Effects of temperature and pressure on interatomic distances in oxygen-based minerals

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Abstract

Variations of metal–oxygen bond distances with temperature and pressure have been compiled from previously published studies of oxides and silicates for eighteen types of cation polyhedra. All metal–oxygen distances vary approximately linearly with both temperature (23° to 1000°C) and pressure (to 100 kbar), and mean coefficients of metal–oxygen bond expansion and compression are proposed. Two empirical relationships between bond expansion, compression, and other bonding variables are:

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

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

where z is the cation charge, p the cation coordination number, d_0 the mean polyhedral metal–oxygen distance at 1 atm and 23°C, $\bar{\alpha}$ the mean coefficient of linear expansion from 23°C to 1000°C, and $\bar{\beta}$ the mean coefficient of linear compression to 100 kbar.

For many cation polyhedra, including $^{IV}Si^{4+}$, $^{VI}Al^{3+}$, $^{IV}Be^{2+}$, $^{VI}Mg^{2+}$, $^{VI}Fe^{2+}$, $^{VI}Ni^{2+}$, and $^{VI}Co^{2+}$, the observed ratio $\bar{\alpha}/\bar{\beta}$ is approximately constant. Consequently, for minerals containing these cations, bond-length changes during thermal expansion will be the inverse of those during compression. Using the two empirical relationships it is possible to predict bond compressions and expansions for other cation polyhedra, and thus provide a basis for estimating structural variations with temperature and pressure for many oxygen-based minerals.

Introduction

A knowledge of the structural response of minerals to changes in temperature and pressure is of fundamental importance to the earth sciences. Prediction of crystal structures at high temperature and pressure requires a detailed understanding of the differential response of different bonds to these parameters. While there is not, as yet, a theoretical model which has successfully predicted expansion and compression of metal–oxygen bonds in solids, recent studies on the variation of mineral structures with temperature and pressure may provide an empirical key to this problem.

Extensive data have been compiled on the variation of room temperature and pressure metal–oxygen bond distances in solids (Shannon and Prewitt, 1969; Shannon, 1976). These relations have proved valu-

able in predicting the physical properties and stabilities of solids. In addition, distance least-squares techniques using the Shannon and Prewitt radii have proved effective in predicting atomic coordinates in oxides and silicates (Dempsey and Strens, 1976). With the growing number of high-temperature and high-pressure crystal-structure studies it seems profitable to examine existing data for systematic trends in bond expansion and compression. The principal objectives of this study are: (1) to determine values of expansion and compression coefficients for several metal–oxygen bonds of importance to earth science; (2) to examine systematic relationships between expansion, compression, and other bonding parameters; and, (3) to provide data for predicting crystal structures of oxygen-based minerals at high temperature and pressure.

Procedures

A systematic literature survey was conducted for sources containing experimental data on the varia-

tion of metal–oxygen distances with temperature and pressure. Sources of two types were used, and are described below.

Simple oxides

In simple oxides of fixed structure (*e.g.,* MgO) or highly symmetric structures (*e.g.,* BeO, Al_2O_3), volume changes and metal–oxygen bond distances are closely related. Consequently, data on oxide thermal expansion and compression provide important information on the variation of metal–oxygen distances with temperature and pressure. More than half of the data were compiled from sources on the expansion and compression of simple oxides.

Silicates

The second group of sources are studies on the variation of silicate structures with temperature and pressure, in which bond distances are tabulated. In these structures the temperature and pressure response of individual bonds within a polyhedron may vary significantly (*e.g.,* Hazen, 1976). However, mean polyhedral rates of expansion and compression appear to be remarkably constant for a given type of cation over a wide range of structures. Thus, mean polyhedral values have been used in this investigation. It should also be noted that bond distances uncorrected for thermal vibrations have been used in all compilations.

