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

Richard J. Reeder
Department of Earth and Space Sciences, State University of New York at Stony Brook, Stony Brook, New York 11794, U.S.A.
Wayne A. Dollase
Department of Earth and Space Sciences, University of California, Los Angeles, Los Angeles, California 90024, U.S.A.

Upon reconsidering the effects of octahedral distortion on the stabilities of ferroan carbonates, Rosenberg (1991) agrees that the cause of the apparent instability of $CaFe(CO_3)_2$ and limited substitution of Fe^{2+} in dolomite does not seem to lie with excessive distortion of the octahedral sites in ankerite. Rather, he now suggests that the lack of significant octahedral distortion in ankerite and the presence of slightly greater Fe^{2+} site distortion in siderite serve to stabilize the latter, thereby favoring the assemblage calcite + siderite solid solutions over ankerite with $CaFe(CO_3)_2$ content greater than roughly 70 mol%. We agree with Rosenberg that the presence of different Fe^{2+} site distortions in these minerals allows for the possibility of differing crystal field stabilization. However, we also believe the magnitudes of the distortion differences that have been documented are sufficiently small that attributing differences of stability to crystal field effects may be unwarranted. Nevertheless, we find Rosenberg's suggestion very interesting and believe that it points to the need for greater study of Fe-bearing carbonates. We also applaud Rosenberg for indicating that observed octahedral distortions in rhombohedral carbonates are not fully consistent with the previously proposed stability series for transition metal dolomites (cf. Rosenberg and Foit, 1979).

Since Rosenberg's arguments are based on differences of the magnitudes of Fe^{2+} site distortion between siderite and ankerite, we examine this first. The sites occupied by Fe^{2+} in both siderite and ankerite have symmetry $\bar{3}$, and static octahedral distortions are constrained to be either trigonal elongations or compressions. Magnitudes of distortion are commonly expressed either by quadratic elongation (Robinson et al., 1971) or, somewhat more conveniently, by deviation from 90° of the octahedral angles. In both siderite and ankerite, the observed static distortion is a trigonal elongation of small magnitude. We have previously noted that cation sites of all calcite- and dolomite-structure carbonates exhibit small trigonal elongations, both larger and smaller in magnitude than the ferroan carbonates discussed here (cf. Reeder, 1983).

The structure refinement of siderite by Effenberger et al. (1981) shows that the O-Fe^{2+}-O angles (the O atoms are situated at different levels along **c**) of the trigonally elongated octahedra deviate from 90° by 2.05°. Refinements of the ankerite structure (Reeder and Dollase, 1989) show that the O-(Fe^{2+},Mg)-O angles of the octahedra filled with just over 70% Fe^{2+} (sample AMNH 8059) deviate from 90° by 1.80°. Thus, it appears that the siderite octahedra are more distorted, but by only 0.25°.

A slightly greater octahedral distortion in siderite is consistent with the observation of a larger quadrupole splitting in the Mössbauer spectra of siderite (Nagy et al., 1975) compared to that of ankerite (Reeder and Dollase, 1989; DeGrave and Vochten, 1985). Similarly, the lower rate of change of quadrupole splitting (QS) as a function of temperature observed in siderite (Nagy et al., 1975) compared to ankerite (DeGrave and Vochten, 1985) is very likely due to slightly greater distortion in the former, and hence, greater splitting of the first excited state above the ground state.

However, the differences observed between siderite and ankerite are very small, especially when compared with examples of Fe^{2+}-bearing silicates. The crystal field energetic consequences of such small differences in distortion are also likely to be small.

Trigonal elongation of the Fe^{2+} octahedra in siderite and ankerite results in splitting of the t_{2g} energy level, producing an orbital doublet ground state and singlet first excited state, for which the splitting is denoted by δ. The additional crystal field stabilization energy (CFSE) for high-spin Fe^{2+} resulting from this trigonal elongation is $\frac{1}{3}\delta$, so that the total CFSE is $\frac{2}{5}\Delta_0 + \frac{1}{3}\delta$. Values of Δ_0 have not been reported for siderite or ankerite, and therefore, evaluation of total CFSE is not possible. However, DeGrave and Vochten (1985) have estimated $\delta = 370$ cm^{-1} for an ankerite based on the temperature dependence of QS. A comparable analysis for siderite using the data given by Nagy et al. (1975) yields approximately 600 cm^{-1}, which is consistent with its slightly greater site distortion. We emphasize, as did DeGrave and Vochten, that these values should be considered little more than rough estimates, since the simple crystal field models used cannot adequately describe the linear temperature dependence of QS observed for both siderite and ankerite. However, these estimates do suggest that the crystal field energetic differences are likely to be small—on the order of only a few hundred cal/mol greater stabilization in siderite.

Further evidence that the additional crystal field stabilization of siderite is minimal as a consequence of its distortion can be found in the linear relationship between the free energies of formation of aqueous metal species and their respective (calcite structure) carbonate shown by Sverjensky (1984). If the distortion of the Fe^{2+} site in siderite contributed significantly to enhancing its stability, one would expect its free energy value to deviate from the straight line connecting the other carbonates (Sverjensky, 1984, Fig. 1), for which there are no crystal field effects.

A small CFSE may (or may not) be significant, as noted by Rosenberg, but it should not be viewed as the only factor affecting the apparent instability of $CaFe(CO_3)_2$ and the limited Fe^{2+} substitution in ankerite. For example, the energetic consequences of mixing in calcite and siderite solid solutions [which are seemingly more stable than $CaFe(CO_3)_2$-rich ankerites] could easily be on the order of hundreds of cal/mol. In view of the lack of data for the various energetic contributions, we believe that it is probably unwarranted to attribute any cause to small differences in octahedral distortions, unless other observations can be found to support it.

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