

KUTNAHORITE: A MANGANESE DOLOMITE, $\text{CaMn}(\text{CO}_3)_2^*$

CLIFFORD FRONDEL AND L. H. BAUER,† *Department of Mineralogy, Harvard University, Cambridge, Mass., and New Jersey Zinc Company, Franklin, N. J.*

KUTNAHORITE FROM CZECHOSLOVAKIA

The name kutnahorite was proposed by Bukowsky (1901) for a supposed manganese member of the dolomite group, ideally $\text{CaMn}(\text{CO}_3)_2$. One of his analyses of pale rose cleavable aggregates from Kutnahora, Czechoslovakia, corresponded approximately to $\text{Ca}(\text{Mn},\text{Mg},\text{Fe})(\text{CO}_3)_2$, with $\text{Mn}:\text{Mg}:\text{Fe}\sim 6:2:1$. Rigorous proof has been lacking that his mineral belonged in the dolomite structure-type, $\text{AB}(\text{CO}_3)_2$, and was not merely a calcite-type solid solution, with the formula $(\text{Ca},\text{Mn},\text{Mg},\text{Fe})(\text{CO}_3)_2$, that fortuitously approached the dolomite ratios.

Through the kind effort of Dr. Jan Kutina of the Department of Mineralogy of the Charles University, Prague, a type specimen of kutnahorite was obtained from the museum of the school in Kutná Hora where Professor Bukowsky taught. The label glued on the specimen reads (translation by Dr. Kutina): "*Kutnohorite (ferroan mangandolomite with cleavage). Kutná Hora, from a stony fencing of a field above the Vašata's quarries. Ant. Bukovský, 1900.*" An analysis also is given, which is stated in recast form in Table 1, column 5. A differential thermal analysis and x -ray study of this specimen has now shown that the mineral is in fact of the dolomite-type. In addition, Dr. Kutina sent us a specimen of a carbonate from Chvaletice, Czechoslovakia, described by Žák (1949), that has a composition very close to that of the original kutnahorite. The analysis of this material is repeated in Table 1, column 6. Žák states that the mineral gives an x -ray pattern similar to that of ankerite (in the old sense of ferroan dolomite), and we have confirmed this identification as a member of the dolomite group by both x -ray and differential thermal analysis. The existence of kutnahorite¹ as a valid member of the dolomite group thus is established.

* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 353.

† Deceased, January, 1954.

¹ The name mangandolomite has been employed by some authors for the theoretical "molecule" $\text{CaMn}(\text{CO}_3)_2$ in the dolomite group. It is objectionable because it has been used with other meanings: by Eisenhuth (1901) for a mineral that may be ideally $\text{MgMn}(\text{CO}_3)_2$, by Doelter (1912) for ordinary dolomite containing small amounts of Mn in solid solution, and by Naumann (cited by Hey (1950)) for rhodochrosite with $\text{Mn}\sim\text{Ca}$. The name greinerite of Boldyrev (1928) also has been applied to manganoan varieties of dolomite.

TABLE 1. ANALYSES OF KUTNAHORITE AND OF MINERALS POSSIBLY IDENTICAL THEREWITH

	1	2	3	4	5	6
CaO	27.44	28.24	26.71	28.83	24.66	24.43
MgO	2.21	2.72		6.88	5.18	5.16
MnO	28.31	26.87	24.61	11.43	23.76	23.39
FeO	0.50	0.47	6.95	8.58	4.27	4.79
CO ₂	41.80	42.09	40.58	43.28	42.62	42.17
Rem.		0.08	1.15			0.17
Total	100.26	100.47	100.00	100.00	100.49	100.11
<i>Molecular Percentages</i>						
CaCO ₃	51.50	52.65	51.77	54.10	45.69	45.38
MgCO ₃	5.77	7.05		17.36	13.34	13.33
MnCO ₃	42.00	39.61	37.71	16.39	34.79	34.35
FeCO ₃	0.73	0.69	10.52	12.15	6.18	6.94
Total	100.00	100.00	100.00	100.00	100.00	100.00
S.G.	3.12	3.052		3.01	3.06	3.09

1. Kutnahorite, Franklin, N. J. C. M. Smink *analyst*, N. J. Zinc Company, 1953 Harvard specimen 85670.
2. Kutnahorite? Franklin, N. J. The "manganesian dolomite" of Roepper (1870). Rem. is insol.
3. Kutnahorite? Vester Silfberg, Dalecarlia, Sweden. The "manganocalcite" of Weibull (1885). Average of two analyses. Rem. is insol.
4. Kutnahorite, Kutnahora, Czechoslovakia. The original material of Bukowsky (1901).
5. Kutnahorite, Kutnahora, Czechoslovakia. The original material of Bukowsky (1901).
6. Kutnahorite, Chvaletice, Czechoslovakia. Called ankerite by Žák (1949) and compared by him to the kutnahorite of Bukowsky (1901). Rem. is insol. 0.14, H₂O 0.03.

