

Temperature, Pressure and Composition: Structurally Analogous Variables

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Abstract. Changes in temperature, pressure and composition cause changes in the ratios of polyhedral sizes in oxygen-based minerals. Polyhedra with large, high-coordination, low-valence cations expand and compress more than polyhedra with small, low-coordination, high-valence cations. Changes in cation composition alter the ratios of polyhedral sizes by changing mean cation radii. Thus temperature, pressure and composition are structurally analogous variables. Since temperature, pressure and composition change structures in similar ways, it is possible to construct isostructural surfaces in $P-T-X$ space. For structures in which stability is limited to specific ranges of polyhedral size ratios (e.g. octahedral-tetrahedral layers in mica), certain $P-T-X$ isostructural surfaces may coincide with phase boundaries. If geometrical constraints on mineral stability are known, then phase equilibria may be predicted. Examples of stability limit calculations are given for several major oxygen-based mineral groups.

Introduction

Solid-solid transformations are among the most important, yet least predictable phenomena in mineralogy. Although thousands of such transformations are known, it has seldom proven possible to predict *a priori* the exact temperature and pressure at which a given structure of a given composition will transform. As the body of experimental data grows, both on phase equilibria and on mineral structures, it appears that many mineral phase transformations are in part geometrically controlled. An understanding of the limiting polyhedral geometries, combined with a knowledge of structural changes resulting from continuous variation of temperature, pressure and composition, thus provides a key to the prediction of a group of solid-solid phase boundaries.

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This study will first review how oxygen-based mineral structures vary continuously with changes in temperature, pressure and composition. Mineral structures will be treated as arrangements of cation-oxygen polyhedra, and variations in the sizes of these polyhedra will provide the basis for defining structural changes. These concepts will then be applied to minerals with known or suspected geometrical limits of stability to illustrate the prediction of phase boundaries from basic structural data.

Hazen and Prewitt (1977) have demonstrated several systematic relationships between metal-oxygen polyhedral thermal expansion and compression, and simple polyhedral bonding parameters. Specifically:

$$\bar{\alpha} = 32.9 (0.75 - z/p) \times 10^{-6} \text{ } ^\circ\text{C}^{-1}, \quad (1)$$

and

$$\bar{\beta} = 37.0 (d_0^3/z) \times 10^{-6} \text{ kbar}^{-1}, \quad (2)$$

where $\bar{\alpha}$ is the mean polyhedral linear thermal expansion between 23° and 1000° C, $\bar{\beta}$ is the mean polyhedral linear compression between room pressure and 100 kbar, z is the cation charge, p is the cation coordination number, and d_0 is the 23° C, 1 atm, metal-oxygen mean polyhedral bond distance. Thus, mean polyhedral thermal expansion is a simple function of bond strength (z/p), and mean polyhedral compression is simply related to a kind of polyhedral charge density (z/d_0^3). The forms of these empirical relationships are in agreement with theoretical predictions by Megaw (1971) and Cameron et al. (1973) for thermal expansion, and with Anderson and Anderson (1970) and Huggins (1974) for compression.

These two simple equations allow the prediction of expansion and compression behavior for any cation-oxygen polyhedron, because valence, coordination number, and metal-oxygen distance are known (metal-oxygen distance may be calculated from ionic radii of Shannon and Prewitt, 1969, and Shannon, 1976). Because the mean expansions and compressions of polyhedra are known, the structural changes of any oxygen-based mineral with temperature and pressure may also be specified. Qualitative predictions of structural variations may be made by inspection of the differing expansion or compression rates of different component polyhedra, and quantitative predictions are also possible using the Distance Least Squares technique (see Dempsey and Strens, 1976).