Compilation of data

For each type of cation polyhedron, plots of $(d_T - d_0)/d_0$ *vs.* temperature, and $(d_P - d_0)/d_0$ *vs.* pressure were made for all available data. Mean coefficients of linear expansion to 1000°C

$$\left(\bar{\alpha} = \frac{1}{d_0} \times \frac{d_{1000} - d_0}{977} °C^{-1}\right)$$

Table 1. Mean coefficients of expansion (23° to 1000°C) and compression (to 100 kbar), and bonding parameters of metal–oxygen bonds in oxygen-based minerals.

Cation	d_0(Å) [§]	z/p	$\bar{\alpha} \times 10^6 \ °C^{-1}$	$-\bar{\beta} \times 10^6 kbar^{-1}$	$\dfrac{\bar{\alpha}}{0.75 - z/p}$	$-\bar{\beta} \times (z/d_0^3)$	$-\bar{\alpha}/\bar{\beta}$	References
Si	1.61	4/4	0.0*	0.0	0	0	–	9, 10, 12, 15, 17, 18, 21-24, 27, 30, 31, 35, 36, 39, 43-50, 53
Al	1.74	3/4	0.0	n.d.	0	–	–	17, 18, 35, 39
Al	1.89	3/6	8.8	110[†]	35.2	43	0.080	1-4, 7, 10, 12, 19, 26, 30, 32, 38, 41, 42
Cr	1.97	3/6	7.3	n.d.	29.2	–	–	10, 12
Fe	2.00	3/6	7.5	n.d.	30.0	–	–	10
Be	1.63	2/4	9.1[†]	110[†,‡]	36.4	41	0.101	2, 12, 25, 52
Ni	2.05	2/6	14.8	160	35.2	37	0.093	2, 5, 13, 27, 33
Mg	2.08	2/6	14.2	160	33.8	36	0.089	1-3, 6, 7, 10, 12, 14, 20, 21, 25, 31, 32, 37, 40, 43, 49, 51, 52
Co	2.11	2/6	13.8	170	32.9	36	0.081	13, 32
Fe	2.14	2/6	14.0	200	33.3	41	0.070	11-13, 22, 46, 50
Mn	2.19	2/6	14.0	210	33.3	40	0.067	8, 13, 32
Ca	2.36	2/6	13.5	250	32.1	38	0.054	3, 6, 12, 25, 32, 34, 37, 52
Sr	2.54	2/6	14.0	300	33.3	37	0.048	3, 25, 29, 52
Ba	2.71	2/6	14.0 & 18.0[‖]	360	33.3	36	0.039	16, 25, 28, 32, 34, 52, 54
Mg	2.25	2/8	15.4	n.d.	30.8	–	–	30
Ca	2.48	2/8	16.0	n.d.	32.0	–	–	10, 30, 49
Li	2.12	1/6	19.5 & 28.0[‖]	n.d.	33.4	–	–	10, 32
Na	2.56	1/8	15.0 & 20.0[‖]	n.d.	32.0	–	–	10, 32

*This coefficient may have a slight negative value.
[†]Data on linear expansion or compression from non-cubic oxides
[‡]Experimental data to 10 kbar only
[§]From ionic radii of Shannon (1976)
[‖]Two different values of expansion were found. Preferred value is underlined.

and mean coefficients of linear compression to 100 kbar

$$\left(\bar{\beta} = \frac{-1}{d_0} \times \frac{d_{100} - d_0}{100} \text{ kbar}^{-1}\right)$$

were determined from these data. In general these expansion or compression coefficients are approximately the same for a given type of metal-oxygen polyhedron in different oxide and silicate structures. For example, Mg–O octahedra have mean expansion coefficients of 13.9, 14.2, and 14.4 $\times$ 10^{-6} °C^{-1} in periclase, forsterite, and diopside respectively. An average value of 14.2 $\times$ 10^{-6} was thus selected for ^{VI}Mg^{2+}-O expansion to 1000°C. Observed linear expansion and compression coefficients are listed in Table 1 with other bonding parameters; the numbered references are listed in Appendix 1. For each of three different cations (^{VI}Ba^{2+}, ^{VI}Li$^+$, and ^{VIII}Na$^+$) two significantly different values of bond expansion were found in the literature, and both are listed in Table 1.

