

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

**JIANZHONG ZHANG\* AND RICHARD J. REEDER**

Center for High-Pressure Research and Department of Geosciences, State University of New York at Stony Brook, Stony Brook, New York 11794, U.S.A.

### **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  $\text{MgCO}_3$  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  $\text{CdCO}_3$ , whose M-O bond length and cell volume are only slightly smaller than those of  $\text{CaCO}_3$ , 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.