KUTNAHORITE FROM FRANKLIN, NEW JERSEY

The writers surveyed a small collection of pink, manganese-containing carbonates from Franklin and Sterling Hill, New Jersey, and found four specimens that gave an x-ray powder pattern resembling that of dolomite. One of these specimens, No. 85670, was found on chemical analysis and differential thermal analysis to be a member of the dolomite group with almost the ideal composition CaMn(CO₃)₂. Small amounts of Mg and Fe are present in substitution for the Mn (analysis 1, Table 1). The grouping of the Mg and Fe with Mn rather than with Ca, here required to make the analysis conform to the dolomite type of formula, is consistent with the closer approach of Mg and Fe in ionic size to Mn than

to Ca. There is also a small excess of Ca over the requirement of the *A* position of the formula. This presumably is in substitution for Mn in the *B* position, analogous to calcian dolomite, $\text{Ca}(\text{Mg},\text{Ca})(\text{CO}_3)_2$, and the complete formula may be written $\text{Ca}(\text{Mn},\text{Mg},\text{Ca},\text{Fe})(\text{CO}_3)_2$.

The differential thermal analysis curve of the material is shown in Fig. 1. It closely resembles the *DTA* curve of ankerite, and to a less extent the curve of dolomite proper (which lacks oxidizable cations).

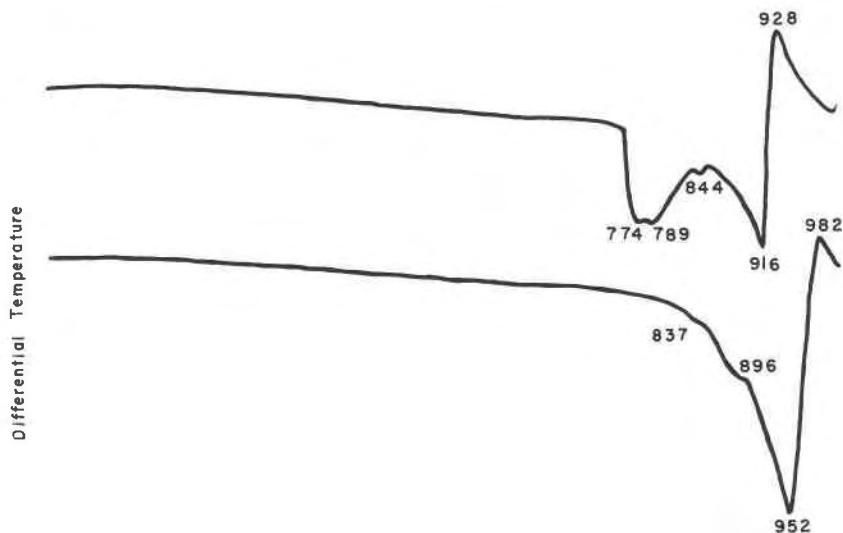


FIG. 1. Top curve, kutnahorite from Franklin, N. J. (no. 85670), analysis 1, Table 1.
Bottom curve, rhodochrosite from Franklin, N. J., analysis 9, Table 2.

It differs completely from the *DTA* curves of calcite and rhodochrosite, which show a single endothermic break marking dissociation into oxide and CO_2 . In dolomite, two endothermic breaks are obtained corresponding to the stepwise dissociation of the two structurally non-equivalent cations. In ankerite and kutnahorite the curves are further complicated by oxidation of the FeO or MnO and reaction with the CaO . Thermal curves for the rhodochrosite-calcite series have been described by Kulp, Wright and Holmes (1949), for ankerite by Kulp, Kent and Kerr (1951) and Beck (1950), for dolomite by Faust (1944, 1949, 1953), Bradley et al. (1953), Graf (1952), Haul and Heystek (1952) and others. The indices of refraction of kutnahorite, $n_{\text{O}} 1.727$, $n_{\text{E}} 1.535$, agree exactly with the values calculated from the indices of refraction of the CaCO_3 , MgCO_3 and FeCO_3 end-members taken in the ratio of the analysis. The specific gravity, 3.12, is slightly lower than the

value 3.15 similarly calculated from the end-members. The indexed x -ray powder spacing data are given in Table 2. The unit cell dimensions obtained are a_0 4.85 Å, c_0 16.34. The pattern contains several of the lines diagnostic of dolomite-type structures. The kutnahorite from Chvalětice analyzed by Žák (analysis 6, Table 1) has the cell dimensions a_0 4.83 Å, c_0 16.18.