It should be noted that thermal expansion between 23°C and 1000°C is not, in general, a constant. Expansivity increases with temperature and, for many metal-oxygen bonds, α doubles over this interval. Thus the values of $\bar{\alpha}$ cited in this report are valid only for metal-oxygen bonds heated significantly above 23°C. Compressibility between 1 atm and 100 kbar decreases slightly for most metal-oxygen bonds, but values of $\bar{\beta}$ provide reasonable approximations throughout the 100 kbar range. The effects of pressure on thermal expansion (and of temperature on compressibility) have not been determined for most metal-oxygen bonds, but are generally small compared to $\bar{\alpha}$ and $\bar{\beta}$ in simple oxides. Thus changes in bond lengths at high temperature and pressure may be determined approximately by adding the changes due to temperature and pressure alone.

Discussion

Bond expansion

Several attempts have been made by previous investigators to relate crystal expansion to bonding parameters. Megaw (1938) suggested that for homodesmic crystals, thermal expansion is a function of Pauling bond strength (z/p, where z is the cation charge and p is the cation coordination). She proposed the empirical relationship: $\alpha \propto p^2/z^2$. This equation agrees well with observed thermal expansion for a variety of simple ionic solids (see Megaw, 1971, Fig. 3). However, this relationship does not

hold for the metal-oxygen bonds listed in Table 1, and especially not for metals with low charge and high coordination.

More recently, Cameron et al. (1973) have related the expansion coefficients of M–O bonds in pyroxenes to bond strengths (defined as $4\nu^2\mu^2\pi c^2$, where ν is M–O stretching frequency, μ is reduced mass, and c is the velocity of light). The mean thermal expansion coefficient was found to be directly proportional to bond strength. Because z/p is also a rough measure of bond strength, a plot of M–O expansion coefficients vs. (z/p) was made (Fig. 1). This figure demonstrates the close relationship between bond expansion and Pauling bond strength, and suggests an empirical function of the form:

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

which is analogous to that observed by Cameron et al. (1973).

A direct consequence of any such empirical formula is that metal-oxygen bonds with cations of the same charge and coordination should have approximately the same expansion rates. In fact the mean expansion coefficients for divalent, octahedrally-coordinated cations Fe, Mg, Ni, Mn, Co, Ca, Sr, and Ba are all close to 14 $\times$ 10^{-6} °C^{-1}. This is in spite of the fact that ^{VI}Ba^{2+}(ionic radius = 1.35 Å) is twice as
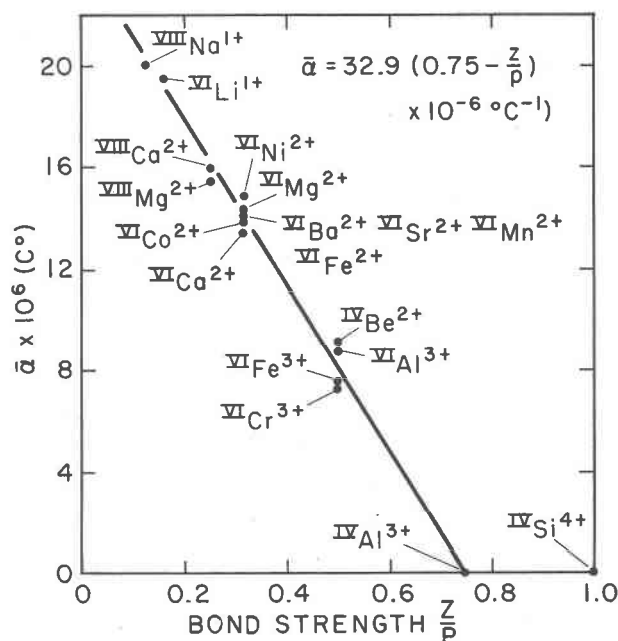