The Structural Analogy of Temperature and Pressure

It is not obvious from Equations (1) and (2) that there are any simple relationships between $\bar{\alpha}$ and $\bar{\beta}$. However, a plot of $\bar{\alpha}$ vs. $\bar{\beta}$ for many types of polyhedra (see Fig. 1) does reveal some useful information. It is first necessary to make an assumption: it is assumed that if $\bar{\alpha}/\bar{\beta}$ is the same for all polyhedra in a mineral, then the reduction in volume during cooling from high temperature will take place in the same structural way as the reduction of volume during compression. In other words, if $\bar{\alpha}/\bar{\beta}$ is constant for a group of polyhedra, then the ratios of polyhedral sizes will change in the same way for cooling or compression. It is clear from

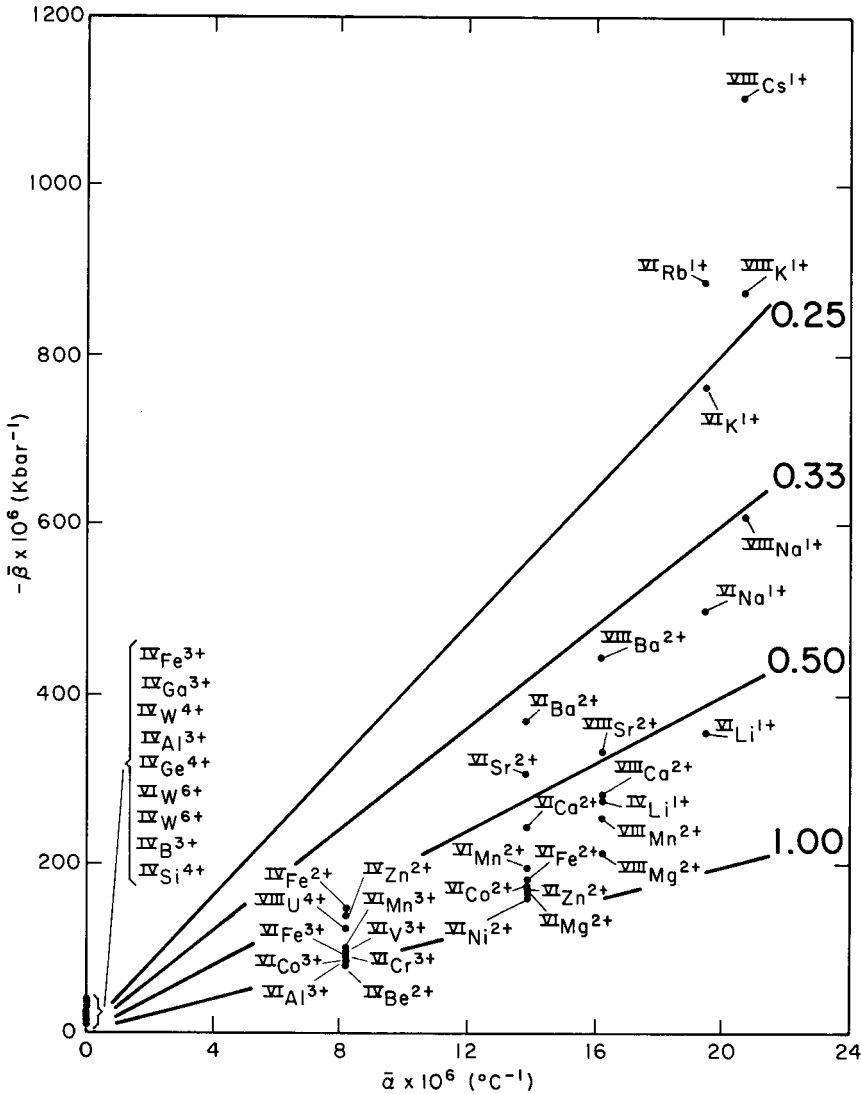


Fig. 1. Mean polyhedral thermal expansion ($\bar{\alpha}$) versus mean polyhedral compression ($\bar{\beta}$) for metal-oxygen polyhedra. Lines are loci of constant $\bar{\alpha}/\bar{\beta}$, with slopes ($\times 10$) in boldface numbers to the right. If all component polyhedra of a mineral lie along such an origin-containing line then structural changes on cooling will be similar to structural changes on compression. Cations are given in the form ${}^pR^z$, where z is the cation charge and p is the coordination number

Figure 1 that many important minerals have the same $\bar{\alpha}/\bar{\beta}$ ratio for all component polyhedra and thus will display this “inverse relationship” between thermal expansion and compression.

