3+}_{0.10}Al_{0.20}Si_{1.60}Al_{0.30}Fe^{3+}_{0.10}O_6$	$Fo_{90}Fa_{10}$

Natural magnesiohastingsite is restricted to SiO_2-undersaturated rocks, reflecting the fact that its stability field would be much less extensive (judging by the synthetic high-temperature assemblages) in the presence of free silica. Typical occurrences are in aureoles of carbonatite complexes and as a major component in late-stage amphiboles occurring in rocks of the alkali-gabbro clan. Although magnesiohastingsite does not seem to be stable at liquidus temperatures in alkaline ultramafics because of attendant low oxygen fugacities, it is suggested that a late-stage melt enriched in alkalis, ferric iron and volatile constituents would react with early-formed olivine, pyroxene, ± melilite and feldspathoid to form hornblende close to the pargasite-magnesiohastings join, as is observed.

HIGH-TEMPERATURE SINGLE-CRYSTAL X-RAY STUDIES OF NATURAL ORTHOPYROXENES

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High temperature single crystal X-ray studies have been carried out on several natural orthopyroxenes of various compositions. Upon heating above 1000°C, two iron-rich orthopyroxenes ($En_{30}Fs_{70}$ and $En_{24}Fs_{76}$) inverted reconstructively to twinned high clinopyroxene (space group $C2/c$), which inverted displacively to low clinopyroxene (space group $P2_1/c$) on cooling. A more iron-rich sample ($En_{12}Fs_{86}Wo_2$) inverted directly to fayalite plus tridymite at $975° \pm 25°C$. No change was observed in a sample of composition $En_{70}Fs_{26}Wo_4$ when held at $1100° \pm 25°C$ for 72 hours.

Sample Bl-9 ($En_{30}Fs_{70}$) was heated to 1050° for 60 hours and gradually inverted to a high clinopyroxene of space group $C2/c$ twinned on $\{100\}$ with a complete reorientation of the crystallographic axes. The silicate chain axis of the new phase was inclined 30° to that of the orthopyroxene, indicating that the inversion required the breaking of silicon-oxygen bonds. Upon cooling, several sharp reflections of the type $h+k=2n+1$ appeared in the pattern of the clinopyroxene, indicating a displacive change of space group to $P2_1/c$. These reflections disappeared rapidly above 800°C but were again present in patterns taken below 700°C. Sample H-8 ($En_{24}Fs_{76}$) was observed to undergo very similar reactions, except that the inversion to high clinopyroxene occurred much more rapidly at 1050°C and gave rise to many smaller crystals of clinopyroxene of apparently random orientation.

THREE-AMPHIBOLE ASSEMBLAGES AND THEIR BEARING ON THE ANTHOPHYLLITE-GEDRITE MISCIBILITY GAP

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Electron microprobe data on the compositions of 2- and 3-amphibole assemblages in amphibolite facies rocks from Telemark, Norway are presented. All assemblages can be successfully projected through plagioclase and quartz in the system $MgO\text{-}FeO+MnO\text{-}Al_2O_3\text{-}CaO+Na_2O\text{-}SiO_2$ The compositions of coexisting anthophyllite and cummingtonite indicate that an anthophyllite solid solution extends to at least $mg = MgO/(MgO+FeO+MnO)\ 100 = 60.0$ mole percent from more magnesian compositions. Cummingtonite ($mg = 57.2$) coexisting with gedrite ($mg = 55.2$) from another compositional layer in the same outcrop further indicates that the anthophyllite series is restricted to compositions more magnesian than that tieline. A close examination of the assemblage revealed a small amount of optically distinct anthophyllite intergrown as irregular patches and lamellae within and around gedrite. Contacts with the slightly pleochroic gedrite are sharp and easily resolved with high magnification and an intense light source. Microprobe data on the anthophyllite where in contact with gedrite and within 0.5 millimeters of coarse cummingtonite gives $mg = 59.5$ mole percent. In the absence of any evidence for a higher temperature event in the surrounding assemblages, a reasonable interpretation is that the three amphiboles represent an equilibrium assemblage formed at the peak of regional metamorphism. If that is the case, then the anthophyllite in the assemblage is the most Fe-rich possible that can coexist with plagioclase and quartz at this grade. The assemblage is also useful in that it restricts the stable occurrence of the pair anthophyllite-gedrite to more magnesian bulk compositions.

Additional information on the compositional range of the anthophyllite-gedrite miscibility gap is provided by the assemblage anthophyllite-gedrite-hornblende. Anthophyllite ($mg=69.6$) is homoaxially intergrown with gedrite ($mg=64.9$), and both occur in mutual contact with blue-green hornblende. Depending on the ferric component in hornblende and gedrite, the three-phase region in projection can have two possible configurations, each providing further compositional constraints on the stable occurrence of the orthorhombic phases.