Fig. 1. Mean coefficients of thermal expansion vs. bond strength (z/p). Cations are given in the form $^pR^z$, where z is the cation charge, and p is the coordination number.
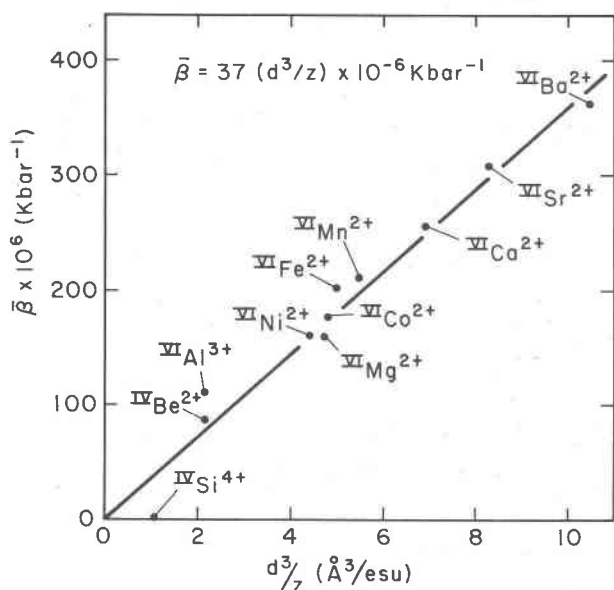
Fig. 2. Mean coefficients of compressibility vs. d^3/z (the inverse of polyhedral charge density). Cations are given in the form $^P R^z$, as described in Fig. 1.
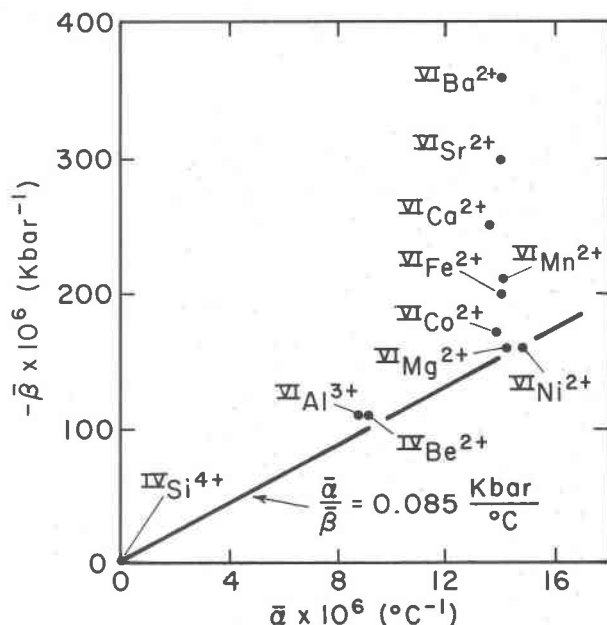

Fig. 3. Observed values of $\bar{\alpha}$ vs. $\bar{\beta}$ for metal–oxygen bonds. $\bar{\alpha}/\bar{\beta}$ should not, in general, be a constant. However, the points for Si, Al, Be, Mg, Ni, Co, Fe, and Mn are coincidently close to a line. Cations are given in the form $^P R^z$, as described in Figure 1.

large as $^{VI}Ni^{2+}$ (0.69 A). Another consequence is that $^{VI}Al^{3+}$ should have approximately the same expansion rate as $^{IV}Be^{2+}$, since $z/p = \frac{1}{2}$ for both bonds. The mean expansion coefficients of 8.8 and 9.1 × 10^{-6} °C^{-1} for Al and Be, respectively, confirm this.

Bond compression

Anderson and Anderson (1970) have demonstrated that for any oxide:

$$KV_o = 0.157\, z_c z_a e^2,$$

Table 2. Predicted values of expansion and compression for metal–oxygen bonds in oxygen-based minerals.