Kutnahorite occurs at Franklin as anhedral masses with curved cleavage surfaces up to three centimeters in size in a small veinlet cutting

TABLE 2. X-RAY POWDER SPACING DATA FOR KUTNAHORITE

Material of analysis 1, Table 1, from Franklin, N. J.

Iron radiation, manganese filter, in Ångstroms.

Relative intensities from spectrometer chart.

<i>I</i>	<i>d</i>	<i>Indices</i>		<i>I</i>	<i>d</i>	<i>Indices</i>	
5	4.268	10 $\bar{1}$ 1	100	3	1.540	2132	211
20	3.753	01 $\bar{1}$ 2	110	7	1.486	2134	310
100	2.935	10 $\bar{1}$ 4	211	3	1.469	02 $\bar{2}$ 8	224
5	2.730	0006	222	3	1.465	1129	432
4	2.593	01 $\bar{1}$ 5	221	5	1.409	1235	320
14	2.437	11 $\bar{2}$ 0	10 $\bar{1}$	5	1.363	000.12	444
19	2.225	11 $\bar{2}$ 3	210	3	1.294	20 $\bar{2}$.10	442
4	2.095	02 $\bar{2}$ 1	11 $\bar{1}$	4	1.258	12 $\bar{3}$ 8	431
19	2.043	10 $\bar{1}$ 7	322	4	1.189	20 $\bar{2}$.11	533
9	1.876	02 $\bar{2}$ 4	220	4	1.145	21 $\bar{3}$.10	532
27	1.837	01 $\bar{1}$ 8	332	4	1.141		
31	1.814	0009	333	5	1.126	13 $\bar{4}$ 4	32 $\bar{1}$
6	1.588	21 $\bar{3}$ 1	20 $\bar{1}$	4	1.089	000.15	555
4	1.566	1232	211	5	1.022	20 $\bar{2}$.14	644
				5	0.9763	11 $\bar{2}$.15	654

the normal franklinite ore. It is translucent, with a pale pink color. The vein is bordered by a thin layer of dark pink rhodochrosite; this has n_D 1.792, corresponding to a content of 85 per cent $MnCO_2$ according to the data of Wayland (1942).

The other three specimens examined appeared on optical, x -ray and thermal analysis to be mechanical mixtures of kutnahorite with a calcite-type carbonate. It is hoped to give a fuller description of this material at a later time.

A few analyses of minerals that may be identical with kutnahorite have been found in the literature. These analyses are listed in Table 1. Crystallographic or other data that would identify the material as belonging to the dolomite structure-type are lacking, and the assigning of these minerals to kutnahorite rests entirely on the closeness to which

the analyses approach the ratio $\text{Ca}:(\text{Mn}, \text{Mg}, \text{Fe})=1:1$. The material of Roepper (1870) from Franklin (analysis 2) is very close in composition to the kutnahorite specimen here described. The material of Weibull (1885) from Sweden (analysis 3) appears to be a ferroan variety of kutnahorite. If this mineral actually belongs to the dolomite-type, it is the only member of the dolomite-ankerite-kutnahorite group so far analyzed that does not contain over about 5 mol per cent MgCO_3 . The kutnahorite of analyses 5 and 6 requires a substitution of Fe for Ca, or a distribution of both Fe and Mn between the *A* and *B* positions, in

TABLE 3. NEW ANALYSIS OF CALCITE AND RHODOCHROSITE
FROM FRANKLIN AND STERLING HILL, N. J.
(all analyses in weight percentages)

	1	2	3	4	5	6	7	8
CaCO_3	98.41		56.44	56.57				3.71
MgCO_3			6.58	2.93				1.44
MnCO_3	0.90	33.38	36.14	40.35	81.47	82.5	83.5	94.93
FeCO_3	0.86		0.93					0.44
PbCO_3		0.07		0.22				
Total	100.17		100.09	100.07				100.02
S.G.	2.73	3.04	3.06	3.06	3.53	3.55	3.50	~3.6
<i>n</i> O	1.658	1.712	1.716	1.716	1.791	1.792	1.792	1.806

1. Calcite, orange brown color. Franklin, N. J. L. H. Bauer, *analyst*.
- 2, 3, 4. Manganian calcite, Franklin, N. J. L. H. Bauer, *analyst*.
- 5, 7. Calcian rhodochrosite, Franklin, N. J. L. H. Bauer, *analyst*.
6. Calcian rhodochrosite, Sterling Hill, N. J. L. H. Bauer, *analyst*.
8. Rhodochrosite, Franklin, N. J. C. M. Smink, *analyst*.

order to make the analyses conform to the requirements of the dolomite formula-type. Analysis 4 requires the entrance of Ca into the *B* position; this material has not been shown directly to belong in the dolomite group.

