

Comparative compressibilities of calcite-structure carbonates: Deviations from empirical relations

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ABSTRACT

Room-temperature volume measurements of the complete set of calcite-structure carbonates in the pressure range 0–8.1 GPa revealed systematic differences in compressibilities that depend on cation type, resulting in significant deviations from empirical relations of an inverse linear correlation between K_0 and V_0 . The bulk modulus for MgCO_3 lies approximately 18 GPa below the trend for the 3d transition metal carbonates, which show an expected inverse linear correlation of bulk modulus with ambient cell volume (and M-O bond length). The bulk modulus of CdCO_3 , whose M-O bond length and cell volume are only slightly smaller than those of CaCO_3 , lies up to 10 GPa above the trend of the 3d transition metal carbonates and about 30 GPa above that of calcite. These deviations in compressibility trends as a function of cell volume (or M-O bond length) are expressed as differences in a axis compressibility but not in c axis compressibility, which shows a nearly linear increase with M-O distance. Hence, systematic behavior is apparently limited to subsets of carbonates in which metal ions share the same valence electron character (i.e., s vs. 3d vs. 4d) and is primarily attributed to unexpected compressibility differences along the a axis.

Crystal-field effects, beyond those reflected in the M-O distances, cannot account for the observed compressibilities. Nonbonded interactions also fail to explain the deviations from predicted trends. Variations of electronegativity and vibrational frequency with ionic radius for the relevant metal ions show differences that are qualitatively similar to the observed trends of bulk modulus, suggesting that differences in bonding character may contribute to the different behaviors among the subsets of calcite-structure carbonates. However, it is most likely that a combination of factors is necessary to account fully for the observed behavior.

INTRODUCTION

For a variety of isostructural compounds, including halides, oxides, and some silicates, it has been found that the ambient bulk modulus, K_0 , shows an approximately linear inverse correlation with ambient volume, V_0 (e.g., Anderson and Anderson 1970 and references therein). Although this relationship is empirical, theoretical arguments in support of it can be derived from a simple two-term bonding potential as described in the work of Anderson (1972). From similar theoretical arguments and high-pressure single-crystal structure refinements on oxygen-based materials, Hazen and Prewitt (1977) and Hazen and Finger (1982) concluded that compressibility of many compounds is controlled primarily by the bulk moduli of their constituent polyhedra, K_p , which are largely determined by the mean cation-oxygen bond length in the polyhedra and independent of the polyhedral linkage. These empirical relations have provided a useful framework for predicting the properties of minerals at high pressure and for understanding the effects of pressure on bonding.

Deviations of the bulk modulus-volume behavior from the empirical relations, however, have been reported in several different structure types. The best known examples are found in ferromagnesian minerals, which have been extensively stud-

ied because of their importance in understanding the Earth's interior. The bulk modulus appears to increase with increasing Fe content (thus increasing volume) in rock-salt oxides (e.g., Jackson et al. 1978; Sumino 1980), olivines (e.g., Sumino 1979; L. Zhang 1998), clinopyroxene (L. Zhang et al. 1997), silicate spinels (Hazen 1993), and carbonates (J. Zhang et al. 1998), even though the absolute difference is typically no more than a few percent for complete substitution. In a broader view, elastic properties are found to be sensitive to the replacement of Mg by the 3d transition metals (Sumino 1979, 1980; Weidner et al. 1982; L. Zhang 1998). These observations suggest that the crystal bulk modulus or compressibility cannot be solely determined by variables associated with the cation size. Systematic studies of minerals of different structure types are needed to understand the effects of compositional variation on crystal compressibility.

The calcite-structure carbonates (space group $R\bar{3}c$) represent a mineral group that is structurally simple and different from oxides and silicates; the slightly distorted octahedra are exclusively corner-linked through shared oxygen anions of CO_3 groups, which are extremely incompressible structural units (Ross and Reeder 1992; Ross 1997). These authors also found that M-O-M and M-O-C angles in magnesite, dolomite, and ankerite showed almost no variation with pressure, indicating that bond bending does not contribute to the compression of these carbonates. Calcite-structure carbonates exist for diva-

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lent cations with ionic radii ranging from 0.69 to 1.0 Å. In addition, their electronic configurations are of three types: alkaline earth elements (Mg, Ca), 3d transition metals (Ni, Co, Fe, Mn, Zn), and 4d transition metal (Cd). Hence, this is an ideal structure-type for exploring effects of different cation type on crystal compressibility. Here, pressure-volume measurements were carried out at room temperature for end-member MgCO_3 , CaCO_3 , NiCO_3 , CoCO_3 , MnCO_3 , ZnCO_3 , and CdCO_3 , which, in combination with our previous results for the join MgCO_3 - FeCO_3 (J. Zhang et al. 1997, 1998), completes a systematic study of crystal compressibility for all calcite-structure carbonates. The present experimental results demonstrate that neither bond length (or cell volume) nor crystal-field effects can account for the observed bulk moduli for the complete set of calcite-structure carbonates. Other possible explanations such as cation-cation interaction and role of covalency in bonding are explored and discussed.

EXPERIMENTAL METHODS

Synthetic powder samples of magnesite (MgCO_3), calcite (CaCO_3), gaspeite (NiCO_3), spherocobaltite (CoCO_3), and otavite (CdCO_3) as well as optically homogeneous natural samples of smithsonite (ZnCO_3) and rhodochrosite (MnCO_3) were used. We previously studied this magnesite (J. Zhang et al. 1997). The spherocobaltite was synthesized by D.H. Lindsley. Calcite (purity 99.95% metal basis) and gaspeite (purity 99%) samples were obtained from Johnson-Matthey Company, and otavite (purity 98%) from Aldrich Chemical Company. The smithsonite [$(\text{Zn}_{0.96}\text{Cu}_{0.03}\text{Pb}_{0.01})\text{CO}_3$] and rhodochrosite [$(\text{Mn}_{0.996}\text{Fe}_{0.003}\text{Mg}_{0.001})\text{CO}_3$] samples were from Kelly Mine, New Mexico, and Sweet Home Mine, Colorado, respectively, and the chemical compositions were obtained from electron microprobe analysis. The two natural carbonates were single crystal specimens and were ground in an agate pestle and mortar for the diffraction work.

Experiments were performed using a DIA-type, cubic-anvil apparatus (SAM85) designed for in-situ X-ray diffraction studies at simultaneously high pressure and temperature (Weidner et al. 1992). An energy-dispersive X-ray method was employed using white radiation from the superconducting wiggler magnet at beamline X17B of the National Synchrotron Light Source, Brookhaven National Laboratory. The experimental technique and cell assembly used in the present study were identical to the ones described by J. Zhang et al. (1997, 1998).

