

## Petrologic and crystal-chemical implications of cation order-disorder in kutnahorite $[\text{CaMn}(\text{CO}_3)_2]^*$

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### ABSTRACT

The crystal structures of kutnahorite from Bald Knob (BK), North Carolina, and Sterling Hill (SH), New Jersey, have been refined. The BK kutnahorite  $(\text{Ca}_{49}\text{Mn}_{50}\text{Mg}_1\text{Fe}_0)$  is disordered in Ca-Mn distribution, but the SH kutnahorite is substantially ordered:  $(\text{Ca}_{0.84}\text{Mn}_{0.16})(\text{Ca}_{0.27}\text{Mn}_{0.73})(\text{CO}_3)_2$ . Long-range cation order in kutnahorite is not detectable using conventional powder X-ray diffraction techniques, but it may be measured by single-crystal techniques. The large ionic radius of Mn relative to Mg in dolomite leads to coupled distortion of the Ca and Mn octahedra that may result in a low ordering potential. Thus, the BK kutnahorite lacks significant cation order despite slow cooling from amphibolite-facies regional metamorphic conditions. Long-range cation order in SH kutnahorite is compatible with a low-temperature solvus between calcite and kutnahorite as well as between kutnahorite and rhodochrosite. Two-phase intergrowths of manganian calcite  $(\text{Ca}_{88}\text{Mn}_{12}\text{Mg}_0)$  and calcian kutnahorite  $(\text{Ca}_{62}\text{Mn}_{35}\text{Mg}_3)$  from SH are interpreted as due to primary coprecipitation of calcite and ordered kutnahorite from solution in the two-phase region at temperatures below the solvus crest. Data on metamorphic Ca-Mn carbonates indicate complete solid solution between calcite and rhodochrosite at 600°C with solvi between kutnahorite-calcite and kutnahorite-rhodochrosite forming at lower temperatures.

### INTRODUCTION

Kutnahorite was originally described by Frondel and Bauer (1955) as having ideal composition  $\text{CaMn}(\text{CO}_3)_2$  and ordering of Ca and Mn, resulting in a dolomite-like structure. The ordering was determined by the apparent presence of  $h0l$ ,  $l = 2N + 1$  reflections (based on hexagonal axes) in the powder-diffraction pattern that are compatible with space group  $(R\bar{3})$  of the ordered compound but incompatible with space group  $(R\bar{3}c)$  of the disordered calcite-type structure. Schindler and Ghose (1970), Wildeman (1970), Lumsden and Lloyd (1984), and Lloyd et al. (1985) showed that  $\text{Mn}^{2+}$  substitutes in both the A and B sites of dolomite, but with a strong preference for the B(Mg) site. This implies strong Ca-Mn order in manganian dolomite, but the results are for very low Mn concentrations and may not apply to  $\text{CaMn}(\text{CO}_3)_2$ . Bolzenius et al. (1985) have briefly described a structure refinement of a magnesian kutnahorite of an unreported composition but did not report on the inferred cation ordering.

The binary system  $\text{CaCO}_3$ - $\text{MnCO}_3$  was experimentally investigated by Goldsmith and Graf (1957) and de Capitani and Peters (1981), who found a solvus between rhodochrosite and kutnahorite but none between kutnahorite

and calcite. The ternary system  $\text{CaCO}_3$ - $\text{MnCO}_3$ - $\text{MgCO}_3$  was evaluated at 500 to 800°C by Goldsmith and Graf (1960), who found wide solvi separating manganian calcite, manganian dolomite, and manganian magnesite. They were unable to detect ordering reflections in synthetic kutnahorite and concluded that the similar scattering powers of Ca and Mn result in very weak and perhaps undetectable ordering reflections even if Ca and Mn are highly ordered. Goldsmith (1983) further pointed out that short-range order may occur in carbonates but be undetectable by X-ray diffraction. Capobianco and Navrotsky (1987) combined experimental and thermodynamic data on synthetic  $\text{CaCO}_3$ - $\text{MnCO}_3$  solid solutions to calculate a solvus for disordered carbonates cresting at ca. 330°C and  $X_{\text{MnCO}_3}$  of 0.44. The calculated solvus is metastable relative to a solvus or solvi involving kutnahorite with short- or long-range order (Capobianco and Navrotsky, 1987). Although the coherent and spinodal solvi were not given, their data suggest that disordered carbonates near the kutnahorite composition are unstable at Earth surface temperatures.

Despite the absence of observed ordering reflections in the synthetic materials, the experimental solvus inferred between kutnahorite and rhodochrosite (Goldsmith and Graf, 1957; de Capitani and Peters, 1981) suggests cation ordering in kutnahorite by analogy with the system  $\text{CaCO}_3$ - $\text{MgCO}_3$ . This also would suggest a solvus between

\* Contribution no. 422 from the Mineralogical Laboratory, Department of Geological Sciences, the University of Michigan.  
0003-004X/87/0304-0319\$02.00

TABLE 1. Microprobe analyses of manganoan carbonates

|                 | Oxide weight percent |          |         |         |
|-----------------|----------------------|----------|---------|---------|
|                 | BK-14                | H-109405 | SH-525K | SH-525C |
| FeO             | 0.2                  | 0.8      | 0.8     | 0.2     |
| MnO             | 32.6                 | 31.8     | 27.6    | 9.6     |
| MgO             | 0.4                  | 0.5      | 1.1     | 0.5     |
| CaO             | 25.6                 | 25.3     | 37.8    | 56.5    |
| ZnO             | n.d.                 | 1.4      | 0.8     | 0.1     |
| CO <sub>2</sub> | 40.6                 | 40.3     | 31.1    | 32.5    |
| Sum             | 99.4                 | 100.1    | 99.2    | 99.4    |
|                 | Atom fraction        |          |         |         |
| Fe              | 0.003                | 0.012    | 0.008   | 0.002   |
| Mn              | 0.496                | 0.477    | 0.351   | 0.117   |
| Mg              | 0.011                | 0.013    | 0.025   | 0.010   |
| Ca              | 0.490                | 0.480    | 0.607   | 0.888   |
| Zn              | n.d.                 | 0.018    | 0.009   | 0.003   |