Any simple oxide (i.e. an oxide with only one type of cation polyhedron) will demonstrate the inverse relationship, and structural changes during cooling and

during compression will occur in the same way. Simple silicates, with only one type of polyhedron other than Si tetrahedra, will also show this behavior, because the Si tetrahedra are inert structural elements (they neither expand nor compress over the T - P range considered). Forsterite, enstatite, wollastonite, and kyanite represent examples of such simple silicates; in each, octahedral cations change size with changes in pressure and temperature, while silicon polyhedra are rigid.

Al-O bonds in tetrahedral coordination, as well as Si-O bonds, undergo little expansion or compression, so minerals with Si-Al tetrahedral groups plus one other cation polyhedron will also demonstrate the inverse relationship. Feldspar, feldspathoids, and many zeolites and layer silicates are among such minerals. Once again, the tetrahedra are rigid, while the less-tightly-bonded cations expand or compress. From Figure 1 it appears that most minerals in the systems SiO_2 - Al_2O_3 - Fe_2O_3 - MgO - FeO and SiO_2 - Al_2O_3 - K_2O - Na_2O - CaO have the inverse relationship. In all such minerals temperature and pressure are analogous variables; cooling from high temperature has the same effect on structure as compression. Furthermore, there will exist lines of constant structure in the P - T plane, since any structural change caused by a variation in pressure may be offset by an appropriate change in temperature.

This inverse relationship does not hold precisely for many oxygen-based minerals. For example, in minerals with coexisting transition metal and alkali metal cations, the ratio of expansion to compression is greater for the transition element polyhedron: $(\bar{\alpha}/\bar{\beta})_{\text{transition}} > (\bar{\alpha}/\bar{\beta})_{\text{alkali}}$. However, even in these minerals the inverse relationship is qualitatively correct, since alkali cation polyhedra expand or compress significantly more than transition cation polyhedra during a given change in T or P , whereas Si-Al tetrahedra do not change size or shape. The extent to which a mineral deviates from the precise inverse relationship between expansion and compression may be ascertained by noting the deviation of polyhedral points from an origin-containing line in Figure 1.

The Structural Analogy of Composition to Temperature and Pressure

Continuous changes of a mineral's cationic composition, as with continuous changes in temperature and pressure, will cause systematic variations in polyhedral sizes. In simple binary oxide solid solutions (e.g. $(\text{Mg}, \text{Fe})\text{O}$; $(\text{Na}, \text{K})_2\text{O}$; etc.) the substitution of a smaller cation has the same effect on structure as an increase in pressure or a decrease in temperature (assuming a disordered cation arrangement). The same is true for silicates such as $(\text{Mg}, \text{Fe})_2\text{SiO}_4$; $(\text{Al}, \text{Fe}^{3+})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$; and $(\text{Na}, \text{K})\text{AlSi}_3\text{O}_8$. In these minerals changes in pressure, temperature or composition vary the size of the large cation polyhedron, while tetrahedra remain rigid. Any change in large-polyhedron composition causes a structural change, which may be offset by a change in temperature or pressure or a combination of both. Thus there exists in P - T - X space a family of isostructural surfaces, analogous to the isostructural lines of the P - T plane.

Isostructural P - T - X surfaces will have several features common to all oxygen-based minerals. For example, $(dT/dP)_\diamond$ of these surfaces will almost always

be positive, since cooling has the same net effect as squeezing.¹ The slope $(\partial T/\partial P)_\diamond$ of isostructural surfaces for minerals in the system $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{MgO} - \text{FeO}$ (e.g. olivines, pyroxenes, garnets) will be less than $(\partial T/\partial P)_\diamond$ for minerals in the system $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{CaO} - \text{Na}_2\text{O} - \text{K}_2\text{O}$ (e.g. feldspars, feldspathoids). This is because pressure, when compared to temperature, has a relatively greater effect on alkali cation polyhedra than on transition cation polyhedra.²

The slopes $(\partial P/\partial X)_\diamond$ and $(T/\partial X)_\diamond$ depend on the nature of the cation substitution. If the substitution takes place in the largest polyhedron, and the substituting cation is the larger (i.e. K for Na in alkali feldspar), then $(\partial P/\partial X)_\diamond$ will be positive and $(\partial T/\partial X)_\diamond$ will be negative. If, however, the substitution takes place in the smallest polyhedron and the substituting cation is the larger (i.e. Ge for Si in alkali feldspar) then $(\partial P/\partial X)_\diamond$ will be negative and $(\partial T/\partial X)_\diamond$ will be positive.