In each experiment two carbonate samples were usually included, separated by a layer of NaCl, which also served as an internal pressure standard. All experiments, except for the one on calcite, were carried out as follows. We first compressed samples at room temperature to 9–10 GPa, followed by heating to the maximum temperature of 1073 K. Data were collected upon quench to room temperature to minimize nonhydrostatic stress built up during the room-temperature compression. The same procedure was repeated several times at lower pressures. For calcite, the data reported here were collected during the room-temperature compression and prior to the phase transition to aragonite.

Pressures were calculated from Decker's equation of state

(Decker 1971), and the uncertainty in pressure measurements is mainly attributed to statistical variation in the positions of diffraction lines and is less than 0.1 GPa in the pressure range of the study. The unit-cell parameters were calculated by least-squares fitting using 8 to 12 diffraction lines based on a hexagonal unit cell. The relative standard deviations in determination of the unit-cell volume are less than 0.1% (see Table 1).

TABLE 1. Unit-cell parameters as a function of pressure at room temperature

Pressure (GPa)	a (Å)	c (Å)	V (Å ³)
NiCO₃			
0.00*	4.602(1)	14.729(8)	270.15(12)
1.58	4.590(2)	14.637(15)	267.04(28)
2.53	4.583(2)	14.572(12)	265.10(20)
4.29	4.569(1)	14.489(15)	261.98(22)
5.20	4.562(2)	14.456(9)	260.53(23)
6.77	4.547(1)	14.394(15)	257.77(27)
7.29	4.542(2)	14.372(17)	256.79(32)
CoCO₃			
0.00†	4.660(2)	14.979(12)	281.67(25)
0.00*	4.659(2)	14.989(11)	281.74(22)
1.30	4.652(1)	14.903(10)	279.26(19)
2.53	4.641(2)	14.827(11)	276.62(23)
4.00	4.627(2)	14.747(9)	273.40(25)
5.69	4.614(2)	14.653(8)	270.18(22)
6.99	4.605(2)	14.575(7)	267.66(20)
8.06	4.599(1)	14.509(13)	265.74(21)
MgCO₃			
0.00†	4.636(2)	15.017(14)	279.53(27)
0.00*	4.636(2)	15.023(14)	279.57(25)
1.30	4.618(1)	14.952(12)	276.11(23)
2.53	4.606(1)	14.876(11)	273.35(22)
4.00	4.592(1)	14.784(10)	270.03(20)
5.96	4.578(1)	14.679(10)	266.40(19)
6.99	4.568(2)	14.590(17)	263.67(32)
8.06	4.561(3)	14.519(20)	261.59(38)
ZnCO₃ Run 1			
0.00†	4.658(1)	15.076(4)	283.27(9)
0.00*	4.654(1)	15.055(7)	282.40(16)
0.93	4.644(1)	14.995(11)	280.07(19)
2.18	4.636(1)	14.916(7)	277.58(17)
2.79	4.630(1)	14.871(12)	276.10(19)
3.74	4.625(1)	14.824(8)	274.62(14)
4.73	4.616(2)	14.746(13)	272.14(21)
5.75	4.610(1)	14.687(8)	270.31(13)
6.92	4.603(1)	14.655(5)	268.84(11)
8.07	4.596(1)	14.575(4)	266.61(10)
ZnCO₃ Run 2			
0.00†	4.657(1)	15.076(8)	283.13(15)
0.00*	4.654(1)	15.058(7)	282.42(15)
1.19	4.644(1)	14.982(8)	279.82(15)
2.38	4.634(1)	14.910(8)	277.26(15)
3.72	4.624(1)	14.838(9)	274.76(13)
4.97	4.615(1)	14.760(9)	272.20(14)
5.86	4.609(1)	14.700(10)	270.47(17)
6.85	4.605(1)	14.619(4)	268.48(8)
7.62	4.599(1)	14.599(6)	267.36(15)
CdCO₃ Run 1			
0.00†	4.926(1)	16.301(2)	342.50(5)
0.00*	4.919(1)	16.289(4)	341.38(10)
1.03	4.910(1)	16.202(9)	338.30(19)
2.38	4.903(2)	16.028(9)	333.74(20)
3.72	4.891(1)	15.879(9)	328.99(16)
4.97	4.887(1)	15.736(12)	325.50(22)
5.86	4.883(2)	15.655(16)	323.25(28)
6.85	4.877(2)	15.574(18)	320.78(31)
7.62	4.874(2)	15.506(13)	319.01(29)

TABLE 1.—Continued

Pressure (GPa)	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
CdCO₃ Run 2			
0.00†	4.925(1)	16.296(4)	342.24(8)
0.00*	4.919(1)	16.281(8)	341.15(20)
0.71	4.912(2)	16.224(18)	339.01(33)
1.97	4.903(1)	16.072(13)	334.56(24)
3.07	4.893(1)	15.967(15)	331.04(27)
4.72	4.883(1)	15.823(11)	326.77(22)
5.69	4.878(1)	15.699(13)	323.54(25)
6.65	4.876(2)	15.607(11)	321.38(20)
7.32	4.872(1)	15.535(8)	319.33(14)
MnCO₃ Run 1			
0.00†	4.776(1)	15.690(10)	309.91(18)
0.00*	4.775(2)	15.697(14)	309.93(25)
1.58	4.765(1)	15.572(6)	306.15(10)
2.53	4.755(1)	15.499(8)	303.42(14)
4.29	4.741(2)	15.334(11)	298.51(17)
5.20	4.731(1)	15.279(12)	296.19(21)
6.77	4.721(3)	15.164(17)	292.66(29)
7.29	4.717(2)	15.137(18)	291.71(28)
MnCO₃ Run 2			
0.00†	4.777(1)	15.666(5)	309.54(9)
0.00*	4.775(1)	15.675(5)	309.55(8)
2.18	4.756(1)	15.535(3)	304.27(10)
3.69	4.741(1)	15.399(10)	299.81(17)
4.89	4.733(1)	15.298(7)	296.74(13)
6.27	4.724(1)	15.197(4)	293.72(8)
7.38	4.716(1)	15.125(17)	291.29(29)
CaCO₃			
0.00	4.989(2)	17.044(12)	367.32(33)
0.68	4.985(2)	16.903(17)	363.81(40)
1.10	4.977(4)	16.834(22)	361.05(50)
1.75	4.965(5)	16.801(34)	358.66(75)

Notes: The values in parentheses are standard deviations.

* Recovered after the high pressure and temperature experiments.

† Obtained at the beginning of the experiments.