Note: CO<sub>2</sub> calculated from stoichiometry; n.d. = not determined; sample 525 from Sterling Hill for kutnahorite (K) and calcite (C).

kutnahorite and calcite, but this solvus has not yet been demonstrated experimentally. The compositions of both synthetic and natural metamorphic phases that fall close to the CaCO<sub>3</sub>-CaMn(CO<sub>3</sub>)<sub>2</sub> binary join are consistent with complete solid solution although some two-phase materials and compositional gaps suggest low-temperature solvi (Fron del and Bauer, 1955; Goldsmith, 1959, 1983; Winter et al., 1981; de Capitani and Peters, 1981; Essene, 1983; Fig. 1). The continuum of compositions could be due to (1) crystallization of metastable, cation-disordered carbonates within a two-phase field as in the calcite-dolomite system (Goldsmith, 1983); (2) location of a solvus at a temperature below that of the formation of the minerals studied; or (3) the lack of resolution of fine-grained, two-phase intergrowths. Extrapolation of the experiments in the ternary system CaCO<sub>3</sub>-MgCO<sub>3</sub>-MnCO<sub>3</sub> (Goldsmith and Graf, 1960) indicates that the solvus will intersect the CaCO<sub>3</sub>-MnCO<sub>3</sub> join at  $T < 400^{\circ}\text{C}$ . This system demonstrates the importance of even minor Mg in generating a solvus assemblage that may be driven by ordering of cations in the dolomite-type structure.

Lastly, the "dolomite problem" has long been an enigma to crystal chemists. It is not at all clear why Ca and Mg are ordered in dolomite, resulting in a phase that determines the form of the CaCO<sub>3</sub>-MgCO<sub>3</sub> system and having far-reaching consequences in natural carbonate systems. Reeder (1983) has reviewed the factors that affect the relative stabilities of possible ordered compounds with the dolomite structure. Interpretation is hindered by a lack of detailed knowledge of steric factors in the structures of several carbonates. As kutnahorite is one of only four known dolomite-structure minerals, it is essential to define its detailed structure so that meaningful comparisons of steric parameters can be made and to provide insight into factors that lead to ordered dolomite-type structures.

As part of a study of Mn minerals from Bald Knob (BK), North Carolina, Winter et al. (1981) characterized a phase having a composition very near to that of stoichiometric kutnahorite, for which no ordering reflections

could be detected in single-crystal X-ray photographs. This specimen contains only small amounts of other cations such as Mg. Because such additional components would have significant effects on order-disorder relations and because relatively pure kutnahorites are unusual, we chose to refine its structure in order to directly determine the state of order-disorder. In addition, Pete J. Dunn kindly made available a specimen of Sterling Hill (SH), New Jersey, kutnahorite that has a composition nearly identical to that from BK. Because some SH Ca-Mn carbonates are two-phase intergrowths (Fron del and Bauer, 1955; Goldsmith, 1959, 1983), the presence of a solvus is implied, and this in turn suggests ordering in these kutnahorites; we therefore chose to refine the structure of a specimen from that locality.

### SAMPLE CHARACTERIZATION

The Bald Knob, North Carolina, sample (BK-14) is from a fine-grained metamorphic rock that equilibrated under middle amphibolite-facies conditions at temperatures of 550–600°C (Winter et al., 1981). This sample and others at Bald Knob display an obvious gneissic layering that reflects differences in proportions and grain sizes of Mn carbonates and silicates, such that the carbonates may vary significantly in composition between layers. However, analyses of six different grains from sample BK-14 gave results that are identical within analytical error. Although the analytical totals of the carbonate analyses in Winter et al. (1981) are erratic, reanalysis of kutnahorite BK-14 with the University of Michigan automated CAMECA Camebax microprobe yields a formula close to that originally reported but with better totals (Table 1). A cleavage fragment was separated from the original specimen, and its composition was assumed to correspond to the average (Ca<sub>0.49</sub>Mn<sub>0.50</sub>Mg<sub>0.01</sub>Fe<sub>0.00</sub>CO<sub>3</sub>) for the specimen (Table 1).

The Sterling Hill sample (SH) was obtained from Harvard University sample H-109405. The kutnahorite occurs as a coarsely crystalline vein cutting zinc ore (Fron del and Bauer, 1955). This sample was chosen because a systematic study of compositions of Sterling Hill and Franklin, New Jersey, kutnahorites (P. J. Dunn, pers. comm.) had shown that it is nearly stoichiometric with only minor amounts of Mg and thus is very close to the Bald Knob sample in composition. Refinement of the SH composition during X-ray structure analysis is consistent with the composition (Ca<sub>0.55</sub>Mn<sub>0.45</sub>)CO<sub>3</sub>. The single crystal that was studied was ground away before microprobe analysis could be obtained; analyses of the crushed grains from which the single-crystal mount was selected yielded (Ca<sub>0.48</sub>Mn<sub>0.48</sub>Zn<sub>0.01</sub>Mg<sub>0.01</sub>Fe<sub>0.01</sub>)CO<sub>3</sub>. However, it is evident that the SH sample is somewhat variable around the ideal kutnahorite composition. In the discussion that follows, it is assumed that the composition derived from the X-ray study is correct.