STRUCTURAL INTERPRETATION OF THE INFRARED ABSORPTION SPECTRA AND OPTICAL PROPERTIES OF GLAUCOPHANE AND RELATED MINERALS

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Infrared spectra of 14 natural glaucophanes and crossites, three crocidolites, and three riebeckites have been analysed using modern computing techniques. In glaucophane (II) and crossite, there is little Fe^{3+} in ($M(1)$, $M(3)$ or alkali in the A-site. In crocidolite and riebeckite, there are variable amounts of Fe^{3+} in $M(1)$, $M(3)$ and alkali in the A-site. Synthetic rossite (I) was found to be deficient in hydroxyl, and it is probably "off composition" in other respects. It is shown that the infrared method of determining site populations in alkali amphiboles is at best semi-quantitative for Fe^{2+} in $M(1)$, $M(3)$, and merely qualitative for Fe^{3+} in $M(1)$, $M(3)$ and alkali in the A-site.

The remarkable color and pleochroism of the alkali amphiboles is attributed to the presence of two $Fe^{2+}\rightarrow Fe^{3+}$ charge-transfer bands at 2.0 and 2.3 eV for light polarized in the *bc* plane. A quantitative treatment of the pleochroism is proposed, which relates the absorption intensity $\|a^*$, b and c to the Fe^{2+} and Fe^{3+} contents of the $M(1)$, $M(2)$ and $M(3)$ positions. The rapid changes in the indicatrix orientation as Fe^{3+} replaces Al have been correlated with the distortion of the $M(2)$ octahedron, whilst the crossed dispersion depends on the combined effects of the gross structure and the distortion of the $M(2)$ octahedron.

VISIBLE-REGION ABSORPTION SPECTRA OF (FE, MG) PYROXENES AND AMPHIBOLES

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We have calculated the 3*d*-orbital energy levels of the Fe^{2+} ion in all the important ferromagnesian silicates for which adequate structural data are available. Among pyroxenes and amphiboles, the calculations cover the octahedral sites in orthopyroxene ($M1$), $M(2)$, clinopyroxene (Ca and Mg sites), cummingtonite, $M(1)$, $M(2)$, $M(3)$, $M(4)$, and glaucophane, $M(1)$, $M(2)$, $M(3)$. The results have enabled unequivocal assignments of the *d-d* absorption bands to be made for all these minerals. Agreement between observed and calculated band energies is typically 200 wavenumbers or better, and we have been able to account for the relative intensities and polarizations of the absorption bands in most cases. It is usually easy to distinguish charge-transfer bands from the *d-d* transitions.

Apart from their use in spectroscopic work, knowledge of the energy levels enables us to calculate the crystal field stabilization enthalpy, and the entropy contribution from the 3*d*-electrons, which are used in calculating site preference energies (abstract A), and also the Mossbauer quadrupole splittings and their temperature variation. The extent of relaxation around large substituent ions (*e.g.* Fe^{2+} replacing Al or Mg) can often be inferred by comparing observed and calculated crystal-field splittings. Interpretation of magnetic data is also simplified.

PHASE RELATIONS OF SYNTHETIC MG-FE-CA PYROXENES

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Clinopyroxenes have been synthesized with compositions on the following joins in the system $MgSiO^3$-$FeSi{:}^3$-$CaSiO^3$:

(a) $Mg_{0.5}Ca_{0.5}SiO_3$-$Fe_{0.5}Ca_{0.5}SiO_3$
(b) $Mg_{0.6}Ca_{0.4}SiO_3$-$Fe_{0.6}Ca_{0.4}SiO_3$
(c) $Mg_{0.4}Fe_{0.1}Ca_{0.5}Si_3$-$Mg_{0.8}Fe_{0.2}SiO_3$
(d) $Mg_{0.35}Fe_{0.15}Ca_{0.5}SiO_3$-$Mg_{0.7}Fe_{0.3}SiO_3$
(e) $Mg_{0.25}Fe_{0.25}Ca_{0.5}SiO_3$-$Mg_{0.5}Fe_{0.5}SiO_3$
(f) $Mg_{0.2}Fe_{0.3}Ca_{0.5}SiO_3$-$Mg_{0.4}Fe_{0.6}SiO_3$

These synthetic materials are Augites for compositions with Wo>30 mol % and pigeonites for Wo<30.

The liquidus surface ($P=1$ atm) has a large central crystal field of clinopyroxene, which may be divided into "augite" and "pigeonite". The boundary between these two fields is a thermal trough which descends from the magnesium-rich side to the iron-rich side at approximately constant calcium content (Wo $=33$). The liquidus also has fields of olivine, in the "En" corner; tridymite, in the "Fs" corner; and wollastonite, in the $CaFeSi_2O_6$ corner.

The solidus surface is planar in the central (clinopyroxene) portion of the system, where it is intersected by a two-pyroxene solvus. At $P=1$ atm, these two pyroxenes are augite+pigeonite. The latter is probably metastable. At $P=20$ kbar, the solvus of augite+orthopyroxene does not intersect the solidus. The closure of this solvus (consolute $T\approx 1000$°C) is due to the expansion of the stability field of augite (decreased content of Ca) with temperature, because of composition of the orthopyroxene remains at Wo ≈ 8 mole percent for temperatures 800 to 950°C.