EXPERIMENTAL RESULTS

Room-temperature volume data were obtained for all carbonates except calcite in the pressure range up to 7.3 to 8.1 GPa (Table 1). At ambient conditions, the lattice parameters and unit-cell volumes of MgCO₃, CaCO₃, CoCO₃, MnCO₃, and CdCO₃ are in good agreement with those of JCPDS cards. The cell volumes of ZnCO₃ in two experimental runs are about 0.5% larger than the JCPDS value. The reagent NiCO₃ was in an amorphous form at ambient conditions and crystallized at high pressure when the temperature was above 773 K. In all the experiments performed, the unit-cell parameters of NaCl recovered at the end of experimental runs are identical to those at the beginning within uncertainties of the refinements, indicating no change in system calibration over the entire experimental *P-T* range. After the experiments, MgCO₃, CoCO₃, and MnCO₃ were recovered with their initial unit-cell parameters (see Table 1), suggesting no structural and compositional changes in these carbonates in the course of experiments. CaCO₃, as expected, underwent a phase change from calcite to aragonite at about 2 GPa at room temperature.

For ZnCO₃ and CdCO₃, however, unit-cell volumes from the samples recovered at the end of experimental runs were about 0.3% smaller than those measured at the beginning. Such differences were duplicated in two experimental runs for both carbonates (Table 1). The differences do not result from a change in system calibration because NaCl behaved normally. They

may be due to compositional changes upon heating at high pressures. For example, it is possible that exsolution of minor components, such as Pb, in ZnCO₃ and release of relict water in CdCO₃ (note that synthetic carbonates are usually made in a hydrothermal environment) occurred during the initial heating up to 1073 K.

As a result of the above observations and discussion, the ambient unit-cell parameters (*a*₀, *c*₀, and *V*₀) used in this work for MgCO₃, CaCO₃, CoCO₃, and MnCO₃ are those measured at the beginning of the experimental runs and for NiCO₃, ZnCO₃, and CdCO₃ those recovered at the end of the experiments. In the calculations of mean axial and volume compressibilities, the ratios *a/a*₀, *c/c*₀, and *V/V*₀ at zero pressure are all fixed at 1. The room-temperature bulk modulus values, *K*₀, were obtained by fitting the *P-V* data to a second-order Birch-Murnaghan equation of state. Because of the limited pressure ranges of the present study, the pressure derivatives of the bulk modulus, *K*₀', could not be constrained and were fixed at 4. The *V*₀ values were also fixed for all carbonates in the data analysis. Errors quoted for compressibilities or *K*₀ values throughout this paper are those of the least-squares fitting; uncertainties in the measurements of pressure and unit-cell parameters were not included for error estimations. For the sake of internal consistency, compressibility data or *K*₀ values obtained from studies using different experimental techniques are not used here for comparison because systematic errors may exist in some or all of the experiments, as is the case for MgCO₃ (e.g., Redfern et al. 1993; Fiquet et al. 1994; J. Zhang et al. 1997; Ross 1997). Nonetheless, the room-temperature bulk modulus values obtained for MgCO₃ and FeCO₃ in our previous studies (J. Zhang et al. 1997, 1998) are in good agreement with those determined from ultrasonic measurements (Christensen 1972) and single-crystal X-ray diffraction study in a diamond-anvil cell (Ross 1997).

Reproducibility of the *P-V* measurements

For MgCO₃, MnCO₃, ZnCO₃, and CdCO₃, representatives of carbonates with different types of cations, two experimental runs were carried out to examine reproducibility of the *P-V* measurements. Examples are given in Figure 1 for ZnCO₃ and in Figure 2 for CdCO₃, showing that unit-cell parameters and cell volumes determined from different experimental runs as a function of pressure are in good agreement. As expected, similar values of *a*, *c*, *v*, and *K*₀ were found from different measurements for both carbonates (Table 2). Excellent reproducibilities are also found for MnCO₃ (Table 1) and for MgCO₃, when the current results are compared to those of J. Zhang et al. (1997).

Examples of deviations from empirical relationships

Empirical relations suggest that the crystal compressibility is primarily controlled by the unit-cell volume or M-O bond length of the constituent polyhedra. Deviations from the empirical relationships are clearly shown from the pressure-volume data for MgCO₃ and CoCO₃ (Fig. 3a). These two carbonates, with nearly identical ambient cell volumes and M-O bond lengths (see Tables 1 and 2), were studied in the same experiment. MgCO₃, however, is considerably more compressible than CoCO₃. Further examination of unit-cell parameters as a function of pressure indicates that the two carbonates have similar

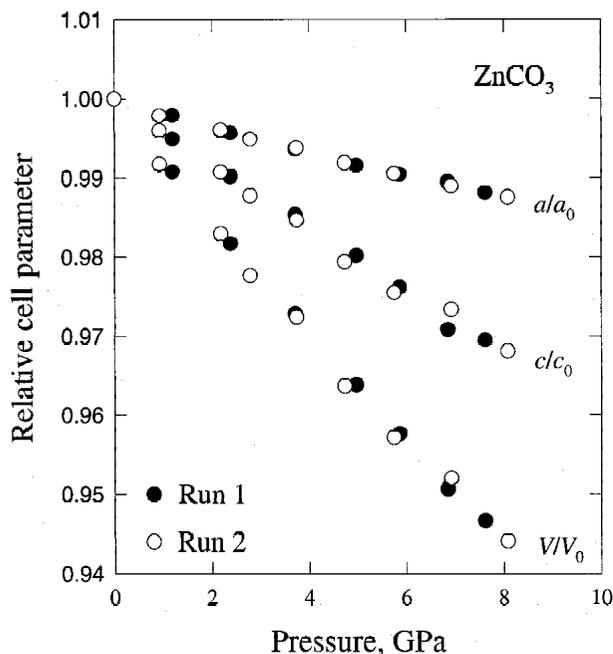


FIGURE 1. Variations of a/a_0 , c/c_0 , and V/V_0 as a function of pressure for ZnCO_3 from two different experimental runs. Error bars of the measurements are equivalent to or smaller than the symbol size.

compressibilities along the c axis, whereas MgCO_3 is significantly more compressible along the a axis (Fig. 3b). Note that these observations are similar to those reported for ferromagnesian carbonates (Zhang et al. 1998), in which the compressibility of the a axis was found to decrease almost linearly with increasing Fe content.

Comparison of results for MgCO_3 and MnCO_3 provides another example of a deviation from the empirical relationships. These two carbonates have almost identical compressibilities in the pressure range studied, even though MnCO_3 has a much larger cell volume (and M-O bond length) than MgCO_3 (Tables 1 and 2). Thus we conclude from these examples that even for isostructural materials the compressibility or bulk modulus cannot be predicted simply from the cation size.