Powder-diffractometer patterns were obtained from both BK and SH kutnahorites. We attempted to index these patterns initially based on the indexing of Fron del

TABLE 2. Powder diffraction data for kutnahorite (Sample BK-14, Bald Knob, North Carolina)

| $hkl$ | $d_{obs}$ | $d_{calc}$ | $hkl$  |
|-------|-----------|------------|--------|
| 9     | 3.76      | 3.75       | 012    |
| 100   | 2.939     | 2.936      | 104    |
| 3     | 2.438     | 2.437      | 110    |
| 4     | 2.225     | 2.224      | 113    |
| 0     | —         | 2.044      | 107    |
| 10    | 2.042     | 2.043      | 202    |
| 2     | 1.875     | 1.875      | 024    |
| 8     | 1.839     | 1.839      | 018    |
| 0     | —         | 1.817      | 009    |
| 11    | 1.816     | 1.816      | 116    |
| 1     | 1.587     | 1.588      | 211    |
| 6     | 1.565     | 1.566      | 122    |
| 3     | 1.486     | 1.486      | 214    |
| 1     | 1.468     | 1.468      | 028    |
| 2     | 1.456     | 1.456      | 119    |
| 1     | 1.435     | 1.434      | 125    |
| 2     | 1.407     | 1.407      | 300    |
| 1     | 1.291     | 1.292      | 02, 10 |
| 2     | 1.256     | 1.257      | 128    |

Note: The ordering reflections (107) and (009) are inferred to have an intensity of 0 based on single-crystal observations.

TABLE 3. Crystal data for Bald Knob and Sterling Hill kutnahorite

|  | BK   | SH                 |
|--|--|--------------------|
| Space group                            | $R\bar{3}$   | $R\bar{3}$         |
| Lattice parameters                     |  |                    |
| $a$ (Å)                                | 4.8732(8)  | 4.894(1)           |
| $c$                                    | 16.349(6)  | 16.50(2)           |
| $V$ (Å <sup>3</sup> )                  | 336.2(1)   | 342.3(3)           |
| Diffractometer                         | Weissenberg geometry $\omega$ -scan                |                    |
| Radiation                              | MoK $\alpha$ , monochromated with graphite crystal |                    |
| Detector                               | Scintillation counter                              |                    |
| Absorption correction                  |  |                    |
| $\mu$ (cm <sup>-1</sup> )              | 50   | 50                 |
| Crystal shape                          | rhombohedron                                       | rhombohedron       |
| average vertex to vertex distance (mm) | 0.26   | 0.20               |
| $\sin \theta/\lambda$ limit            | 0.65   | 0.65               |
| Reflections measured                   | $h > 0; h + k > 0$                                 | $h > 0; h + k > 0$ |
| Number of reflections                  | 322  | 319                |
| Number of unobserved reflections       | 78   | 54                 |
| Final residuals                        |  |                    |
| $R$ (all data)                         | 3.9%   | 4.0%               |
| $R$ (observed data)                    | 3.1%   | 3.1%               |
| Largest $\Delta/\sigma$                | 0.12   | 0.09               |

and Bauer (1955) in order to obtain data for least-squares refinement of lattice parameters. Ambiguities became apparent in the indexing of the ordering reflections, however, and we therefore reindexed the pattern (Table 2). This showed that all observed reflections for both the BK and SH samples, as well as those of Frondel and Bauer (1955), are explained by nonordering reflections alone.

#### CRYSTAL-STRUCTURE REFINEMENTS

Rhombohedral cleavage fragments of kutnahorite from both localities were mounted along  $c$  on a Supper-Pace diffractometer system. MoK $\alpha$  radiation, monochromated by a flat crystal of graphite, was used. Intensities of reflections with  $\sin \theta/\lambda < 0.65$  were measured and corrected for Lorentz, polarization, and absorption effects, resulting in 322 and 319 reflections for the BK and SH kutnahorites, respectively. Absorption corrections were carried out using a modified version of a program written by Burnham (1962a). Lattice parameters were determined by least-squares refinement of powder-diffractometer data, obtained using CuK $\alpha$  with Si as an internal standard and utilizing the program LCLSQ (Burnham, 1962b). The refined values are  $a = 4.8732(8)$  and  $c = 16.349(6)$  Å for BK and  $a = 4.894(1)$  and  $c = 16.50(2)$  Å for SH (Table 3).

Before proceeding with measurements of intensity values, single-crystal X-ray scans were carefully made at coordinates corresponding to ordering reflections. Scans for the Bald Knob specimen showed no observable intensities for any ordering reflections except a barely observable peak for (107). This confirmed the single-crystal film observations for which no ordering reflections were observed. By contrast, several ordering reflections were observed to have weak-to-medium intensities for the SH crystal. These data imply that the BK sample has a highly

disordered distribution of Ca and Mn and that the SH kutnahorite is at least partially ordered. In order to test the BK sample for the possibility of short-range order that might occur in anti-phase domains of a size so small as to be undetectable using X-ray diffraction, a sample was studied using transmission-electron microscopy. An ion-thinned sample was observed using the University of Michigan JEOL JEM 100CX electron microscope. The relatively featureless images so obtained are consistent with a randomly disordered structure.

Refinement was carried out with the program RFINE2 (Finger and Prince, 1975) using neutral scattering factors of Doyle and Turner (1968) with equal Ca and Mn occupancies initially assumed for the A and B sites of both kutnahorites. The occupancies were not constrained by the analytical data, and the only restriction was that the total site occupancies are 1.0. The weighting scheme of Cruickshank (1965) was used. All refinements were carried out assuming space group  $R\bar{3}$  for the ordered structure. No correction for extinction was utilized because examination of the structure factors implied that there was no significant extinction factor. Refinement converged after refinement of anisotropic temperature factors and occupancy factors for both cation sites. Including unobserved reflections, the final  $R$  factors are 3.9% for BK and 4.0% for SH kutnahorite. Final structure factors are listed in Table 4,<sup>1</sup> structure parameters in Table 5, data from thermal ellipsoids in Table 6, and selected distances and angles in Table 7. Distances and angles were calculated using the program ORFFE (Busing et al., 1964),

<sup>1</sup> To obtain a copy of Table 4, order Document AM-87-332 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 5. Structure parameters for Bald Knob (upper lines) and Sterling Hill (lower lines) kutnahorite

| Atom | x         | y         | z         |  |  |  |
|------|-----------|-----------|-----------|--|--|--|
| A    | 0         | 0         | 0         |  |  |  |
|      | 0         | 0         | 0         |  |  |  |
| B    | 0         | 0         | 1/2       |  |  |  |
|      | 0         | 0         | 1/2       |  |  |  |
| C    | 0         | 0         | 0.2495(2) |  |  |  |
|      | 0         | 0         | 0.2461(2) |  |  |  |
| O    | 0.2634(3) | 0.9995(4) | 0.2496(2) |  |  |  |
|      | 0.2568(3) | 0.9850(4) | 0.2472(1) |  |  |  |