Cation	$\bar{\alpha}$*	$-\bar{\beta}$†	$-\bar{\alpha}/\bar{\beta}$	Cation	$\bar{\alpha}$*	$-\bar{\beta}$†	$-\bar{\alpha}/\bar{\beta}$	Cation	$\bar{\alpha}$*	$-\bar{\beta}$†	$-\bar{\alpha}/\bar{\beta}$	Cation	$\bar{\alpha}$*	$-\bar{\beta}$†	$-\bar{\alpha}/\bar{\beta}$
Al^{3+}_{IV}	0	65	0	Cs^{+}_{VIII}	20.6	1102	0.019	Li^{+}_{VI}	19.5	353	0.055	Si^{4+}_{IV}	0	39	0
Al^{3+}_{VI}	8.2	83	0.099	Fe^{2+}_{IV}	8.2	146	0.056	Mg^{2+}_{VI}	13.8	167	0.071	Sr^{2+}_{VI}	13.8	303	0.046
B^{3+}_{IV}	0	39	0	Fe^{2+}_{VI}	13.8	181	0.076	Mg^{2+}_{VIII}	16.4	211	0.067	Sr^{2+}_{VIII}	16.4	333	0.049
Ba^{2+}_{VI}	13.8	368	0.038	Fe^{3+}_{IV}	0	78	0	Mn^{2+}_{VI}	13.8	194	0.071	U^{4+}_{VIII}	8.2	122	0.067
Ba^{2+}_{VIII}	16.4	442	0.037	Fe^{3+}_{VI}	8.2	99	0.083	Mn^{2+}_{VIII}	16.4	231	0.106	V^{3+}_{VI}	8.2	99	0.083
Be^{2+}_{IV}	8.2	80	0.103	Fe^{3+}_{IV}	0	76	0	Mn^{3+}_{VI}	8.2	100	0.082	W^{4+}_{VI}	0	76	0
Ca^{2+}_{VI}	13.8	243	0.057	Ge^{4+}_{IV}	0	50	0	Na^{+}_{VI}	19.5	499	0.063	W^{6+}_{IV}	0	41	0
Ca^{2+}_{VIII}	16.4	282	0.058	K^{+}_{VI}	19.5	761	0.026	Na^{+}_{VIII}	20.6	606	0.034	W^{6+}_{VI}	0	46	0
Co^{2+}_{VI}	13.8	174	0.079	K^{+}_{VIII}	20.6	875	0.024	Ni^{2+}_{VI}	13.8	159	0.087	Zn^{2+}_{IV}	8.2	139	0.059
Co^{3+}_{VI}	8.2	89	0.092	K^{+}_{XII}	27.4	999	0.027	Rb^{+}_{VI}	19.5	884	0.022	Zn^{2+}_{VI}	13.8	171	0.081
Cr^{3+}_{VI}	8.2	94	0.087	Li^{+}_{IV}	16.4	274	0.060	Rb^{+}_{VIII}	20.6	969	0.021	Zn^{4+}_{VI}	2.7	83	0.033