Geometrically-Constrained Structures and the Prediction of Mineral Stability

The stability of many minerals is limited by geometrical packing restrictions on adjacent groups of ions or polyhedra. In these minerals it is the ratios of ionic radii or polyhedral sizes that must be considered. Since variation in temperature or pressure or composition all have an effect on ionic radii and polyhedral size ratios, it is not surprising that all three variables influence mineral stability. The nature of bond-distance variation with temperature, pressure, and composition has been established above, so if critical limits of ionic radii or polyhedral size ratios are known then mineral stability can be predicted. The prediction of mineral stability limits, based on isostructural $P-T-X$ critical surfaces, is illustrated with several examples below.

In the examples which follow, several assumptions have been made to simplify calculations. It has been assumed that the effects of temperature on compressibility and the effects of pressure on thermal expansion are negligible. This is true to a first approximation for many silicates. It has also been assumed that thermal expansion is independent of temperature, and compressibility is independent of pressure. These assumptions are generally not valid at high temperature and pressure, since mean polyhedral compression decreases at high pressure and mean polyhedral thermal expansion increases at high temperature. For most polyhedra, quadratic equations in P or T are sufficient to define $\bar{\beta}$ or $\bar{\alpha}$. The use of average values of $\bar{\alpha}$ and $\bar{\beta}$ in the following discussions may therefore be modified for more precise calculations in the future.

¹ The symbol \diamond will be used to indicate structure as a constant in partials. Note that

$$(\partial P/\partial T)_\diamond = (\partial P/\partial T)_V = -\alpha_p/\beta_T,$$

which is positive for minerals, except for a few Si-rich substances with α_p slightly negative or zero (e.g. β quartz)

² In fact, given the average geothermal gradient of 15°/km, minerals in the system $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{MgO} - \text{FeO}$ will expand slightly with increasing depth, while feldspars and feldspathoids compress significantly at depth in the earth. Since the structures of Mg-Fe olivine, pyroxene, and garnet are little-changed along the average $P-T$ gradient of the earth, it is not surprising that these minerals are stable deep within the earth

The Sheet Silicates: Breakdown of the Talc-like Layer

A basic structural feature common to many sheet silicates is an octahedral layer sandwiched between two tetrahedral layers. The composition of both layers is variable: the tetrahedral layer is predominantly Al and Si, while numerous cations may enter the octahedral layer. The stability of these sheet silicates is limited by the fit of adjacent octahedral and tetrahedral layers (Hazen and Wones, 1972). Since individual Al and Si tetrahedra neither expand nor compress with changing temperature or pressure, the angles between tetrahedra must change to allow the tetrahedral layers to conform with the changing size of the octahedral layer (i.e. tetrahedral rotation). However, if the octahedral layer becomes too large then the tetrahedral layers can no longer rotate, and the sheet silicate will become unstable. The critical ratio of mean tetrahedral to mean octahedral metal-oxygen distance is $d_t/d_o = 0.784$.³ If d_t/d_o is less than 0.784 then the sheet silicate must be unstable. The mean tetrahedral metal-oxygen distance can be increased by increasing the Al/Si ratio, while the octahedral distance d_o may be decreased by substitution of smaller cations. The coupled substitution $\text{MgSi} \rightarrow \text{AlAl}$ will accomplish both changes at once, and thus will stabilize a sheet silicate near its critical structure. An increase in pressure or a decrease in temperature will also increase d_t/d_o and stabilize the talc-like layer sandwich.

For a given Al/Si ratio, d_t is fixed. Therefore, the critical size of the octahedral layer, d_o , is also fixed, and the stability field of the sheet silicate will be limited by a $P-T-X$ surface of constant d_t and d_o . In talc, which is composed of repeated tetrahedral-octahedral-tetrahedral layer sandwiches, this $P-T-X$ surface will also be an isostructural surface. However, in the micas and chlorites only the three-layer subunits will be isostructural units, while the interlayer cations will generally vary in size along the critical $P-T-X$ surface. (This is because $(\bar{\alpha}/\bar{\beta})_{\text{interlayer cation}} \neq (\bar{\alpha}/\bar{\beta})_{\text{octahedral cation}}$.)