Eight new analyses, four complete and four partial, on members of the calcite-rhodochrosite series from Franklin and Sterling Hill are reported in Table 3. The nine analyses of calcite-rhodochrosite that have been reported in the literature from these localities are summarized in Table 4. The material of analyses 3, 4, 5, and 8 of Table 3 and of analysis 8 of Table 4 was verified as of the calcite-type by differential thermal analysis. The curve of the material of analysis 8 of Table 3 is reproduced in Fig. 1.

The analytical data of Tables 3 and 4 are plotted in Fig. 2 in order

TABLE 4. PUBLISHED ANALYSES OF CALCITE AND RHODOCHROSITE FROM FRANKLIN AND STERLING HILL, N. J.

	1	2	3	4	5	6	7	8	9
CaCO ₃	85.96	79.96	85.57		82.33	63.90	77.94	65.98	20.59
MgCO ₃	0.59	1.94	2.54			11.05		n.d.	3.80
MnCO ₃	2.98	11.09	11.55	15.40	16.57	17.43	22.35	32.34	74.99
FeCO ₃		0.60			0.50	0.30		n.d.	0.36
ZnCO ₃	2.88	0.58				0.32		0.69	0.26
Rem.	7.70	5.67			1.20	7.00			
Total	100.11	99.84	99.66		100.50	100.00	100.29	99.01	100.00
S.G.				2.856				3.021	3.47
<i>n</i> O				1.680				1.713	
<i>n</i> E				1.503				1.519	

1. Calcite, black color. Franklin, N. J. Jenkins and Bauer analysis cited by Palache (1935). Rem. is SiO₂ 0.50, ZnO 1.86, Fe₂O₃ 0.17, Al₂O₃ 0.24, Mn₂O₃ 4.93, due to inclusions.
2. Manganoan calcite ("spartaite"), Sterling Hill, N. J. Jenzsch (1855). Rem. is CaF₂ 5.35, H₂O 0.32.
3. Manganoan calcite ("spartaite"), Sterling Hill, N. J. Richter analysis cited by Rammelsberg (1860).
4. Manganoan calcite, Franklin, N. J. Bauer analysis cited by Krieger (1930).
5. Manganoan calcite, Sterling Hill, N. J. Van Dyke analysis cited by Cook (1868). Rem. is H₂O 1.00, insol. 0.20.
6. Manganoan calcite, Franklin, N. J. Levison (1916). Rem. is insol.
7. Manganoan calcite, Sterling Hill, N. J. Shepard and Tyler (1865).
8. Manganoan calcite, Franklin, N. J. Bauer analysis cited by Krieger (1930). Mg and Fe present but not determined.
9. Calcian rhodochrosite, Franklin, N. J. Bright pink color. Browning (1890). Recalculated after deducting SiO₂ 0.32 as willemite, Fe₂O₃ 0.16, and excess ZnO as zincite.

of increasing weight per cent of MnCO₃. The figure also contains new data on the MnCO₃ content of 29 specimens of calcite-rhodochrosite from Franklin. These were determined from the indices of refraction using the graph of Wayland (1942), with a supplementary linear graph for the region from 50 per cent MnCO₃ to pure CaCO₃. The values for the MnCO₃ content thus obtained are not very precise because the content of Fe, Zn and, in particular, Mg is not known. Figure 2 indicates that the calcite-rhodochrosite series is incomplete under the particular genetic conditions obtaining at Franklin. At this locality a solid solution series apparently extends from the end-composition CaCO₃ up to manganoan calcite containing about 40 weight per cent MnCO₃, with a gap then extending up to calcian rhodochrosite containing about 75 weight

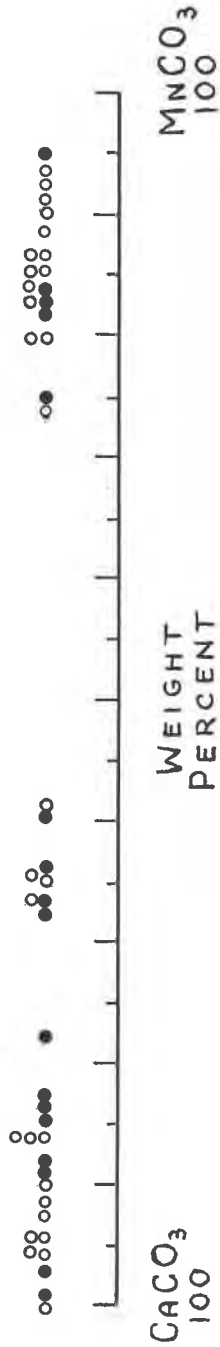


FIG. 2. Graph showing the content in weight per cent of MnCO_3 of 46 specimens of the calcite-rhodochrosite series from Franklin, New Jersey. Solid circles are the analyzed samples of Tables 2 and 3. Open circles based on optical determination of specimens in the Harvard collection.