Compressibility and bulk modulus systematics

The room-temperature bulk moduli for all calcite-structure carbonates (Table 2) are shown in Figure 4 as a function of

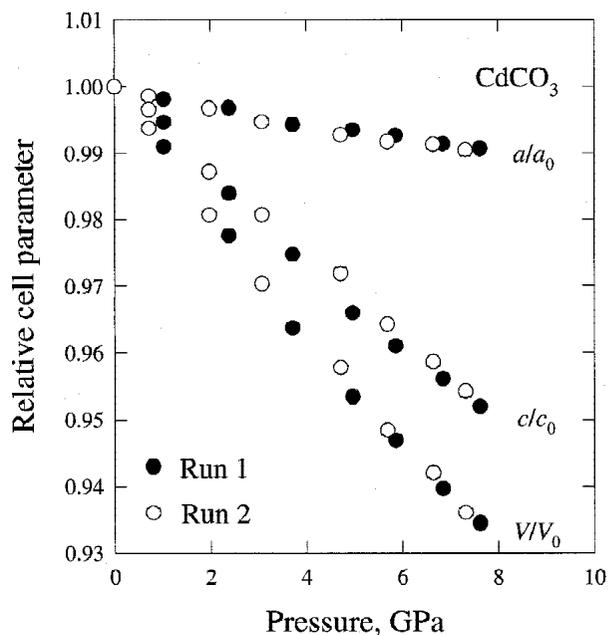


FIGURE 2. Variations of a/a_0 , c/c_0 , and V/V_0 as a function of pressure for CdCO_3 from two different experimental runs. Uncertainties are less than or equal to symbol size.

ambient cell volume. For all 3d transition metal carbonates, the K_0 values show a good linear correlation with the ambient cell volumes (also true if plotted against the ambient M-O bond length) and, thus, as a subset are consistent with the empirical predictions. MgCO_3 , plots well below the trend established by the 3d transition metal carbonates and CaCO_3 slightly below. Notably, the measured bulk modulus of MgCO_3 lies nearly 18 GPa below those of CoCO_3 and ZnCO_3 despite similar M-O bond lengths and cell volumes, and Fe^{2+} substitution for Mg results in a linear increase of the room-temperature bulk modulus (Zhang et al. 1998). In contrast, the bulk modulus of CdCO_3 , whose ambient M-O bond length and cell volume are only slightly smaller than those of CaCO_3 (see Table 1 and 2), is about 30 GPa greater than that of calcite and lies 10 GPa above the trend of the 3d transition metal carbonates. As a result, three subsets of carbonates can be identified in Figure 4, and metal ions within each subset share the same character of their valence electrons, that is, s vs. 3d vs. 4d types, respectively.

TABLE 2. The mean axial and volume compressibilities and room-temperature bulk moduli of calcite-structure carbonates

Carbonate	o. e. c. of metal ions	$d_{\text{M-O}}$ (Å)	α ($\times 10^3$) (GPa $^{-1}$)	c ($\times 10^3$) (GPa $^{-1}$)	v ($\times 10^3$) (GPa $^{-1}$)	K_0 (GPa)
NiCO_3	$3d^8 4s^2$	2.076	1.74(3)	3.48(10)	6.86(7)	131(1)
MgCO_3	$3s^2$	2.102	2.13(7)	4.03(5)	8.15(10)	107(1)
CoCO_3	$3d^7 4s^2$	2.110	1.67(3)	3.87(2)	7.10(5)	125(1)
ZnCO_3	$3d^{10} 4s^2$	2.111	1.60(3)	4.07(5)	7.18(6)	124(1)
			1.62(4)	4.06(7)	7.20(13)	124(1)
FeCO_3	$3d^6 4s^2$	2.145	1.66(5)	4.36(15)	7.58(8)	117(1)
MnCO_3	$3d^5 4s^2$	2.190	1.71(3)	4.96(6)	8.25(9)	107(1)
			1.80(5)	4.72(7)	8.18(9)	108(1)
CdCO_3	$4d^{10} 5s^2$	2.288	1.28(4)	6.51(9)	8.95(13)	97(1)
			1.40(5)	6.21(5)	8.90(10)	98(1)
CaCO_3	$4s^2$	2.360	2.42(30)	9.34(93)	14.10(51)	67(2)

Note: o. e. c. = outer electron configuration. Values of M-O interatomic distance ($d_{\text{M-O}}$) are taken from Reeder (1983).

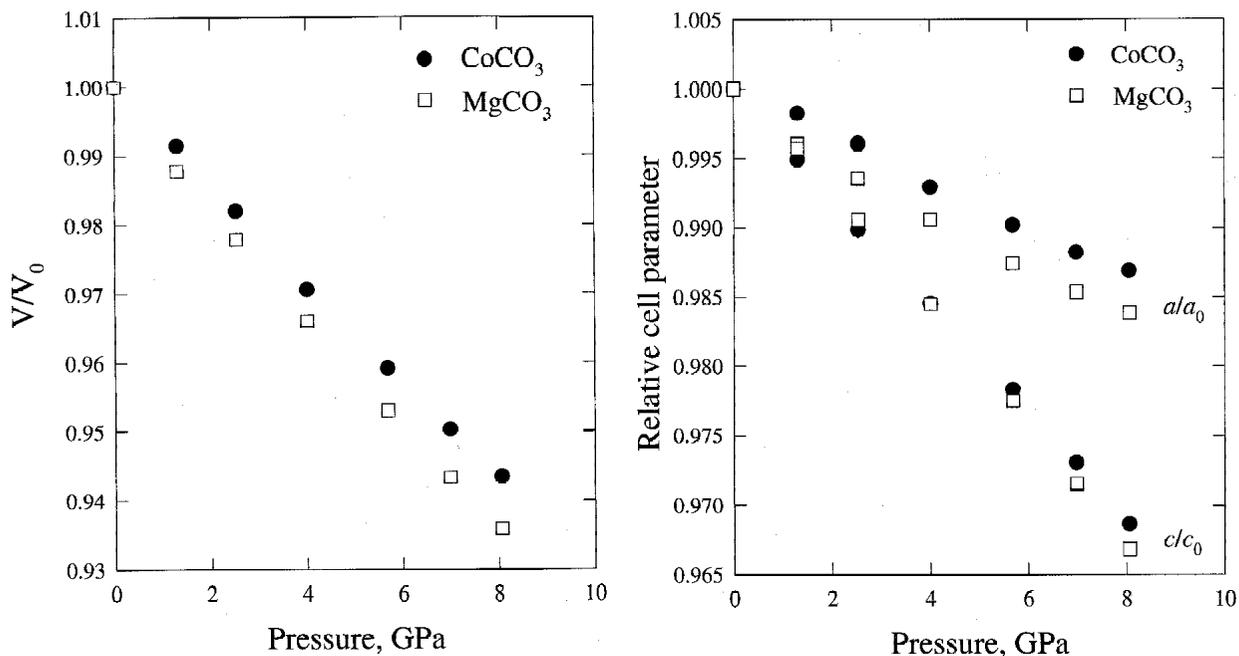


FIGURE 3. Comparisons of the mean volume (a) and axial (b) compressibilities for MgCO_3 and CoCO_3 . These two carbonates have nearly identical ambient cell volumes and M-O bond lengths (see Tables 1 and 2). The measurements were made simultaneously in the same experiment. Uncertainties are less than or equal to symbol size.