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|------|--------------|--------------|--------------|--------------|--------------|--------------|
| A    | 0.0115(3)    | 0.0115       | 0.0010(1)    | 0.0057       | 0            | 0            |
|      | 0.0120(2)    | 0.0120       | 0.0011(1)    | 0.0060       | 0            | 0            |
| B    | 0.0012(3)    | 0.0012       | 0.0010(1)    | 0.0056       | 0            | 0            |
|      | 0.0108(2)    | 0.0108       | 0.0011(1)    | 0.0054       | 0            | 0            |
| C    | 0.0122(9)    | 0.0122       | 0.0011(2)    | 0.0061       | 0            | 0            |
|      | 0.0124(10)   | 0.0124       | 0.0013(1)    | 0.0062       | 0            | 0            |
| O    | 0.0131(5)    | 0.0272(6)    | 0.0019(1)    | 0.0125(4)    | -0.0001(1)   | -0.0003(1)   |
|      | 0.0122(6)    | 0.0244(7)    | 0.0017(1)    | 0.0111(6)    | -0.0004(1)   | -0.0007(1)   |

standard errors in lattice parameters, and the full variance-covariance matrix of the structure refinement.

## DISCUSSION

### Site occupancies

The results for the BK and SH kutnahorites are very different, as anticipated from the absence and presence of ordering reflections in single-crystal photographs of the respective samples. The BK kutnahorite is almost completely disordered in Ca-Mn distribution; the SH kutnahorite is largely ordered.

The disorder of BK kutnahorite is clearly indicated by the near-equivalence of structure parameters for both the A and B cation sites (Tables 5-7). The average M-O distances, for example, are 2.277(2) and 2.267(2) Å, respectively. Final refined occupancies correspond to site com-

positions  $\text{Ca}_{0.49(4)}\text{Mn}_{0.51}$  and  $\text{Ca}_{0.53(4)}\text{Mn}_{0.47}$  for the A and B sites, respectively. The high occupancy value of Ca relative to Mn in the B site may in part be attributed to ordering of the small amount of Mg in the site in that the form factor of Mg will be accommodated by that of Ca.

Refined occupancies for the SH kutnahorite are  $\text{Ca}_{0.84(4)}\text{Mn}_{0.16}$  and  $\text{Ca}_{0.27(5)}\text{Mn}_{0.73}$  for the A and B sites, respectively, which correspond to the composition  $\text{Ca}_{0.55}\text{Mn}_{0.45}\text{CO}_3$ , neglecting the small contributions of Mg and Fe. By comparison, the composition implied by the lattice parameters is  $\text{Ca}_{0.55}\text{Mn}_{0.45}$ , assuming an ideal composition in the  $\text{CaCO}_3$ - $\text{MnCO}_3$  binary and Vegard's law. This also is in fair agreement with the composition as determined by electron-microprobe analysis.

The Ca-O and Mn-O distances determined by Effenberger et al. (1981) for calcite and rhodochrosite are 2.362 and 2.190 Å, respectively. Assuming the site occupancies given above, linear interpolations between these dis-

TABLE 6. Thermal-ellipsoid data for Bald Knob (upper lines) and Sterling Hill (lower lines) kutnahorite

| Atom | R | Amplitude (Å) | Angle to $a^*$ (°) | Angle to $b^*$ (°) | Angle to $c^*$ (°) |
|------|---|---------------|--------------------|--------------------|--------------------|
| A    | 1 | 0.102(1)      | —                  | —                  | 90                 |
|      |   | 0.104(1)      | —                  | —                  | 90                 |
| 3    |   | 0.118(2)      | 90                 | 90                 | 0                  |
|      |   | 0.122(2)      | 90                 | 90                 | 0                  |
| B    | 1 | 0.100(1)      | —                  | —                  | 90                 |
|      |   | 0.099(1)      | —                  | —                  | 90                 |
| 3    |   | 0.118(2)      | 90                 | 90                 | 0                  |
|      |   | 0.124(2)      | 90                 | 90                 | 0                  |
| C    | 1 | 0.105(4)      | —                  | —                  | 90                 |
|      |   | 0.106(3)      | —                  | —                  | 90                 |
| 3    |   | 0.124(8)      | 90                 | 90                 | 0                  |
|      |   | 0.137(9)      | 90                 | 90                 | 0                  |
| O    | 1 | 0.094(2)      | 176(1)             | 94(2)              | 91(2)              |
|      |   | 0.093(3)      | 174(2)             | 96(2)              | 89(2)              |
| 2    |   | 0.154(2)      | 93(2)              | 36(11)             | 126(12)            |
|      |   | 0.143(2)      | 95(2)              | 36(7)              | 126(7)             |
| 3    |   | 0.162(2)      | 93(2)              | 54(11)             | 36(12)             |
|      |   | 0.160(2)      | 92(2)              | 54(7)              | 36(7)              |

TABLE 7. Selected interatomic distances (Å) and angles for Bald Knob and Sterling Hill kutnahorite

|                   | Bald Knob  | Sterling Hill |
|-------------------|------------|---------------|
| A polyhedron      |            |               |
| Ca-O              | 2.277(2)   | 2.351(2)      |
| O-O'              | 3.152(3)   | 3.244(3)      |
| O-O''             | 3.288(3)   | 3.404(3)      |
| O-Ca-O'           | 87.59°(9)  | 87.76°(8)     |
| O-Ca-O''          | 92.41°(9)  | 92.74°(8)     |
| QE                | 1.0017(5)  | 1.0022(3)     |
| B polyhedron      |            |               |
| Mn-O              | 2.267(2)   | 2.217(2)      |
| O-O'              | 3.146(3)   | 3.074(3)      |
| O-O''             | 3.264(3)   | 3.196(3)      |
| O-Mn-O'           | 87.90°(9)  | 87.76°(7)     |
| O-Mn-O''          | 92.10°(9)  | 92.24°(8)     |
| QE                | 1.0013(12) | 1.0015(10)    |
| Carbon polyhedron |            |               |
| C-O               | 1.285(1)   | 1.296(1)      |
| O-O               | 2.225(2)   | 2.244(2)      |
| O-C-O             | 120.00°(1) | 119.98°(2)    |

tances result in predictions of M–O distances of 2.334 and 2.236 Å, which are different than the observed values of 2.351 and 2.217 Å. If such a linear interpolation is valid, this implies either that the degree of order is higher than indicated by the site occupancies, or perhaps that some stress factor prevents their adjustment to ideal values.