*Calculated from equation 1 (see text).
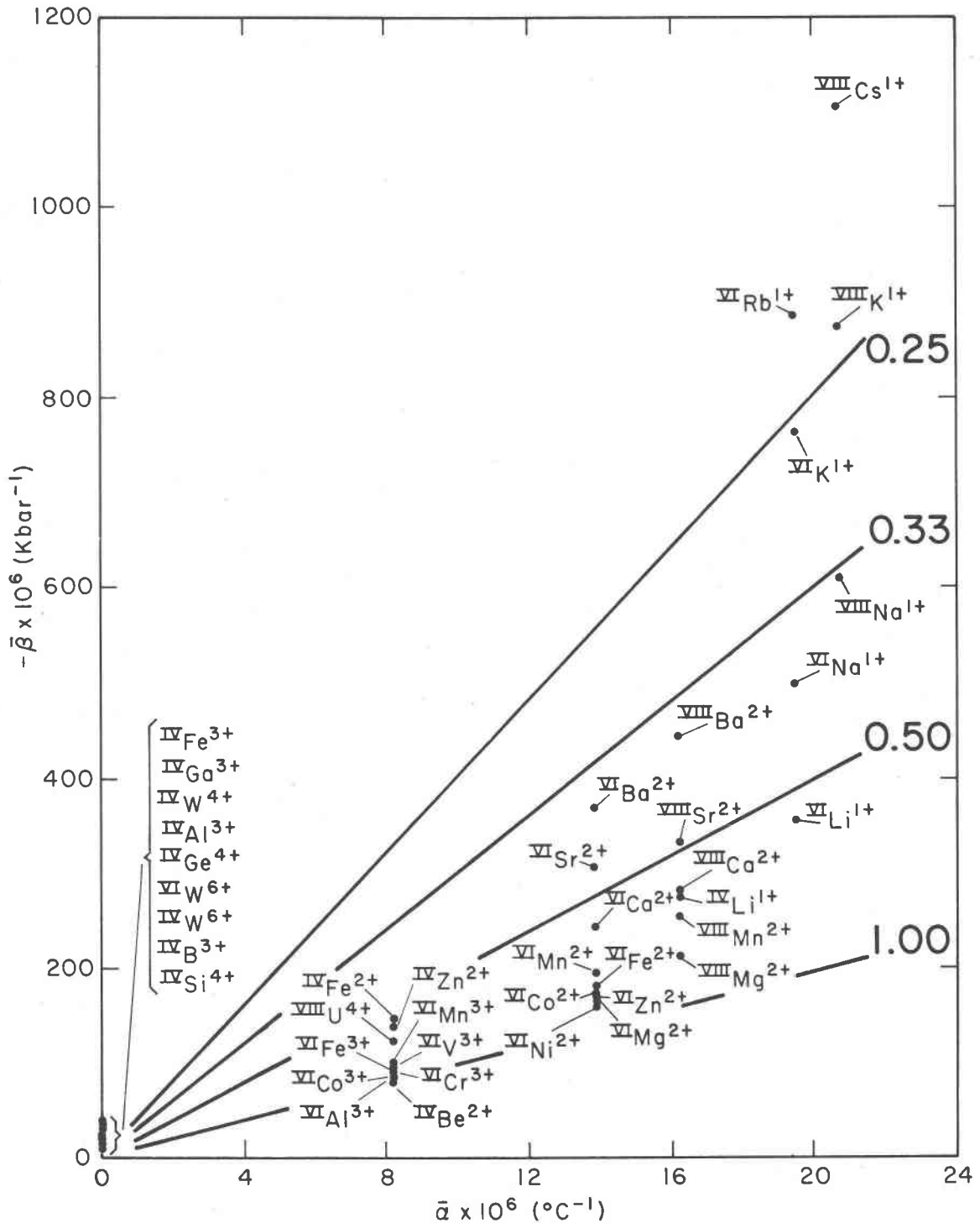
†Calculated from equation 2 (see text).

Fig. 4. Predicted values of $\bar{\alpha}/\bar{\beta}$ for metal–oxygen bonds. Several lines of constant $\bar{\alpha}/\bar{\beta}$ are drawn. If all the cation polyhedra in a given mineral fall near one such line, then the structural changes during cooling from high temperature will be the same as the structural changes during compression. Cations are given in the form $^{P}R^{z}$, as described in Fig. 1.

where K is the bulk modulus, V_o the molar volume, z_c and z_a the cation and anion charges, and e the electrostatic charge. Since z_a and e^2 are constant, and $3\bar{\beta} \approx 1/K$, it follows directly that:

$$3\bar{\beta} \approx 1/K \propto \frac{V_o}{z_c} \quad \text{(Huggins, 1974), or}$$

$$\bar{\beta} \propto \frac{d_o^3}{z},$$

where d_o is the metal–oxygen distance. Figure 2 demonstrates the validity of this equation for a variety of metal–oxygen bonds, and the function proposed is:

$$\bar{\beta}_{100} = 37.0 \, (d_0^3/z) \times 10^{-6} \text{ kbar}^{-1} \quad (2)$$

Note that z/d^3 is a form of charge density, and that compressibility is inversely proportional to this polyhedral charge density.