per cent MnCO_3 , and a continuous series extending from there to the end-composition MnCO_3 . Vegard (1947) found in material synthesized at room temperature that the gap was larger, extending from 12.5 mol per cent MnCO_3 up to 75 mol per cent MnCO_3 . Under some geologic conditions the series may be complete. A study of synthetic material to determine the temperature dependency of the solid solubility would be highly desirable.

ORDERED PHASES IN THE CALCITE AND OLIVINE GROUPS

The extent of solid solution in binary disordered solid solutions involving Ca, Mn, Fe or Mg ions and the occurrence of ordered phases in these systems appears to be controlled principally by the relative size of the cations involved. The term ordering is here used to mean the two cations that are structurally equivalent in the disordered phase become structurally non-equivalent in the ordered phase, without implying that the overall crystal structures of the ordered and disordered phases are closely related. With increasing closeness in ionic size, the olivine-type nesosilicates and the NaCl-type oxides of the four cations mentioned in general show: (1) increasing solid solubility in the disordered binary series; (2) decreasing tendency to form ordered phases. The observations are summarized² in Table 5.

Further more or less complete examples of the relations described are shown by other minerals. Thus in the idealized $\text{A}_3''\text{Al}_2(\text{SiO}_4)_3$ members of the garnet group complete series apparently exist between Mg-Fe and Mn-Fe, partial series between Mg-Mn and Ca-Mn, and very small series between Ca-Mg and Ca-Fe, in natural material.

The reciprocal relation between extent of solid solution in the binary disordered series and the occurrence of ordered phases is primarily a matter of structural strain. Ordering relieves the strain caused by the random fitting together of ions of different sizes, and the ordering potential should increase as the strain or difference in size increases. The ordered phases listed in Table 5 have crystallized directly from solution, and not in the solid state from a parent solid solution, but this does not alter the general reasoning. The geometry of the ordering is facilitated at or near simple whole number ratios of the ion species involved; the most common ratios observed are 1:1, 1:2 and 1:3. With increasing similarity in ionic size, the ordering potential decreases and the formation of random substitutional solid solutions is favored.

² Data on the extent of solid solubility in the binary systems cited were obtained from Hall and Insley (1947); Dana's System of Mineralogy (1951); Ford (1917); Kulp, Kent, and Kerr (1951); Greer (1932); Passerini (1930); Natta and Passerini (1929); Petterson (1946); Jay and Andrews (1944, 1946).

TABLE 5. RELATION OF IONIC SIZE TO SOLID SOLUBILITY AND ORDERING IN SOME IONIC COMPOUNDS OF Ca, Fe, Mn AND Mg
(Ionic radii: Ca 1.06, Mn 0.91, Fe 0.83, Mg 0.78 kX)

Difference in ionic size	Extent of solubility in binary disordered systems	Occurrence of 1:1 ordered phases	Occurrence of other ordered phases
Large Ca—Mg (26.5%)	Very small solubility CaCO ₃ —MgCO ₃ , small solubility Ca ₂ SiO ₄ —Mg ₂ SiO ₄ , no solubility? CaO—MgO, very small solubility	Common Ca ₂ Mg(CO ₃) ₂ , dolomite CaMg(SiO ₄), monticellite	Ca ₂ Mg ₃ (CO ₃) ₄ , huntite Ca ₃ Mg(SiO ₄) ₂ , merwinite
Moderate Ca—Fe (21.7%)	Moderate solubility CaCO ₃ —FeCO ₃ , extensive solubility Ca ₂ SiO ₄ —Fe ₂ SiO ₄ , moderate solubility CaO—FeO, moderate solubility	Less common Ca(Fe, Mg)(CO ₃) ₂ , ankerite CaFe(SiO ₄), (synthetic)	None
Small Ca—Mn (14.3%)	Large or complete solubility CaCO ₃ —MnCO ₃ , large or complete solubility Ca ₂ SiO ₄ —Mn ₂ SiO ₄ , extensive solubility CaO—MnO, extensive solubility	Rare CaMn(CO ₃) ₂ , kutnahorite CaMn(SiO ₄), glaucocochroite	None
Mg—Mn (14.3%)	MgCO ₃ —MnCO ₃ , large solubility MgSiO ₄ —MnSiO ₄ , complete solubility? MgO—MnO, extensive solubility	None?	None
Fe—Mn (8.8%)	FeCO ₃ —MnCO ₃ , complete solubility FeSiO ₄ —MnSiO ₄ , nearly complete solubility? FeO—MnO, large or complete solubility	None	None
Very Small Mg—Fe (6.0%)	Complete solubility MgCO ₃ —FeCO ₃ , complete solubility Mg ₂ SiO ₄ —Fe ₂ SiO ₄ , complete solubility MgO—FeO, complete solubility	None	None