The stability limit of a talc-like layer may be calculated given d_t , d_o and the expansion and compression coefficients of the octahedral cations. For example, phlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$) has $d_t = 1.649$, and $d_o = 2.064 \text{ \AA}$ (Hazen and Burnham, 1973), while for ${}^{\text{VI}}\text{Mg}^{2+}$, $\bar{\alpha} = 13.8 \times 10^{-6} \text{ C}^{-1}$ and $\bar{\beta} = 163 \times 10^{-6} \text{ kbar}^{-1}$ (from equations 1 and 2). The critical value of d_o is $1.649/0.784 = 2.103 \text{ \AA}$, thus giving an equation for the critical $P-T$ curve for phlogopite:

$$2.064(1 - 0.000163 P + 0.0000138 T) = 2.103,$$

or

$$T = 11.81 \cdot P + 1370. \quad (3)$$

Phlogopite will be geometrically unstable at room pressure and temperatures above 1370°C . Furthermore, each pressure increase of 10 kbar will raise the critical temperature by 118°C . These are maximum stability limits; other phase regions

³ The critical value of d_t/d_o is obtained as follows. As demonstrated by Hazen and Wones (1972) $\cos \alpha = b_m/4 \sqrt{2} d_t$, where α is the tetrahedral rotation angle, b_m the b cell dimension, and d_t tetrahedral metal-oxygen distance. Also, $b_m = 3 \sqrt{3} d_o \sin \psi$, where ψ is a measure of octahedral flattening, and is usually about 59° . Thus, at the critical limit of stability when $\alpha = 0^\circ$,

$$1 = b_m/4 \sqrt{2} d_t = 3 \sqrt{3} d_o \sin 59^\circ/4 \sqrt{2} d_t, \quad \text{and} \quad d_t/d_o = 0.784$$

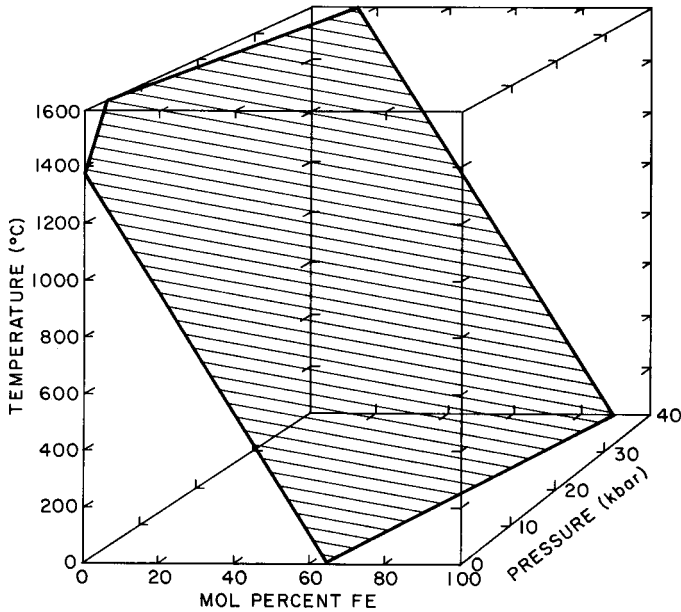


Fig. 2. Predicted geometrical stability limit for trioctahedral micas of the form $K(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$. The P - T - X surface is calculated on the basis of 0° tetrahedral rotation angle

intersect the critical P - T line and phlogopite is not in fact stable under these extreme conditions.

The equation for a critical P - T - X surface may be derived in the same way. Consider micas of the form $K(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$. The value of d_t is still 1.649 \AA ; d_o is a function of composition, $d_o = 2.064 + 0.06 \cdot X_{\text{Fe}}$; $\bar{\alpha}$ is still $13.8 \times 10^{-6} \text{ C}^{-1}$; $\bar{\beta}$ is also a function of composition which may be approximated by $\bar{\beta} = (163 + 14 \cdot X_{\text{Fe}}) \times 10^{-6} \text{ kbar}^{-1}$, where X_{Fe} is the octahedral mole fraction of iron. The resulting equation, analogous to Equation (3) above, is:

$$(2.064 + 0.06 X_{\text{Fe}}) [1 - (0.000163 + 0.000014 X_{\text{Fe}}) P + 0.0000138 T] = 2.103,$$

or

$$T \cong 11.8 \cdot P - 2105 \cdot X_{\text{Fe}} + 1370, \quad (4)$$

eliminating the negligible $X_{\text{Fe}} P$, $X_{\text{Fe}} T$, and $X_{\text{Fe}}^2 P$ terms. This isostructural limiting P - T - X surface for (Mg, Fe) trioctahedral micas is illustrated in Figure 2. Several important aspects of mica stability are apparent from this figure. At room conditions, micas of the form $K(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ with greater than $0.65 X_{\text{Fe}}$ are not stable. Such micas have too large an octahedral cation radius for the AlSi_3 tetrahedral layer. In nature, micas with greater than 65% Fe in the octahedral layer are known, but these are invariably Al-rich, with aluminum substituting in both octahedral and tetrahedral layers. A second aspect of Figure 2 worth noting is that $(\partial P / \partial T)_\diamond$ is approximately $12^\circ/\text{kbar}$, which is considerably less than the average crustal geothermal gradient. Thus, if a mica is unstable at surface conditions it will likely be unstable at depth. Furthermore, most micas which are

stable under near-surface conditions will not be stable at depths greater than several tens of kilometers.

Pyroxenes and amphiboles have chain geometries that are closely related to the three-layer sandwich of talc and mica. In both chain silicates groups of octahedra are between two linear groups of tetrahedra. As in the sheet silicates, there are octahedral expansion limits, beyond which the tetrahedral-octahedral-tetrahedral chains are unstable. As with the trioctahedral micas, pyroxenes and amphiboles will approach their critical structures at depth in the earth. The formation of aluminous pyroxenes at high temperatures and pressures is well documented (e.g. Wyllie, 1971). The substitution of ${}^{\text{IV}}\text{Al}{}^{\text{VI}}\text{Al}$ for ${}^{\text{VI}}\text{Mg}{}^{\text{IV}}\text{Si}$ has the same effect on pyroxene stability that it had on mica stability, namely to increase the size of tetrahedral groups while decreasing the size of octahedral groups, and thus stabilize the mineral.

Reversible Monoclinic-To-Triclinic Transformations in the Alkali Feldspars

Disordered monoclinic albite (monalbite) transforms reversibly to a triclinic form (high albite) at temperatures below 1100°C due to collapse of the Al-Si framework about the alkali site (Prewitt et al., 1976). The transformation temperature decreases with increasing K/Na ratio, and at room temperature metastable disordered alkali feldspars more potassic than $\approx\text{Or}_{38}$ are monoclinic (high sanidine). Since changes on compression are similar to those on cooling from high temperature, it was predicted that high sanidine should transform to a triclinic form, analogous to high albite, at elevated pressure, with higher pressures required for more potassic alkali feldspars. This transformation was then observed for Or_{67} at 12 kbar and for Or_{82} at 18 kbar. Furthermore, it was demonstrated that unit-cell parameters at the monoclinic-to-triclinic transformation were independent of composition. For albite at 1100°C , Or_{38} at room conditions, Or_{67} at 12 kbar, and Or_{82} at 18 kbar the critical monoclinic cell dimensions are all $a=8.30$, $b=12.96$, $c=7.15$ Å, and $\beta=116.1^{\circ}$ within experimental error (Hazen, 1976a).

The constancy of unit-cell dimensions at the reversible transition implies that this is a structurally-controlled event. The size of individual tetrahedra within the Al-Si framework do not change, but the angles between tetrahedra do change to accommodate the varying size of the alkali cation site. If the alkali site is sufficiently large the framework will maintain monoclinic symmetry. However, if the alkali site drops below the critical size, either by cooling or compression or sodium substitution, the framework will collapse to triclinic symmetry. Based on this model Hazen (1976a) predicted stability limits for $(\text{K}, \text{Na})\text{AlSi}_3\text{O}_8$ monoclinic and triclinic forms.