### Stereochemistry vs. ordering

Insofar as the SH and BK kutnahorites are the substantially ordered and disordered equivalents of nearly stoichiometric kutnahorite, they provide a unique opportunity to compare structure parameters in dolomite-type structures. The most striking comparison of parameters is in the thermal ellipsoid data, which are nearly identical for both structures (Table 6). This implies that the values for BK kutnahorite do not include a contribution due to positional disorder. Even though different individual oxygen sites must be associated with different species in A and B sites, the positions of all oxygen atoms must be virtually identical. This implies a lack of short-range order below the level of detectability by X-ray diffraction for BK kutnahorite, as also concluded from TEM observations. Reeder (1983) tabulated rms amplitudes of thermal ellipsoids for available refinements of dolomite (Althoff, 1977; Reeder and Wenk, 1983; Reeder, 1983) and ankerite (Beran and Zemann, 1977). These values are all smaller than those for BK and SH kutnahorites, including those for vibration parallel to *c*. Similarly, Reeder listed values for several calcite-type structures for refinements carried out by Althoff (1977) and Effenberger et al. (1981). They are also smaller than those for kutnahorite, although those for calcite are almost as large. We have no explanation for the disparity. We re-emphasize, however, that the same factors must have equivalent effects in both the ordered and disordered structures.

The octahedra in calcite- and dolomite-type structures are trigonally distorted. Several authors (Althoff, 1977; Beran and Zemann, 1977; Rosenberg and Foit, 1979; Effenberger et al., 1981; Reeder, 1983) have discussed the significance of the distortion using the quadratic elongation (QE) parameter of Robinson et al. (1971). It is a function of rotation of the CO<sub>3</sub> groups about *c*, resulting in rotation in an opposite sense of the vertices of both A and B octahedra. The rotation results in an increase in the A–O distance and a decrease in the B–O distance.

Reeder (1983) has plotted QE versus mean A–O and B–O distances for both calcite- and dolomite-type structures. In general there is an increase in QE with distance (and therefore with increase in ionic radius) for calcite-type structures, where no CO<sub>3</sub> rotation is possible and all octahedra are equivalent. However, rotation in dolomite causes a nonequivalence in both QE and mean bond distance for the A and B sites. QE for the B site (1.0008–1.0009) is only slightly less than for magnesite (1.0009–1.0010), but that for the A site (1.0016) is significantly less than that for calcite (1.0020). Rotation of the carbonate groups thus results in smaller octahedral distor-

tion while accommodating the large difference in ionic radius of Ca and Mg. Reeder (1983) has emphasized this coupling of the steric effects of the A and B sites; both the absolute and relative ionic radii are significant in stabilization of a dolomite-type structure.

Attempts to explain the lack of a dolomite-type structure for CaFe(CO<sub>3</sub>)<sub>2</sub> compared to CaMg(CO<sub>3</sub>)<sub>2</sub>, CaMn(CO<sub>3</sub>)<sub>2</sub>, CaZn(CO<sub>3</sub>)<sub>2</sub>, and CdMg(CO<sub>3</sub>)<sub>2</sub> and to explain their relative stabilities on the basis of factors such as ionic radii or octahedral site-preference energies have not been successful. The coupling of dimensions of the A and B sites through a common oxygen atom may be the critical factor (combined with site-preference energies for certain transition-element ions), but we can find no simple function for correlating such parameters.

Lacking a more appropriate function, the parameter QE appears to be the best available one for evaluating the relative stability of a dolomite-type structure. For BK kutnahorite, the QE values (Table 7) for the A and B sites are only slightly different than the average value (1.0014) for rhodochrosite and calcite, as expected for a disordered structure (Reeder, 1983). The QE value for the A site of the ordered SH kutnahorite is much greater than the averages of the calcite-type structures (Table 7). Thus, the CO<sub>3</sub> group rotation results in interatomic distances approximately consistent with ionic radii, but at the price of significant A-site octahedral distortion. Although the distortions in kutnahorite are not significant enough to cause instability of the structure, they may be important in constraining the order-disorder transition to low temperatures. The B–O distances in SH kutnahorite are slightly larger and A–O distances smaller than those predicted from radii, and site occupancies may possibly be due to the coupling of distortions in the A and B sites.

Reeder (1983) and Reeder and Wenk (1983) have pointed out that the C atom is displaced from the plane of three coordinating oxygen atoms in dolomite-type structures. The displacement is in response to differences between the ordered cations in layers above and below the carbonate groups. In BK kutnahorite, this displacement is nearly zero (0.002 Å), but in SH kutnahorite, it is 0.016 Å. It therefore provides a significant measure of the degree of cation order as in the case of dolomite.