One may also expect that in two isostructural binary series separated by a gap, $(A, B)X$ — $(B, A)X$, that the smaller ion B will substitute to a larger extent for A in $(A, B)X$ than the larger ion A will substitute for B in $(B, A)X$, since the strain introduced by the substitution should be less. This follows since the introduction of a large ion in place of a smaller one at constant A — X distance involves work against a high-power exponential repulsive force arising in the overlap of the electron clouds about the nuclei, while the introduction of a smaller ion involves work against the weaker, inverse square attractive force between oppositely charged ions. The series CaCO_3 — MgCO_3 appears to illustrate the rule, with Mg present in $(\text{Ca}, \text{Mg})\text{CO}_3$ up to about 29 mol per cent and Ca present in $(\text{Mg}, \text{Ca})\text{CO}_3$ only up to about 7 mol per cent, according to the data of Ford (1917) and Chave (1952). The solubility of Mg in $(\text{Ca}, \text{Mg})\text{O}$ also is greater than that of Ca in $(\text{Mg}, \text{Ca})\text{O}$ according to Petterson (1946). The partial series between MgCO_3 — MnCO_3 and CaCO_3 — CdCO_3 also show the expected relation, as do the partial series between CaO — FeO , MnO — CaO , MnO — MgO , MnO — CdO and CaO — SrO from the data of Passerini (1930), Natta and Passerini (1929), Petterson (1946) and Primak et al. (1948). Under other conditions the series CaO — MnO and MgO — MnO may be complete (Jay and Andrews (1944, 1946) and Petterson (1946)). In the partial binary series between ZnO and NiO , MgO , MnO and CdO the greater solubility is of the larger ion substituting for the smaller, as shown by Rigamonti (1946), but in this case the structure-type and the bond-type is different at opposite ends of the series.

One might also expect that the solvus curves in continuous high-temperature random solid solution series would tend to be asymmetrically displaced toward the end-component with the smaller ionic radius.

Ordered phases with ratios other than 1:1 are found in the calcite and olivine groups only with the ion pair Ca-Mg, in which the difference in ionic size is a maximum. The cation ratios in these instances appears to be related to the asymmetry in the central gap between the two partial disordered solid solution series. Thus $\text{CaMg}_3(\text{CO}_3)_4$, huntite, apparently is more stable than $\text{Ca}_3\text{Mg}(\text{CO}_3)_4$ because the ordering potential is greater towards the Mg end of the binary series, as indicated by the greater extent of solid solubility towards the Ca end of the series. The compound $\text{Ca}_3\text{Mg}(\text{CO}_3)_4$ was described as a mineral, conite, by Retzius in 1795, but his material was shown to be a mixture. A highly calcian dolomite $\text{Ca}(\text{Mg}, \text{Ca})(\text{CO}_3)_2$ in which the actual ratios are close to the the formula $\text{Ca}_3\text{Mg}(\text{CO}_3)_4$ was analyzed by Strobentz (1926), indicating that the magnesian calcite and calcian dolomite series virtually overlap

in this region of composition. The supposed mineral $\text{CaMg}_2(\text{CO}_3)_3$, leesbergite, of Blum (1907) also was shown to be a mixture.

An ordered compound of the dolomite-type between Mg and Mn appears to be as likely as that between Ca and Mn, since the difference in ionic size in the two cases is the same. A possible example may be a mineral from Greiner, Switzerland, called mangandolomite by Eisenhuth (1901). If his analysis, cited below, is accepted as of a dolomite-type compound, and no evidence was given to justify this, the interpretation suggested by the relative sizes of the ions involved is $(\text{Mg, Fe, Mn})(\text{Mn, Ca})(\text{CO}_3)_2$. Mn is then distributed between the *A* and *B* positions to fit the requirements of the formula, somewhat analogous to the dolomite solid solutions $\text{Ca}(\text{Mg, Ca})(\text{CO}_3)_2$ and $(\text{Ca, Mg})\text{Mg}(\text{CO}_3)_2$ described by Foote and Bradley (1914) and Ford (1917). Ankerite with Fe in both the *A* and *B* positions was analyzed by Strobenz (1926).