Systematic differences between the three subsets of carbonates are also evident if, in Figure 4, the bulk modulus is replaced by the mean volume compressibility, ν . Because the ν values (Table 2) were obtained directly from linear fits of the volume ratios V/V_0 vs. pressure, potential errors are avoided in determination of the K_0 values of Figure 4 from the use of the equation of state. The Birch-Murnaghan equation of state was not originally developed for materials that are highly anisotropic, such as carbonates (see discussion below), and the K_0 values for all calcite-structure carbonates were assumed to be the same in calculations of the K_0 values plotted in Figure 4. A similar trend in the ν -cell volume relationship, however, suggests that these two concerns are unlikely to be important factors in drawing conclusions using the K_0 values because of the comparative nature of the present study.

The present observations (Fig. 4) differ from those reported by Martens et al. (1982), in which no deviation was detected in the compressibility of MgCO_3 from other carbonates with the calcite structure. Moreover, the conclusions of Martens et al. (1982) should be viewed with caution because some of their compressibility data were taken from other studies, and systematic errors in the compressibility measurements may exist in some or all of the experiments. For example, the compressibility data for FeCO_3 and MnCO_3 used by Martens et al. (1982) differ from those of Christensen (1972) and the present study.

Compressibilities along the a axis (ν_a) and c axis (ν_c) (Table 2) are shown in Figures 5 and 6, respectively. We do not use the CaCO_3 data of the present study for the following reasons: (1) only three P - V data points were obtained in a small pressure range 0–1.75 GPa (Table 1) and (2) calcite was not heated to eliminate deviatoric stress, which resulted in more scatter of

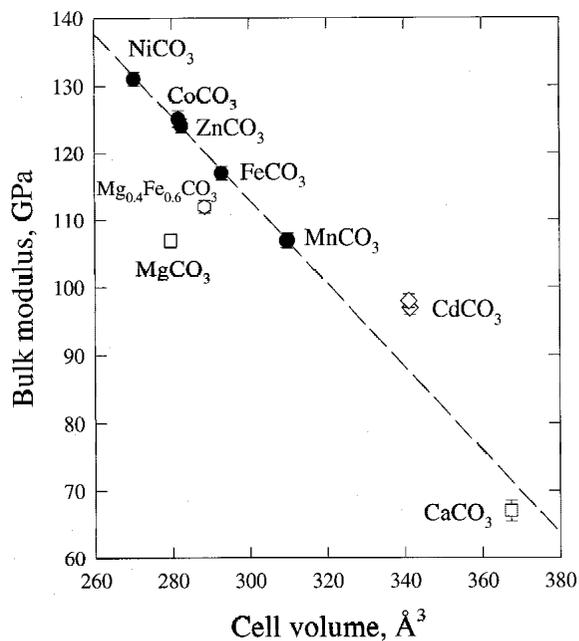


FIGURE 4. Relationship between the bulk modulus and the ambient cell volume for all calcite-structure carbonates. A similar trend is found if the horizontal axis is ambient M-O bond length. Although the assumption of $K'_0 = 4$ was used to obtain the bulk moduli using the Birch-Murnaghan EOS, the same trend still holds as long as the carbonates studied have values of K'_0 that are similar to one another. The data for FeCO_3 and $\text{Fe}_{0.6}\text{Mg}_{0.4}\text{CO}_3$ plotted here and throughout the paper are taken from Zhang et al. (1998).

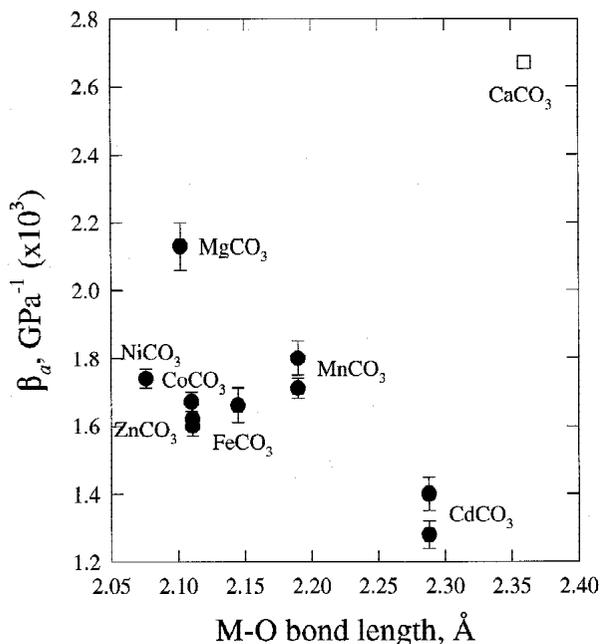


FIGURE 5. The a axis compressibilities of the calcite-structure carbonates as a function of ambient M-O bond length. Systematic differences exist between MgCO_3 and CaCO_3 , the 3d transition metal carbonates, and CdCO_3 . For CaCO_3 , the data point shown is the average value from Dandekar (1968) in the pressure range 0–0.6 GPa (see text), thus providing an upper limit for the axial compressibility when compared with those of other carbonates studied over the pressure range up to 7.3–8.1 GPa.

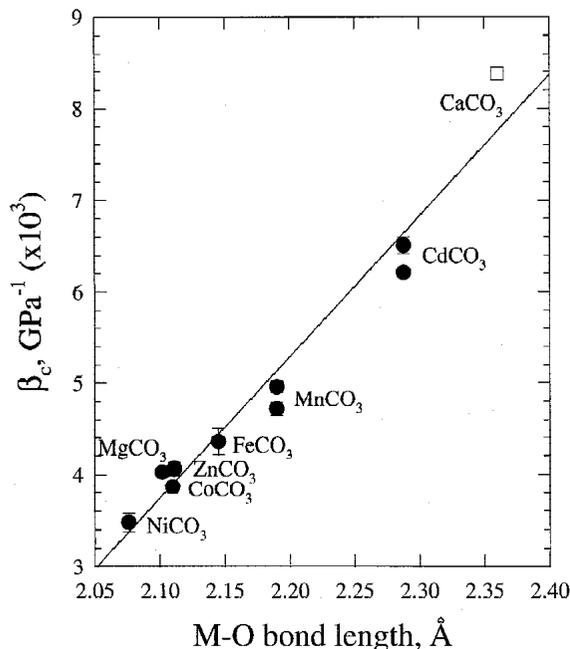


FIGURE 6. The c axis compressibilities as a function of ambient M-O bond length. β_c shows a good linear correlation with interatomic distance for all carbonates. Deviations shown by MgCO_3 and CdCO_3 in Figure 4 are apparently attributable to the compressional behavior of the a axis. CaCO_3 provides an upper limit.

lattice parameter data compared to those of all other carbonates (Tables 1 and 2). Instead, the average a and c values in the pressure range 0–0.6 GPa, calculated from the single-crystal elastic compliances of Dandekar (1968) are used. Because both a and c of calcite in the work of Dandekar (1968) showed a small pressure dependence, the values given in Figures 5 and 6 can only provide an upper limit for the axial compressibilities when compared with those of other carbonates studied over the much larger pressure ranges (Table 1). Inspection of Figures 5 and 6 demonstrates that the c axis is 2 to 5 times more compressible than the a axis. Such anisotropic compressional behavior is typical of all rhombohedral carbonates.