The original powder pattern of kutnahorite (Frondele and Bauer, 1955) was incorrectly indexed as to ordering reflections. The scattering factors of Ca and Mn are so similar that such reflections are much weaker than in dolomite where they are a function of the large difference in scattering power of Ca and Mg (Goldsmith, 1983). If these reflections could be identified in powder patterns, the degree of ordering would be much more easily determined than through single-crystal patterns. We therefore obtained a diffractometer scan using a portion of the Sterling Hill sample, maximizing conditions for observation of weak reflections, but no ordering reflections could be detected. This implies that powder-diffraction data should not be used to infer ordering in nearly pure Ca–Mn carbonates unless special care is used, as is the case with

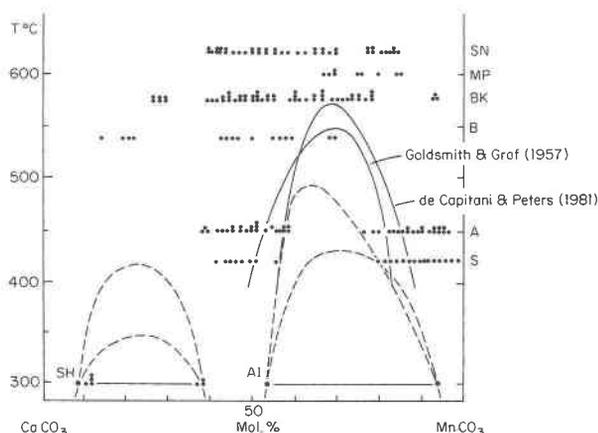


Fig. 1. Manganous carbonates with less than 10 mol%  $\text{MgCO}_3$  and  $\text{FeCO}_3$  projected onto the  $\text{CaCO}_3$ - $\text{MnCO}_3$  binary join modified from de Capitani and Peters (1981). SN = Serro do Navio, MP = Muretto Pass, B = Buritirama, A = Alagna, S = Scerscen. Additional data are BK (Bald Knob, North Carolina; Winter et al., 1981), AI (Andros Island, Greece; Reinecke, 1983), and SH (Sterling Hill, N.J.; this work). Solid lines are the inferred solvi of Goldsmith and Graf (1957) and of de Capitani and Peters (1981), and dashed lines are possible solvi consistent with experimental and natural data.

Rietveld-type refinements. Single-crystal patterns, however, clearly show ordering reflections.

### Nomenclature

In describing kutnahorite we have faced a seemingly trivial, yet complicating aspect of nomenclature. The name *kutnahorite* was clearly meant to be applied to the ordered phase with ideal composition  $\text{CaMn}(\text{CO}_3)_2$  (Fron del and Bauer, 1955). The probability that the type material was ordered is high, even though ordering reflections were erroneously identified. The name *kutnahorite* should not be applicable to disordered phases, *sensu stricto*. However, we recommend its use for all phases near  $\text{CaMn}(\text{CO}_3)_2$  in composition, with adjectives such as "disordered" or "calcian" specifying aspects of structure and chemistry as they become determined. No confusion seems to result from such usage.

### Implications of ordered vs. disordered kutnahorite

The occurrence of disordered kutnahorite at Bald Knob and ordered kutnahorite at Sterling Hill presumably restricts the order-disorder transition to a temperature between those of the formation of these two carbonates. The formation of ordered kutnahorite in late, low-temperature veins at Sterling Hill is inferred to indicate growth of an ordered phase within its stability field. Unfortunately the equilibration temperature of the SH carbonate is uncertain. Our prejudice, based on estimates of late-stage hydrothermal parageneses at Sterling Hill would place the formation of the SH carbonate veins and the order-disorder transition somewhere in the range of 200 to 400°C with the former at lower temperatures than the latter. The survival of disordered BK kutnahorite dem-

onstrates that the kinetics of the ordering process are sluggish even for the geologic times attendant with slow cooling of a regional metamorphic terrane (Winter et al., 1981).

### Compositions of natural Mn carbonates in the system $\text{CaCO}_3$ - $\text{MnCO}_3$

Observation of solid solutions and possible solvus pairs of natural Mn carbonates provides insight into their phase equilibria. Data on natural carbonates close to the  $\text{CaCO}_3$ - $\text{MnCO}_3$  join give some constraints on solvi along this join. Using estimated equilibration temperatures, de Capitani and Peters (1981) projected the compositions of natural carbonates onto a  $\text{CaCO}_3$ - $\text{MnCO}_3$  binary in comparison with experiments on the kutnahorite-rhodochrosite (KR) solvus. Their figure has been expanded to include data from Winter et al. (1981), Reinecke (1983), and this paper (Fig. 1). The compositions of the natural carbonates are generally consistent with the experiments of Goldsmith and Graf (1957) and de Capitani and Peters (1981) on the KR solvus (Fig. 1). However, its location is constrained only as a maximum because of the unreversed nature of their experiments. Successful experiments involving homogeneous solid solutions with equilibrium distributions of cations and initially located *within* the KR solvus are needed to reverse its location (Essene, 1983). Attempts have yielded no detectable reaction to form two-phase materials (Goldsmith and Graf, 1957; de Capitani and Peters, 1981). Experiments would have to involve kutnahorites with the equilibrium ordering. For a complete understanding of this system by analogy with  $\text{CaCO}_3$ - $\text{MgCO}_3$  (Burton and Kikuchi, 1984), the temperature of order-disorder transition of kutnahorite in relation to the equilibrium solvi and tricritical points needs to be determined for different Ca/Mn ratios.

Few two-phase pairs of carbonates near the join  $\text{CaCO}_3$ - $\text{MnCO}_3$  have been reported. Some analytical data are available on coexisting Mn carbonates that are close to the  $\text{CaCO}_3$ - $\text{MnCO}_3$  join: kutnahorite-rhodochrosite (KR) from blueschists at Andros Island, Greece (Reinecke, 1983), and calcite-kutnahorite (CK) from Sterling Hill. From the appearance of the sample 525 (Fig. 2A), we tentatively infer that it formed by epitaxial growth rather than by exsolution. Sample 526 shows a more complex intergrowth of earlier euhedral calcite and later replacive (?) calcite in a calcian rhodochrosite host (Fig. 2B). The textures of the two-phase materials do not resemble those commonly observed for high-temperature calcites containing exsolved dolomite. However, an exsolution or replacement origin for the Sterling Hill intergrowths cannot at present be ruled out. In any case, this assemblage provides direct evidence (Table 1) for the existence of a low-temperature solvus between calcite and kutnahorite, but its shape and location remains ill-constrained.