<i>Eisenhuth</i> (1901)		<i>Molecular Percentages</i>
CaO	10.48	CaCO_3 19.25
MnO	23.41	MnCO_3 34.03
FeO	6.59	FeCO_3 9.45
MgO	14.58	MgCO_3 37.27
CO_2	45.59	
Insol.	0.16	
	100.81	53.28
		46.72
		100.00

An ordered compound of the formula $\text{MgFe}(\text{CO}_3)_2$ seems to be the least likely for the four cations under consideration. Nevertheless, two analyses of material from Thurnberg, Germany, by Fritzsche (1847) and Ettling (1853), and analyses of material from Traversella, Italy, by Stromeyer (1875) and Saarbruecken, Germany, by Weiss (1885) approach the ratio $\text{Mg}:\text{Fe}=1:1$ closely. Stromeyer's analysis has $\text{Fe}:\text{Mg}=1:1.02$. Crystallographic or other evidence (aside from the analytical ratios) which definitely place any of these four samples in either the dolomite or calcite groups is lacking. The name pistomesite was proposed by Breithaupt (1847) for the material from Thurnberg. We have examined two specimens from Traversella and a third specimen from Brozzothal, Italy, containing Fe and Mg in almost equal proportions, as indicated by the indices of refraction. These specimens proved on differential thermal analysis to belong in the calcite structure-type.

ACKNOWLEDGMENTS

We wish to express our thanks to Mr. Brian Skinner, Department of Mineralogy, Harvard, for making numerous differential thermal analysis runs, and to Dr. George T. Faust, U. S. Geological Survey, for inde-

pendently verifying the *DTA* curves on three of our samples. Dr. Faust's thermal curves are used in the present report.

REFERENCES

- BECK, C. W., Differential thermal analysis curves of carbonate minerals: *Am. Mineral.*, **35**, 985 (1950).
- BLUM, L., Leesbergite, un nouveau carbonate calcaréo-magnésique: *Ann. géol. Belg., Bull.* **34**, 118 (1908).
- BOLDYREV, A. K., Kurs opisatelnoi min., Leningrad, Pt. 2, 162 (1928).
- BRADLEY, W. F., BURST, J. F., & GRAF, D. L., Crystal chemistry differential and thermal curves of dolomite: *Am. Mineral.*, **38**, 207 (1953).
- BREITHAUP, J., Carbonites Pistomesites, etc.: *Ann. Phys.* **70**, 147 (1847).
- BROWNING, P. E., Analysis of rhodochrosite from Franklin Furnace, N. J.: *Am. J. Sci.*, **40**, 375 (1890).
- BUKOWSKY, A., Kuttenger manganmineralien. Anz. der III Congr. Böhm. Naturforsch. und Ärzte. Prague, 293 (1901). Abstracted in *Jb. Min.*, **II**, 338 (1903), and *Zeits. Krist.*, **39**, 400 (1903).
- CHAVE, K. E., A solid solution between calcite and dolomite: *J. Geol.*, **60**, 190 (1952).
- COOK, G. H., Geology of New Jersey. 69 (1868).
- DOELTER, C., Handbuch der Mineralchemie, Leipzig, **I**, 360, 376 (1912).
- DANA'S SYSTEM OF MINERALOGY by C. Palache, H. Berman and C. Frondel, New York, 7th ed., 141 (1951).
- EISENHUTH, K., Beiträge zur kenntnis der bitterspätze: *Zeits. Kryst.*, **35**, 582 (1901).
- ETTLING, C., Untersuchung einiger rhomboedrischen Karbonspätze: *Ann. Chem.* **99**, 203 (1853).
- FAUST, G. T., Differentiation of magnesite from dolomite in concentrates and tailings: *Econ. Geol.*, **39**, 192 (1944).
- Dedolomitization, and its relation to a possible derivation of a magnesium-rich hydrothermal solution: *Am. Mineral.*, **34**, 789 (1949).
- FOOTE, H. W., & BRADLEY, W. M., On solid solution in minerals. V. The isomorphism between calcite and dolomite: *Am. J. Sci.*, **37**, 339 (1914).
- FORD, W. E., Studies in the calcite group: *Trans. Conn. Acad. Arts Sci.*, **22**, 211 (1917).
- FRITZSCHE, J., cited in Breithaupt (1847).
- GRAF, D. L., Preliminary report on the variations in differential thermal curves of low-iron dolomite: *Am. Mineral.*, **37**, 1 (1952).
- GREER, W. L. C., Mix-Crystals of CaMnSiO_4 and Mn_2SiO_4 : *Am. Mineral.*, **17**, 135 (1932).
- HALL, F. P., & INSLEY, H., Phase diagrams for ceramists: *J. Am. Ceram. Soc.*, Pt. **II**, Bov. (1947).
- HAUL, R. A. W., & HEYSTEK, H., Differential thermal analysis of the dolomite decomposition: *Am. Mineral.*, **37**, 166 (1952).
- JAY, A. H., & ANDREWS, K. W., Composition of some binary oxide systems: *J. Iron Steel Inst.*, **152**, 15 (1946), *Nature*, **154**, 116 (1944).
- JENZSCH, G., Fluor im Kalkspath und Aragonit: *Ann. Phys.*, **96**, 145 (1855).
- KRIEGER, P., Notes on an x-ray diffraction study of the series calcite-rhodochrosite: *Am. Mineral.*, **15**, 23 (1930).
- KULP, J. L., KENT, P., & KERR, P. F., Thermal study of the Ca-Mg-Fe carbonate minerals: *Am. Mineral.*, **36**, 643 (1951).
- KULP, J. L., WRIGHT, H. D., & HOLMES, R. J., Thermal study of rhodochrosite: *Am. Mineral.*, **34**, 195 (1949).

