

## Structural variation in the dolomite-ankerite solid-solution series: An X-ray, Mössbauer, and TEM study—Discussion

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In the recent study of the dolomite-ankerite solid-solution series by Reeder and Dollase (1989), the cause of the instability of  $\text{CaFe}(\text{CO}_3)_2$  and the limited substitution of  $\text{Fe}^{2+}$  for  $\text{Mg}^{2+}$  in the dolomite structure is reconsidered but left unresolved. Excessive octahedral distortion has been proposed as a possible explanation (Rosenberg and Foit, 1979), but because of the lack of structural data for Fe-bearing dolomites a decade ago, octahedral distortion in ferroan dolomites was inferred from estimates for siderite ( $\text{FeCO}_3$ ). Now that structural refinements and other crystal chemical data are available for ferroan dolomites (Reeder and Dollase, 1989) a reassessment of the effects of octahedral distortion is possible.

In their recent paper, Reeder and Dollase (1989) have shown convincingly that little or no octahedral distortion exists in ferroan dolomites. The  $\text{CaO}_6$  octahedron in ankerite is apparently no more distorted than in calcite, whereas the  $(\text{Fe}^{2+}, \text{Mg})\text{O}_6$  octahedron is somewhat less distorted in ankerite than it is in siderite. Therefore, Reeder and Dollase (1989, 1991) conclude that the energetic differences favoring two-phase assemblages of calcite and siderite solid solutions over ankerite richer in  $\text{CaFe}(\text{CO}_3)_2$  than approximately 70 mol% are probably not due to octahedral distortion.

The distortion of  $\text{FeO}_6$  octahedra in siderite should result in a lower energy configuration, thus stabilizing the siderite structure. Consequently, the free energy of formation of siderite should be more negative than it would be if  $\text{Fe}^{2+}$  were constrained to more regular coordination octahedra. However, the  $(\text{Fe}^{2+}, \text{Mg})\text{O}_6$  octahedron in ferroan dolomite is less distorted than it is in siderite (Reeder and Dollase, 1989). The greater octahedral distortion in siderite than in ferroan dolomite may provide an explanation for these phase relations, inasmuch as  $\text{Fe}^{2+}$ , an ion subject to the Jahn-Teller effect, substitutes preferentially in distorted sites (Walsh et al., 1974).

Octahedral distortion is present in all of the rhombohedral carbonates in the form of trigonal elongation (Reeder, 1983; Reeder and Dollase, 1991). Although static Jahn-Teller effects are not to be expected in trigonal fields, dynamic effects are anticipated (Walsh et al., 1974). These effects are due to distortions along symmetry-equivalent directions and, therefore, do not lower the symmetry of the affected polyhedra. Since they cause no static (i.e., permanent) structural changes, dynamic Jahn-Teller effects can be detected only by optical spectroscopy. The magnitude of dynamic effects in the rhombohedral carbonates cannot be evaluated at present.

However, the  $t_{2g}$  ground state of  $\text{Fe}^{2+}$  is split by a trigonal field resulting in an orbital doublet (degenerate) ground state and a singlet excited state (Walsh et al., 1974), thus increasing the stability of  $\text{Fe}^{2+}$  in trigonally elongated octahedral sites. If two such sites are available,  $\text{Fe}^{2+}$  will favor the more distorted site. The additional stabilization energy due to the slightly greater trigonal distortion in siderite than in ankerite is likely to be small (Reeder and Dollase, 1991). Nevertheless, substitution of  $\text{Fe}^{2+}$  into the octahedral sites in the ferroan dolomite structure should result in a slightly more positive free energy of formation than would be the case if the  $\text{FeO}_6$  octahedra were more distorted as they are in siderite.

A linear correlation has been shown to exist between the standard free energies of formation of the calcite-type carbonates and those of the divalent aqueous ions at 25 °C and 1 bar (Sverjensky, 1984). Inasmuch as the aqueous  $\text{Fe}^{2+}$  complex is essentially undistorted, the splitting of the  $t_{2g}$  ground state in siderite appears to have no effect on its free energy of formation. However, the errors inherent in this comparison (several hundred calories per mole) are of the same order of magnitude as the crystal field effects (Reeder and Dollase, 1991).

Although the additional stabilization energy caused by greater octahedral distortion in siderite is probably small, it may well be significant. If so, then substitution of  $\text{Fe}^{2+}$  in the dolomite structure would be energetically favorable until

$$\Delta G_{f, \text{dol}}^0 = \sum \Delta G_{f, \text{two disordered solid solutions}}^0$$

With further substitution, ferroan dolomite would become metastable with respect to a two-phase assemblage of calcite and siderite solid solutions. The free energies of mixing of these solid solutions must also be taken into consideration.

Similar reasoning may account for the instability of  $\text{CaCo}(\text{CO}_3)_2$  and the limited substitution of  $\text{Co}^{2+}$  for  $\text{Mg}^{2+}$  in the dolomite structure (Goldsmith and Northrop, 1965), but it would not apply to other transition metal ( $R^{2+}$ ) cations ( $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ) that do not gain stabilization energy because of trigonal elongation of octahedra in carbonate structures.  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$ , like  $\text{Mg}^{2+}$ , receive no crystal field stabilization energy in octahedral coordination, and they substitute completely for  $\text{Mg}^{2+}$  in the dolomite structure. [Substitution of  $\text{Zn}^{2+}$  for  $\text{Mg}^{2+}$  in the dolomite structure is very extensive and may be complete (Rosenberg and Champness, 1989).] Thus, trigonal

elongation has little or no effect on the relative stability of  $Mn^{2+}$ - and  $Zn^{2+}$ -bearing carbonates.

$Ni^{2+}$  does not gain additional stabilization energy in distorted sites (Burns, 1970, p. 123). However,  $Ni^{2+}$  is unique among the cations that form rhombohedral carbonates in that it has the smallest ionic radius and the shortest M-O bond length (2.076 Å, Pertlik, 1986). Unlike the other transition metal cations,  $Ni^{2+}$  prefers smaller sites than  $Mg^{2+}$ , which enhance the magnitude of its crystal field splitting (Rajamani et al., 1975). Thus, substitution of  $Ni^{2+}$  for  $Mg^{2+}$  is limited (Goldsmith and Northrop, 1965; Gaines and Goldsmith, 1971);  $Ni^{2+}$  acquires greater stabilization energy by forming  $Ni^{2+}$  minerals (i.e.,  $NiCO_3$ ) rather than solid solutions.

$CuCO_3$  has a distorted, monoclinic structure that is unstable under ambient conditions; the coordination of  $Cu^{2+}$ , an  $e_g$  degenerate Jahn-Teller ion, is five (Seidel et al., 1974). Thus, it is not surprising that little or no  $Cu^{2+}$  has been reported in natural dolomite (Rosenberg and Foit, 1979).

Although the transition metal dolomite stability series proposed by Rosenberg and Foit (1979),



may be valid, the sequence of relative stabilities cannot be attributed solely to octahedral distortion. However, octahedral distortion may account for the instability of  $CaFe(CO_3)_2$  and the energetic differences favoring calcite and siderite solid solutions over ankerite more ferroan than approximately 70 mol%  $CaFe(CO_3)_2$ . Further studies of Fe-bearing carbonates will be required to put this long-standing problem to rest.

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