In spite of the fact that three subsets of carbonates can be identified based on the relationship between the bulk modulus (or crystal compressibility) and cell volume (or M-O bond length) (Fig. 4), the c axis appears to behave normally, in the sense that compressibilities of the c axis in all carbonates studied show a nearly linear increase with interatomic distance (Fig. 6). Compressibilities of the a axis, however, decrease in the order MgCO_3 and CaCO_3 , the 3d transition metal carbonates, and CdCO_3 (Fig. 5). This behavior, although unexpected, is consistent with the observations shown in Figure 4 defining three subsets on the basis of cation type. Because in all calcite-structure carbonates the a axis is expected to contribute approximately twice as much to the crystal compressibility as the c axis (i.e., $\nu \approx 2 \nu_a + \nu_c$), the observed systematic difference between the three subsets of carbonates is primarily attributed to the compressibility of the a axis. It may not be obvious from Figure 4 that CdCO_3 deviates from the trend of the 3d transition metal carbonates. It is its unexpectedly low compressibility along the a axis that supports our conclusion that CdCO_3 should be considered as a separate “group” that differs from the other two. This conclusion, however, should be viewed with some caution because the calculations of the bulk modulus and axial compressibilities are sensitive to the choice of V_0 , a_0 , and c_0 . The initial unit-cell parameters for CdCO_3 differed from those recovered after the experiments, and it is likely that our synthetic CdCO_3 starting material contained some H_2O , we used cell parameters from the recovered samples. If we use the V_0 values measured at the beginning of the experiments for the fitting, a value of $K_0 = 91(1)$ GPa is obtained, which deviates less from the trend of the 3d transition metal carbonates in Figure 4. Similarly, the use of the initial a_0 values would result in the a -axis compressibilities ($1.52 - 1.62 \times 10^{-3} \text{ GPa}^{-1}$) that are within the range of those of the 3d transition metal carbonates (Fig. 5). Therefore, unless the discrepancy between initial and final V_0 values can be understood, there is a possibility that CdCO_3 may in fact deviate very little from the trends established by the 3d transition metal carbonates (Figs. 4 and 5).

DISCUSSION

Deviations from the empirical relations between K_0 and V_0 or between K_p and M-O bond length have been noted in other systems. Like the calcite group, there are other groups whose members have different constituent cations but share the same structure. Among these, room-temperature bulk moduli have been extensively studied for members of the rock-salt oxides and the olivine group. Deviations of the room-temperature bulk

modulus of the Mg compounds from the trend of the 3d transition metal compounds for both structure types (Fig. 7) are remarkably similar to that observed for the calcite-structure carbonates (Fig. 4), even though for the rock-salt monoxides MnO appears to lie closer to the trend defined by MgO and CaO. In general, these observations are consistent with earlier suggestions that elastic properties are particularly sensitive to the replacement of Mg by 3d transition metals (e.g., Weidner et al. 1982). Figure 7 also reveals that the bulk modulus of CdO is more than 30 GPa larger than that of CaO despite the small difference in cell volume and M-O bond length between these two oxides. The behavior of CdO is thus similar to that of CdCO₃ when both are compared to the Ca compounds, suggesting that crystal compressibility may also be sensitive to the differences between 4d and 3d transition metals and alkaline earth elements. In fact, the existence of different K_0 - V_0 relations for different valence electronic structures was also noted by Anderson (1972) when the 4d and 5d transition metal elements, regardless of the structure type, were considered.

For a series of isostructural solids, three types of properties of the constituent atoms are generally considered in explaining their compressional behavior: size, charge, and electronic configuration. We have just demonstrated that crystal compressibility cannot be explained solely by the M-O bond length or cell volume (Figs. 4 and 7). For carbonates of the calcite structure, we can ignore differences in formal charge. Therefore, it is likely that aspects of electronic structure of the divalent cations are partly responsible for the observed differences of crystal compressibilities. Here we evaluate a few possibilities that may be related to the problem; some of this discussion is unique to the gross features of the calcite structure, whereas other aspects may also apply to other structure types.

Crystal field effects

It is well known that properties of transition metal compounds are subject to crystal field effects. Perhaps the best illustration is the variation of interatomic distance in ionic compounds containing different 3d transition metals (e.g., Hush and Pryce 1958). Ohnishi and Mizutani (1978) have proposed that the deviation from constant K_0V_0 of the divalent metal oxides NiO, CoO, and FeO having the NaCl structure (i.e., metal ions in a regular octahedral coordination) can be explained by considering the crystal field stabilization energy (CFSE).

Crystal-field theory predicts that structures with a transition metal in octahedral or tetrahedral coordination gain stability for certain electronic configurations. For example, Ni²⁺(3d⁸), Co²⁺(3d⁷), and Fe²⁺(3d⁶) in high-spin states gain stability in a regular octahedral environment, whereas high-spin Mn²⁺(3d⁵) and Zn²⁺(3d¹⁰) do not. This enhanced stability is commonly expressed as a CFSE, which for a given electronic configuration depends on the crystal field splitting, Δ_o , and, in turn, on the coordination and metal-ligand distance.

In the calcite-structure carbonates, the MO₆ octahedra are very slightly distorted relative to an ideal octahedron. However, this slight distortion does not provide any stabilization for Mn²⁺ or Zn²⁺. Therefore, among the transition metal carbonates, no crystal field effects are expected in MnCO₃, ZnCO₃, and CdCO₃. Figure 4, however, shows that ZnCO₃ and MnCO₃