### Compositions of natural Mn carbonates in the system $\text{CaCO}_3$ - $\text{MnCO}_3$ - $\text{MgCO}_3$

Before accepting that the compositions of natural carbonates in Figure 1 properly constrain the binary solvi,

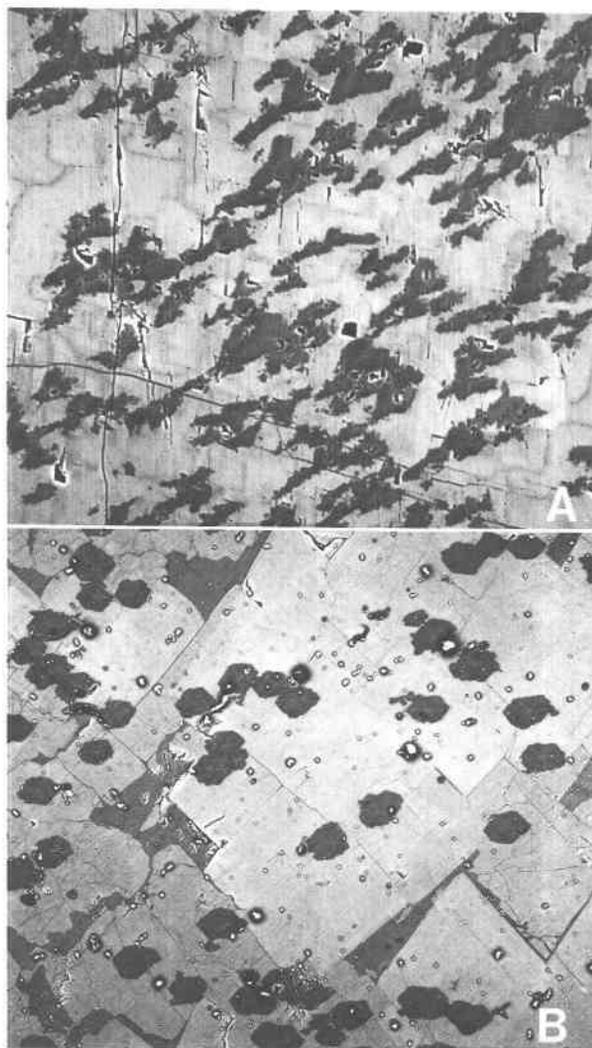


Fig. 2. Backscattered-electron images of manganian calcite (dark) intergrown in calcian kutnahorite (light) from Sterling Hill, N.J. (A) (SH-525) shows irregular "arrowheads" of manganian calcite in kutnahorite (length of photo 335  $\mu\text{m}$ ). Fine dark lines are cracks and cleavages. (B) (SH-526) shows hexagonal intergrowths and late fracture fillings (?) of manganian calcite in coarse kutnahorite (length of photo 720  $\mu\text{m}$ ). Spots with dark circles are from surface dust.

it is important to consider the possible effects of additional components on the solvi. Compositions of most natural manganian carbonates are more completely represented by the ternary system  $\text{CaCO}_3\text{-MnCO}_3\text{-MgCO}_3$  because they commonly have 5 to 10 mol% substitution of  $\text{MgCO}_3$  (Fig. 3). The solid solution of  $\text{FeCO}_3$  is generally much less important; analyses with  $> 5$  mol%  $\text{FeCO}_3$  have been excluded from the plot. Despite the wide ternary solvi of Goldsmith and Graf (1960), few equilibrium two- or three-phase manganian carbonate assemblages have been reported. The Andros Island kutnahorite coexisting with rhodochrosite has significant  $\text{MgCO}_3$ , whereas the Sterling Hill kutnahorite coexisting with calcite, though low in  $\text{MgCO}_3$ , varies erratically in  $\text{CaCO}_3$ ,

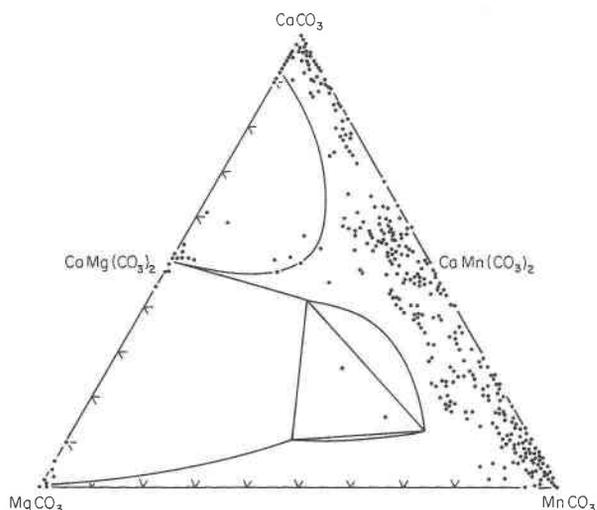


Fig. 3. Manganian carbonates with less than 5 mol%  $\text{FeCO}_3$  projected onto the  $\text{CaCO}_3\text{-MnCO}_3\text{-MgCO}_3$  ternary in comparison with the experimental solvi of Goldsmith and Graf (1960) at 600°C. References: Doelter (1912, 1914, 1917), Krieger (1930), Wayland (1942), Ham and Oakes (1944), Frondel and Bauer (1955), Goldsmith and Graf (1955), Lee (1955), Stankevich (1955), Graf and Lamar (1956), Muta (1957), Karado (1959), Van Tassel and Scheere (1960), Deer et al. (1962), Pavlishin and Slivko (1962), Sundius (1963), Saliya (1964), Trdllicka (1964), Gabrielson and Sundius (1965), Pisa (1966), Sundius et al. (1966), Trdllicka and Sevcu (1968), Calvert and Price (1970), Wenk and Maurizio (1970), Della-Salla et al. (1973), Koritning et al. (1974), Shibuya and Harada (1976), Kashima and Motomura (1977), Peters et al. (1977, 1978, 1980), Sanford (1978), Cortesogno et al. (1979), Suess (1979), Dabitzias (1980), Melone and Vurro (1980), Sivaprakash (1980), Bello et al. (1981), Fukuoka (1981), Green et al. (1981), Tanida and Kitamura (1981, 1982), Winter et al. (1981), Zak and Povondra (1981), Pedersen and Price (1982), Iwafuchi et al. (1983), Nahon et al. (1983), Reinecke (1983). Point lying near center of three-phase triangle is from Nahon et al. (1983) and deserves further study.