Expansion versus compression

Relationships between thermal expansion and compression may prove extremely useful in describing crystalline behavior at high temperature and pressure. Plots of $\bar{\alpha}$ vs. $\bar{\beta}$ for cubic metals and alloys by Hanneman and Gatos (1965) demonstrate unique, continuous functions for each cubic metal structure type. Furthermore, these functions are linear for a wide range of metals. Similar relationships in oxides and silicates would be especially valuable in predicting the compressibility of metal–oxygen bonds, since compression data are at present rather few.

Figure 3 illustrates $\bar{\alpha}$ vs. $\bar{\beta}$ for ten metal–oxygen bonds for which reliable data are available for both expansion and compression. Combining equations (1) and (2) above:

$$\bar{\alpha}/\bar{\beta} = [32.9 \, (0.75 - z/p)]/[37.0 \, (d_0^3/z)]. \quad (3)$$

This quantity should not be a constant, since $\bar{\alpha}$ and $\bar{\beta}$ have different physical origins. Fortuitously, the $\bar{\alpha}/\bar{\beta}$ ratio is observed to be roughly constant for a number of ions including $^{IV}Si^{4+}$, $^{VI}Al^{3+}$, $^{IV}Be^{2+}$, $^{VI}Mg^{2+}$, $^{VI}Fe^{2+}$, $^{VI}Co^{2+}$, and $^{VI}Mn^{2+}$, as illustrated in Figure 3. While this relationship reflects the general tendency for more compressible bonds also to be more expansible, $\bar{\alpha}/\bar{\beta}$ will not be a constant for all types of M–O polyhedra.

The observation that $\bar{\alpha}/\bar{\beta}$ is approximately constant for several important metal–oxygen bonds (i.e., Si, Al, Mg, Fe) has significant implications regarding the response of oxygen compounds to temperature and pressure. Assuming that structural parameters are determined primarily by polyhedral topology and cation–anion bond distances, it appears that the way in which such a solid decreases volume during cooling from high temperature is *structurally the same* as the way in which the solid decreases volume during compression. This observation has been documented for ferromagnesian olivines (Hazen, 1977) and albite (Hazen and Prewitt, 1977) and is now proposed as a general rule for compounds in which all cation polyhedra have similar ratios of $\bar{\alpha}$ to $\bar{\beta}$.

Predictions of $\overline{\alpha}$ and $\bar{\beta}$

Table 2 presents predicted values of $\bar{\alpha}$, $\bar{\beta}$, and $\bar{\alpha}/\bar{\beta}$ (based on equations 1–3) for oxygen–cation polyhedra of importance to the earth sciences. As stated above, oxygen-based minerals in which all cations have similar values of $\bar{\alpha}/\bar{\beta}$ will respond in structurally similar ways to increasing pressure and decreasing temperature. In Figure 4 predicted values of $\bar{\alpha}$ vs. $\bar{\beta}$ are plotted, and lines of constant $\bar{\alpha}/\bar{\beta}$ are illustrated. Substances with component metal–oxygen bonds which lie along only one such line should have inverse expansion and compression behavior. Mg–Fe silicates such as olivine and Na–Al silicates such as albite should demonstrate this behavior. Furthermore, the slope of the appropriate line in Figure 4 should give the relative $\bar{\alpha}/\bar{\beta}$ of the bulk solid.

Several important minerals, notably where one cation is K, Na, or Ca, and another is Mg or Fe, are not expected to demonstrate a precise inverse relationship between thermal expansion and compression. In these minerals the large alkali cations should respond relatively more to pressure than to temperature, since the $\bar{\alpha}/\bar{\beta}$ ratio is small for such cations. However, even in these minerals an approximate inverse relationship may be observed since alkali cations in general show significantly greater expansion or compression than Mg or transition metals, which in turn show greater $\bar{\alpha}$ and $\bar{\beta}$ than Al or Si. Thus most rock-forming minerals will respond to changes in temperature and pressure in closely related ways.

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