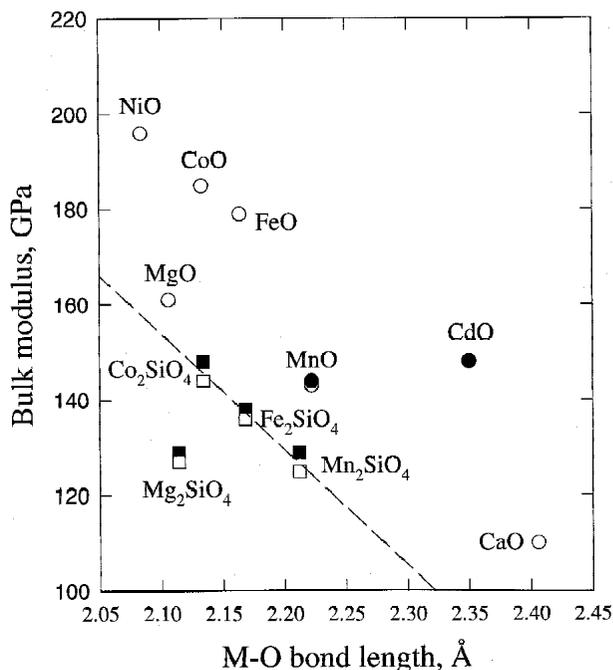


FIGURE 7. The bulk modulus systematics for rock-salt oxides and olivines as functions of M-O bond length. For olivines, the bulk moduli are taken from Sumino (1979) (solid squares) and Zhang (1998) (open squares). MgO and CaO have been well studied, and the data shown here are from Anderson and Isaak (1995). For CoO and MnO, the bulk moduli are taken from Sumino (1980); for NiO the bulk modulus is from Hazen and Finger (1982). For Fe oxide, there appears to be a difference between nonstoichiometric Fe_xO and stoichiometric FeO. In the former case, the bulk modulus values are in the range 146–155 GPa (Fei 1996 and references therein), hence smaller than that of MgO. The predicted bulk modulus for stoichiometric FeO based on the crystal field models for transition metal oxides (Ohnishi and Mizutani 1978; Jeanloz and Sato-Sorensen 1986; Webb et al. 1988) is plotted here and is consistent with the trends observed in olivines and carbonates. The dashed line is the linear fit for the 3d transition metal olivines. The two solid circles are our unpublished data for MnO and CdO, which were studied simultaneously in a single experiment using the same technique as in the present study.

are co-linear with NiCO₃, CoCO₃, and FeCO₃. The bulk moduli of ZnCO₃ and CoCO₃ are essentially identical, as are their ambient M-O bond lengths and volumes. Therefore, no crystal field effect other than that contained within the interatomic distances is observed for the 3d transition metal carbonate subset. In addition, MgCO₃, CaCO₃, and CdCO₃, like MnCO₃ and ZnCO₃, also have no crystal field influence, yet they do not fall on the same trend. Therefore we conclude that the systematic difference between three subsets of carbonates cannot be explained by crystal field effects.

Covalent character in bonding

In many models relating the lattice energy to the equation of state, such as the well-known Born-Mayer formulation, crystals are considered to be ideally ionic for simplicity. However, deviations from the ionic model are also well known, and it appears that such deviations are always in the direction of smaller

compressibility than would be predicted from an ideally ionic model (e.g., Drickamer et al. 1966). It is generally regarded that bonding in these crystals is accompanied by a component of covalency. In its simplest form, increased covalency in bonding is reflected by increased electron density between cations and anions, which is associated with decreased crystal compressibility. A more rigorous evaluation for calcite-structure carbonates, however, requires a quantitative description of the electron density distribution between oxygen and three groups of cations.

Electronegativity is a parameter that, on a relative basis, predicts the tendency of a bonded atom to attract electrons and offers some indication of polarity or covalent character in a bond. Two sets of values that are commonly used (Pauling and Allred-Rochow) are shown in Figure 8 as a function of ambient ionic radius for the metals forming calcite-structure carbonates. Using either set of values, it is seen that electronegativities of alkaline earth elements are systematically lower than those of the transition metals. This difference is similar to that observed for crystal compressibility between the alkaline earth and transition metal carbonates (see Fig. 4). Therefore, it is possible that the relative incompressibility of the transition metal carbonates may be related to the increased covalency or polarity in the M-O bonding. However, when the bulk modulus is plotted as a function of electronegativity (Fig. 9), MgCO_3 and CaCO_3 (and to a lesser degree CdCO_3) show a different correlation from the 3d transition metal carbonates. Therefore, it is clear that polarity or covalent character in bonding alone (or strictly, the electronegativity) cannot explain the complete set of calcite-structure carbonates, nor is it expected to do so. Moreover, the trend in electronegativity (Fig. 8) offers no insight for the different behavior of CdCO_3 .

Vibrational spectra support the view that differences in bond-

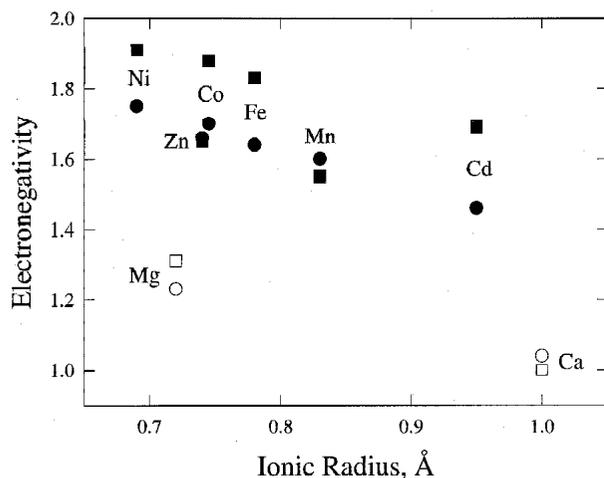


FIGURE 8. Electronegativity vs. ionic radius for cations forming calcite-structure carbonates. Circles: Allred-Rochow values (Pauling scale); squares: Pauling values. For both sets of electronegativities, there is a systematic difference between alkaline earth elements and the trend shown for the transition metals. The nearly linear trend observed for the Allred-Rochow values for the transition metals reflects the radius term used in their calculations. Values of ionic radius are for sixfold coordination and are taken from Shannon and Prewitt (1970) throughout the paper.

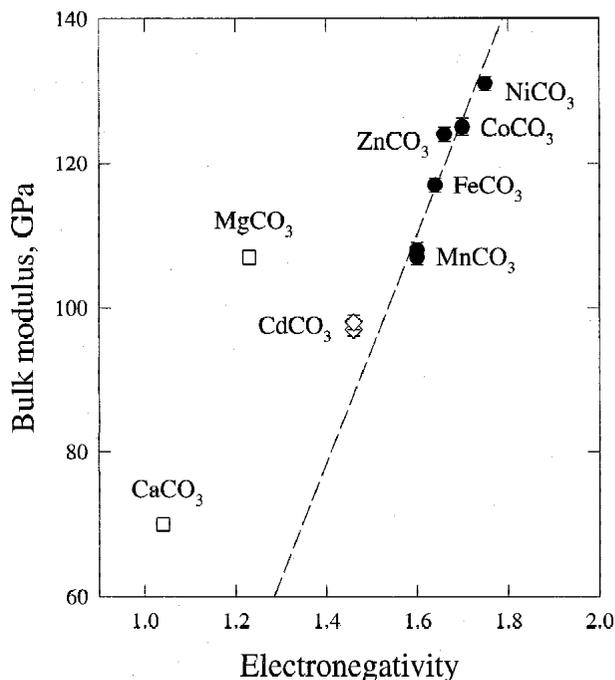


FIGURE 9. The bulk moduli of the calcite-structure carbonates plotted as a function of Allred-Rochow electronegativity (Pauling scale). Some correlation is evident for the 3d transition metal carbonates only.

ing character contribute to our observed difference in compressibility trends. Infrared data for a suite of calcite-structure carbonates (Adler and Kerr 1963) show parallel but offset trends for the internal modes ν_2 , ν_3 , and ν_4 as a function of ionic radius of the metal cation. The observation that the trends for the 3d transition metal carbonates lie at lower frequencies than the trend for MgCO_3 and CaCO_3 is consistent with our finding that MgCO_3 has a systematically lower bulk modulus than the transition metal carbonates. Moreover, this observation is consistent with the conclusion drawn by Hofmeister (1991) that the bulk modulus is correlated with the sum of the squares of the vibrational frequencies as well as structural parameters for the phase. Therefore, differences in bonding character, associated with different valence electronic structure, seem to explain the differences in compressibility trends between different subsets of the calcite-structure carbonates.