The Olivine-Spinel Transformation

Kamb (1968) described the olivine-spinel transformation as a geometrically-controlled event.⁴ The olivine structure was shown to be stable when d_o/d_t (the

⁴ Olivine and spinel are essentially close-packed oxides with six-coordinated R^{2+} and four-coordinated R^{4+} . A significant difference in polyhedral packing of these two structures is the number and type of shared edges; the greater number of $\text{R}^{2+}-\text{R}^{2+}$ shared edges in spinel allows the close approach of more octahedral cations in that structure. Thus, spinel is the denser form

ratio of mean octahedral to mean tetrahedral metal-oxygen distance) was greater than a critical value. In olivines of the form $R_2^{2+}GeO_4$ Kamb noted that the critical value was between 1.15 and 1.22. Insufficient data was available to determine d_o/d_t for the silicate olivine-spinel inversion, but forsterite ($d_o/d_t = 1.30$) and fayalite (1.33) are well within the olivine field.

Assuming a critical value of $d_o/d_t = 1.20$ for Mg_2GeO_4 it is possible to reproduce the magnesium germanate olivine-spinel transformation $P-T$ curve, using the same procedure outlined in the sheet silicate section above. For Mg_2GeO_4 : $d_t = 1.780 \text{ \AA}$; $d_o = 2.110 \text{ \AA}$; $\bar{\alpha} = 1.38 \times 10^{-6} \text{ C}^{-1}$ and $\bar{\beta} = 174 \times 10^{-6} \text{ kbar}^{-1}$. Since d_t is fixed, the critical octahedral size is also fixed at $d_{o, \text{critical}} = 2.135 \text{ \AA}$.

The $P-T$ transition curve is thus:

$$2.110(1 - 0.000174 P + 0.0000138 T) = 2.135,$$

or

$$T = 12.6 P + 859. \quad (5)$$

This compares well with the experimentally determined curve of Dachille and Roy (1960) of $T = 24.0 \cdot P + 810$; presumably agreement with experimental values would be even better if the effects of temperature on thermal expansion were included.

It is possible to determine d_o/d_t at the olivine-spinel transition for silicates using the known stability field of Mg_2SiO_4 . The $P-T$ stability equation of forsterite is approximately $T = 16P - 1400$ (Wyllie, 1971, Fig. 6-14). Since $d_t = 1.649$ and d_o at room conditions is 2.110 \AA (Hazen, 1976b), and $\bar{\alpha}$ and $\bar{\beta}$ for Mg_2SiO_4 are 0.0000138 C^{-1} and $0.000174 \text{ kbar}^{-1}$ respectively, the value of d_o at the olivine-spinel transition is 2.07 \AA . Thus the critical value of d_o/d_t for forsterite appears to be approximately $2.07/1.649 = 1.26$. Using this value it should be possible to predict the olivine-spinel transition curves for other silicates. However, the predicted value for Ni_2SiO_4 of $T = 12P - 350$, and for Fe_2SiO_4 of $T = 14P - 3300$ are in poor agreement with experimental determinations by Akimoto et al. (1965; for Ni, $T = 83P - 1583$, and for Fe, $T = 22P - 267$). Therefore, it appears that the olivine-spinel transition is not always controlled by octahedral and tetrahedral geometries in the way suggested by Kamb (1968).

Rare-Earth Phosphates, Vanadates and Arsenates: Xenotime vs. Monazite

Rare-earth phosphates, vanadates and arsenates of the form $M^{3+}R^{5+}O_4$ may crystallize in either the monazite or the xenotime structure, depending on the ratio of $^{VIII}M^{3+}$ radius to $^{IV}R^{5+}-O$ distance. Carron et al. (1958) have demonstrated that compounds with $\frac{d_{R-O}}{r_M} < 1.50$ adopt the monazite structure (with M in 8-coordination and R in 4-coordination).⁵ Compounds with $\frac{d_{R-O}}{r_M} > 1.50$ form the xenotime structure (R is in 4-coordination and M has four short and four long M-O distances).