Except for carbonates along the magnesite-calcite binary join, most one-phase manganian carbonates lie outside the 600°C isotherm consistent with formation at or below that temperature (Fig. 3). However, if disordered kutnahorites grow metastably at low temperatures, it is also possible that phases with metastable intermediate compositions may form as authigenic or diagenetic minerals in sediments (Suess, 1979; Pedersen and Price, 1982; Beran et al., 1983; Boyle, 1983). No low-Fe carbonates are known to occur as solid solutions between magnesite and rhodochrosite (Essene, 1983, Fig. 3). A solvus could be generated between magnesite and rhodochrosite by expansion of the experimental two-phase region between calcian magnesite and calcian rhodochrosite at 600°C (Fig. 3) down to the  $\text{MgCO}_3\text{-MnCO}_3$  binary at low temperatures (Fig. 4A). Alternatively, it is possible that appropriate protoliths have not yet been found that would yield these solid solutions (Essene, 1983). Permissive evidence for a low-temperature magnesite-rhodochrosite solvus is provided by the experiments of Erenburg (1961), who

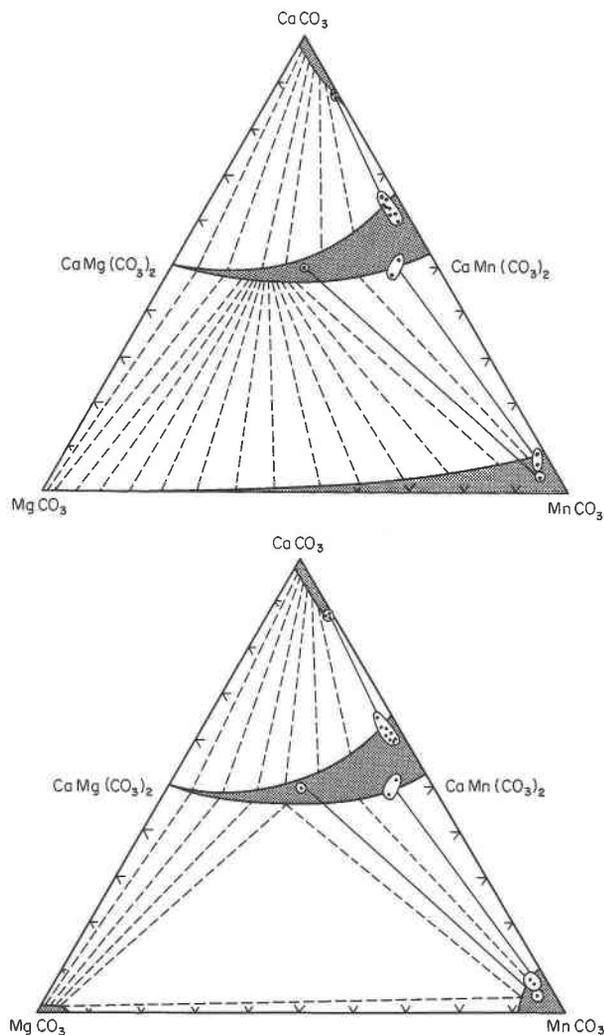


Fig. 4. Ternary diagrams showing the compositions of two-phase manganese carbonates from Andros Island, Greece (Reinecke, 1983), and from Sterling Hill, N.J. (this work). Possible solvi at  $300 \pm 100^\circ\text{C}$  are consistent with these data and the experimental solvi of Goldsmith and Graf (1960) at higher  $T$ . Diagram A shows no miscibility gap between rhodochrosite and magnesite; diagram B extends the ternary gap down to intersect this binary join.

precipitated two carbonate phases when starting with a high Mn/Mg ratio in aqueous experiments on this binary. The rare magnesian rhodochrosites (Fig. 3) need to be examined carefully for coexistence with or exsolution of manganese magnesite to test these two alternatives. We have speculated in Figures 4A and 4B as to possible relations of the  $300^\circ\text{C}$  isotherms in the ternary system using the two-phase pairs from Andros Island and Sterling Hill in combination with single-phase carbonates and the experiments at higher temperatures. If equilibrium prevails, a third magnesian kutnahorite-rhodochrosite pair (Tsusue, 1967) suggests either strong compositional effects on the  $K_D$  for Mg-Mn distribution between these two car-

bonates (Fig. 4A) or formation of a three-phase field (Fig. 4B). Shibuya and Harada (1976) and Zak and Povondra (1981) have described patchy-to-oscillatory variations between manganese ankerite and magnesian kutnahorite that they ascribe to disequilibrium processes. These carbonates may bear upon possible solvi in the quaternary system  $\text{CaCO}_3\text{-MnCO}_3\text{-MgCO}_3\text{-FeCO}_3$ , but no reversed experiments are available for comparison in this system.

#### ACKNOWLEDGMENTS

We again thank W. B. Simmons, Jr., for introducing us to the Bald Knob manganese deposit. C. Capobianco and A. Navrotsky kindly provided us with a preprint of their manuscript in advance of publication. C. B. Henderson, L. A. Marcotty, and W. C. Bigelow of the University of Michigan Microbeam Laboratory are acknowledged for technical assistance. We are grateful to R. J. Reeder, W. B. Simmons, Jr., and an anonymous reviewer for their insightful comments on our manuscript. We also acknowledge NSF Grants EAR-8212764, 85R-83 and EAR-8408168 in partial support of this research.

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MANUSCRIPT RECEIVED MARCH 23, 1986

MANUSCRIPT ACCEPTED NOVEMBER 7, 1986