Nonbonded interactions

O'Keeffe and Hyde (1981) have argued that nonbonded interactions play an important role in determining structural properties. Their emphasis on cation-cation distances contrasts with many conventional interatomic potential models (e.g., Davis 1981; Weidner and Price 1988; Dove et al. 1992), in which only second-neighbor anion repulsive forces are taken into account and interactions between adjacent cations are generally ignored. Recently, Hazen (1993), on the basis of room-temperature pressure-volume measurements, suggested that the incompressibility of Fe^{2+} end-member silicate spinel relative to its Mg counterpart might be partially attributed to d electron repulsion across the shared edges of FeO_6 octahedra, and thus provided experimental grounds that appear to argue for the

importance of nonbonded interactions in determining crystal compressibility.

Cation-cation distances and bond angles involving cations and anions are important parameters describing nonbonded interaction in crystals, and are among several aspects that have been discussed in detail by O'Keeffe and Hyde (1981). For calcite-structure carbonates, the closest M^{2+} - M^{2+} and M^{2+} - C^{4+} distances and the M^{2+} -O- M^{2+} and M^{2+} -O- C^{4+} angles, calculated from ambient single-crystal structure refinements, are shown in Figures 10 and 11. In all calcite-structure carbonates, the closest cation-cation distances and the bond angles correlate approximately linearly with the ionic radii of the corresponding metal ions. It is therefore unlikely that the observed differences in crystal compressibility between alkaline earth, 3d, and 4d transition metal carbonates can be attributed to differences in the nonbonded interactions.

Consideration of the nonbonded interactions also cannot explain the unexpected a axis compressional behavior of the

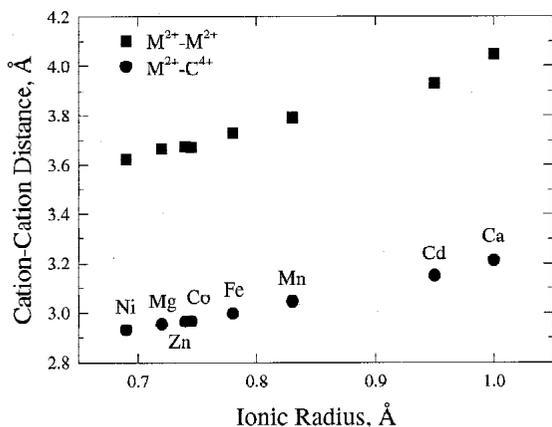


FIGURE 10. Nearest cation-cation distances (ambient conditions) as a function of ionic radius for all calcite-structure carbonates. For comparison, the nearest M^{2+} - M^{2+} distances are 2.7–2.9 Å in the rock salt oxides and 3.0–3.2 Å in the olivines.

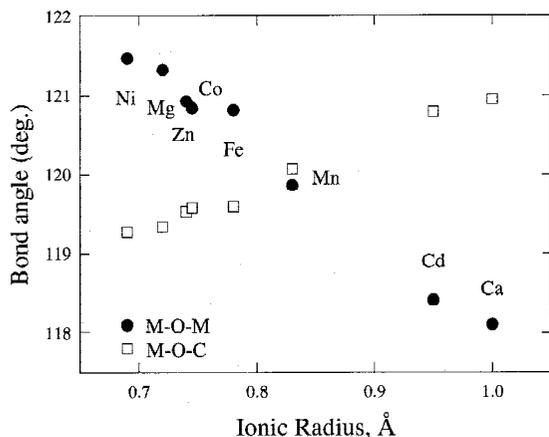


FIGURE 11. Relationship between ambient-condition bond angles and ionic radii in the calcite-structure carbonates.

calcite-structure carbonates (Fig. 5). As shown in Figure 10, the shortest cation-cation distance in the calcite structure is between M^{2+} and C^{4+} (2.93–3.21 Å) whereas the shortest M^{2+} - M^{2+} distance (3.62–4.05 Å) is considerably longer compared to those in rock-salt oxides and olivines. The vectors of the M^{2+} - C^{4+} connections in the calcite structure are aligned more closely with the a axis than the c axis. Therefore, one might expect the compressibility of the a axis to be roughly proportional to the M^{2+} - C^{4+} distance if cation-cation repulsion played an important role in the compressibility of the calcite-structure carbonates. From Figures 5 and 10, however, the experimental observations show that no such trend exists.

For nonbonded interactions, the repulsions are normally ascribed to overlap of electron clouds when atom separations are less than their sum of the van der Waals radii (O'Keeffe and Hyde 1981). One aspect that has not been discussed in the preceding paragraphs is the role of the d electrons. For the transition metal calcite-structure carbonates, one might expect enhanced cation-cation repulsion depending on the occupancy of the 5 d-electron orbitals and their directionality. Therefore, it is possible that the observed incompressibilities of the transition metal carbonates relative to $MgCO_3$ and $CaCO_3$ (Fig. 5), when compared to the empirical relations between K_0 and V_0 or between K_P and M-O bond length, may be partially attributed to enhanced repulsion of the d electrons, as suggested by Hazen (1993) to explain the compressional behavior in $(Mg,Fe)_2SiO_4$ silicate spinels. Further consideration of this aspect would require theoretical calculations to characterize the electron-electron interactions between metal ions of different types and their pressure dependence.

CONCLUDING REMARKS

Our observed correlations between the room-temperature bulk modulus and ambient M-O bond length, shortest cation-cation distances, and cation electronegativity show that systematic behavior is limited to subsets of the calcite-structure carbonates whose metal ions share the same character of their valence electrons. No single structural parameter or electronic property of the cation can account for the behaviors of the complete set of carbonates, suggesting that a combination of factors must be considered in explaining compressibility trends among members of a calcite-structure type. Differences in bonding character, associated with different valence electronic structure, seem to explain the differences in compressibility trends between different subsets. There is every reason to believe that systematic characterization of other isostructural series will show similar deviations from empirical relations based solely on cell volume or M-O bond lengths. Because electronic structure of the constituent cations appears to be an important factor, in addition to cation size, quantum chemical calculations may be particularly important for understanding differences in compressional behavior that are demonstrated by experiments.

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