⁵ Values cited by Carron et al. (1958) have been revised to agree with ionic radii of Shannon and Prewitt (1969)

Consider the system $(\text{Eu}, \text{Y})\text{PO}_4$, assuming complete solid solution between Eu and Y end members. EuPO_4 has the monazite structure $\left(\frac{d_{P-0}}{r_{\text{Eu}}} = 1.45\right)$, while YPO_4 has the xenotime structure $\left(\frac{d_{P-0}}{r_{\text{Y}}} = 1.53\right)$. PO_4 tetrahedra are rigid ($P-0 = 1.55 \text{ \AA}$), and will not change size or shape with changes in P , T or Eu/Y . Thus the size of the 8-coordinated (Eu, Y) site will determine which of the two structures is stable; the critical cation size is $r_M = \frac{1.55}{1.50} = 1.033 \text{ \AA}$. Thermal expansion of the $\text{VIII}M^{3+}$ polyhedron is $12.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, compression (assuming $d_{M-0} \approx 2.47 \text{ \AA}$) is $186 \times 10^{-6} \text{ kbar}^{-1}$, and effects of Eu/Y on radii are

$$r_o = 1.015 + 0.055 X_{\text{Eu}} \text{ \AA},$$

where X_{Eu} is the fraction of Eu in the M site. Thus the equation for the $(\text{Eu}, \text{Y})\text{PO}_4$ transformation surface is:

$$(1.015 + 0.055 X_{\text{Eu}})(1 + 0.0000123 T - 0.000186 P) = 1.033,$$

or

$$T \cong 15.1 P - 4400 X_{\text{Eu}} + 1440. \quad (6)$$

Because PO_4 groups are rigid, this transformation surface is also an isostructural surface. Similar stability equations may be derived for any pair of rare-earth phosphates, vanadates, or arsenates.

Simple Ionic Structures

Pauling (1960) demonstrated that many simple ionic compounds have structures which are largely governed by the ratio of cation-to-anion radii

$$\frac{\text{radius cation}}{\text{radius anion}} = \rho.$$

For example, compounds of the form $M^{2+}X^2$ assume the rutile structure (M in 6-coordination) if $\rho < 0.73$, or the fluorite structure (M in 8-coordination) if $\rho > 0.73$. Similarly, compounds of the form $M^{2+}\text{CO}_3$ or $M^+\text{NO}_3$ or $M^{3+}\text{BO}_3$ crystallize in the calcite structure (M in 6-coordination) if $\rho < 0.67$, or in the aragonite structure (M in 9-coordination) if $\rho > 0.67$. In each of these compounds, larger cations are stabilized in the higher-coordinated, more closely-packed structures.

Temperature, pressure, and composition all influence ionic radii ratios, and thus have analogous effects on the stabilities of simple ionic structures. An increase in pressure will stabilize the denser, closepacked structures: thus higher pressure increases ρ . An increase in temperature stabilizes the less dense, open structures: thus higher temperature decreases ρ . Substitution of different cations will also change ρ . If the stability of a given ionic structure is a function of cation-to-anion radius ratio, then the $P-T-X$ transition surface for that substance will also be a surface of constant ρ . Such a surface will not, in general, be isostructural, since the absolute values of cation and anion radii are not fixed.

As in the case of structures which are constrained by polyhedral geometries, several generalizations may be made about the $P-T-X$ transition surfaces which are constrained by ionic radii ratios. If ρ is a constant along a transition surface, then $(\partial P/\partial T)_\rho$ will always be positive, because pressure favors the less-dense polymorph. If the substituting cation is larger, then $(\partial P/\partial X)_\rho$ will be negative and $(\partial T/\partial X)_\rho$ positive, while if the substituting cation is smaller then $(\partial P/\partial X)_\rho > 0$ and $(\partial T/\partial X)_\rho < 0$. In other words, for simple ionic structures, an increase in temperature, a decrease in pressure, or substitution of a smaller cation have the same effects on structure: all three changes decrease ρ .

Conclusions

One of the ultimate goals of mineralogy and petrology is the capability to predict a stable mineral assemblage, given temperature, pressure and composition. This goal is still far from realization, yet studies on natural and synthetic mineral systems are bringing us closer to an understanding of the factors which govern solid phase equilibria. It is now possible to predict the effects of temperature, pressure and composition on the crystal structures of oxygen-based minerals. Furthermore, if the mineral's stability is constrained by polyhedral packing geometry, then stability limits may also be predicted from calculated isostructural $P-T-X$ surfaces. Thus the structural analogy of temperature, pressure and composition can enhance our understanding of mineral behavior within the earth.

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