- LEVISON, W. G., Columnar manganocalcite from New Jersey: *Am. Mineral.*, **1**, 5 (1916).
- NATTA, G., & PASSERINI, L., Soluzioni solide—I sistemi CaO-MnO, CaO-MgO, etc.: *Gazz. chim. Ital.*, **59**, 129 (1929).
- NAUMANN, C. F., Cited by Hey, M. L., An index of mineral species and varieties, London, **76**, 1950.
- PALACHE, C., The minerals of Franklin and Sterling Hill, Sussex County, New Jersey: *U. S. Geol. Surv., Prof. Paper* **180** (1935).
- PASSERINI, L., Soluzioni solids III—I sistemi MnO-CdO, MnO-MgO: *Gazz. chim. Ital.*, **60**, 535 (1930).
- PETTERSON, H., Investigation of the solubility in the solid state in the binary systems of the oxides, CaO, MnO, MgO and FeO: *Jernkont. Ann.*, **130**, 653 (1946).
- PRIMAK, W., KAUFMAN, H., & WARD, R., X-ray diffraction studies of systems in the preparation of alkaline earth sulfide and selenide phosphors: *J. Am. Chem. Soc.*, **70**, 2043 (1948).
- RAMMELSBERG, C. F., Handbuch der Mineralchemie, 209 (1860); **II**, 231 (1875).
- RETZIUS, A. J., Försök till mineralrikets uppställn., etc.: *Lund*, **136** (1795).
- RIGAMONTI, R., Soluzioni solide tra ossido di zinco ed ossido di metalli bivalenti: *Gazz. chim. Ital.*, **76**, 474 (1946).
- ROEPPER, W. T., Notice of some minerals from New Jersey: *Am. J. Sci.*, **50**, 35 (1870).
- ROZSA, M., Die entstehung des dolomites, etc.: *Zbl. Min.*, **229**, (1926).
- SHEPARD, C. U., & TYLER, S. W., Analysis of a carbonate of lime and manganese from Sterling, Sussex County, N. J.: *Am. J. Sci.*, **39**, 174 (1865).
- STROBENTZ, H., Analysen von ungarischen dolomitkrystallen: *Föld Kőzl.*, **55**, 49 (1926).
- STROMEYER, H., Analysis cited in Rammelsberg (1875).
- VEGARD, L., Mixed crystals of carbonates of the calcite group: *Norske Vid.-Akad. Skrifter, Oslo, Nat.-Nat. Kl., No. 2*, 6 (1947).
- WAYLAND, R. G., Composition, specific gravity and refractive indices of rhodochrosite: *Am. Mineral.*, **27**, 614 (1942).
- WEIBULL, M., Untersuchung schwedischer minerale: *Min. Mitth.*, **7**, 108 (1885).
- WEISS, C. E., Einige carbonate aus der steinkohlenformation: *Jb. preuss. geol. Landesanst.*, **113** (1885).
- ŽÁK, L., Paragenesis of the manganese carbonates of the ore deposit of Chvaletice in Železná Hory, East Bohemia: *Bull. Int. Acad. Czech. Sci.* (1949); *Rozpravy tř. České Akad.*, **59**, No. 25 (1950).

Manuscript received July 20, 1954