ORDER-DISORDER OF FERROUS IRON AND MAGNESIUM IN PYROXENES

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The Fe^{2+}, Mg distribution over the octahedrally coordinated sites $M(1)$ and $M(2)$ in orthopyroxenes with compositions close to the system $Fe_xMg_{1-x}SiO_3$ was investigated at different temperatures and pressures in the orthorhombic phase field. Fe^{2+} distribution and site occupancy numbers were obtained from the electric quadrupole splittings of Fe_{57} at $M(1)$ and $M(2)$ determined from nuclear gamma ray resonant absorption spectra taken at liquid nitrogen temperature. The analysis of nine orthopyroxenes equilibrated at 1000°C revealed that in the region $0 \leq x < 0.6$ the site occupancy is in agreement with the assumption of ideal Fe^{2+}, Mg distribution at each site. The experimental data can therefore be interpreted by simple thermodynamical considerations.

The distribution equilibrium constant was determined for 1000°C, and approximately determined for 800, 700, 600, and 500°C. Fe^{2+}, Mg disordering apparently reaches a partially disordered steady state at about 1000°C. No further disorder could be observed in orthopyroxenes by heating at temperatures higher than 1000°C. At about 480°C, ordering is quenched, and no further ordering appears to occur at lower temperatures even within geological times. Between 500 and 1000°C the standard free energy difference $\Delta G°/$ for Fe^{2+}, Mg exchange between $M(1)$ and $M(2)$ is apparently constant: 3.6 kcal per mole [formula unit $(Fe,Mg)Si_2O_5$].

From kinetic experiments with an orthopyroxene $x=0.574$, the rate constants for disordering at 500°C, and at 1000°C were estimated. The average activation energy for disordering is about 20 kcal per mole and that for ordering about 15–16 kcal per mole.

In the region $0.7 > x \geq 1$, the Fe^{2+}, Mg equilibrium distribution isotherm at 1000°C exhibits a marked, well-defined deviation from ideal solution. No effect of pressure on the distribution could be detected.

It is concluded that the Fe^{2+}, Mg exchange between the octahedral sites in orthopyroxenes is a rapid process characterized by small energy barriers. In fact, the activation energies for ordering and disordering are considerably lower than those for Al, Si exchange between tetrahedral sites in feldspars. Consequently, orthopyroxenes in metamorphic rocks are generally expected to exhibit equilibrated distributions. Rapidly cooled orthopyroxenes in volcanic rocks, however, may have metastable distributions, the critical range for the cooling rate between 600 and 500°C.

MELTING CURVES OF SOME PYROXENES

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The melting of several pure pyroxenes has been investigated by differential thermal analysis and quenching techniques to approximately 55 kbar in piston-cylinder apparatus. After correcting the raw data for frictional losses and for the effect of pressure on the thermocouple emf, our results lie at higher temperatures at high pressure than previously published melting curves. When the melting temperature at high pressure is plotted against the isothermal compression of the solid phase at the same pressure, these results give much straighter lines than those from previous work.

CALCULATION OF SITE PREFERENCE ENERGIES AND CATION DISTRIBUTIONS IN (FE, MG) AMPHIBOLES AND PYROXENES FROM STRUCTURAL DATA

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Given accurate modern structure data, it has been found possible to calculate the site preference energies (*SPE*) of Fe^{2+} in ferromagnesian silicates, including several amphiboles and pyroxenes. The results have been used to calculate the distribution of Fe^{2+} and Mg between sites within crystals, and between different phases, as a function of temperature, pressure and composition. We start by writing:

$$SPE=(\Delta H_{\mathrm{el}}+\Delta H_{\mathrm{latt}}+P\Delta V_{\mathrm{exch}}-T\Delta S_{\mathrm{el}}+C)$$

where H_{el} and S_{el} are the enthalpy and entropy contributions from the 3*d* electrons of Fe^{2+}, H_{latt} is the sum of Madelung and strain-energy terms, ΔV_{exch} is the volume change associated with the exchange of one gram ion of Fe^{2+} between sites or phases, and C is a constant (small compared with ΔH_{el} or ΔH_{latt}) required to fit observed and calculated distributions: often C may be taken as zero, *i.e.* the *SPE* calculated from the atomic coordinates alone is sufficiently accurate. The electronic terms are calculated from the crystal-field splittings (Strens and Wood, abstr. above), whilst the H_{latt} terms are obtained from simple lattice sums.

So far, we have succeeded in reproducing the observed intersite distributions in glaucophane ($M(1):M(3)$, cummingtonite ($M1+M3:M2:M4$) and orthopyroxene ($M1:M2$) assuming that $C=0$. We can also account for the distribution of Fe^{2+} between such minerals pairs as olivine orthopyroxene, olivine-clinopyroxene and orthopyroxene-clinopyroxene.

Comparison of observed and calculated distributions suggests that intersite distributions are frozen in at a much lower temperature than equilibria between different crystals. Quantitative treatment is consistent with an activation energy for diffusion of Mg of 60 kcals, and freezing of the intersite distributions at about 750°K during slow cooling of metamorphic rocks or large intrusions.