Crystal structure refinement of huntite, CaMg$_3$(CO$_3$)$_4$, with X-ray powder data

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Abstract

Peak-fitting of CuK$\alpha_{1,2}$ X-ray powder diffraction data to sin $\theta/\lambda = 0.57$ gave 86 integrated (Bragg) intensities which have been used to refine the crystal structure of huntite, CaMg$_3$(CO$_3$)$_4$, to $R(F) = 5.3\%$. A March distribution model was used as the basis of a correction for the effects of preferred orientation of the platey, micrometer-sized crystals. The atomic arrangement in space group $R32$, $a = 9.5027(6)$ Å, $c = 7.8212(6)$ Å, proposed by Graf and Bradley (1962), is confirmed. Ca and Mg atoms occur within the same cation plane but are ordered with Ca's in trigonal prism sites (Ca occupancy = 0.99(2) and Mg's in edge-sharing octahedral sites. Interatomic distances are nearly identical to those of dolomite, CaMg(CO$_3$)$_2$.

Introduction

Huntite, CaMg$_3$(CO$_3$)$_4$, is a naturally occurring rhombohedral carbonate whose composition lies half way between dolomite, CaMg(CO$_3$)$_2$, and magnesite, MgCO$_3$. Despite structural similarity, the polyhedral connectivity of huntite is not the same as found in these latter, more common carbonates.

Huntite is produced in low temperature surface or near surface environments. The mineral seems to form either by direct precipitation from Mg-rich, aqueous solutions or as the result of interaction of such solutions with pre-existing carbonates (for a summary see Kinsman, 1967; Cole and Lancucki, 1975). Grain size of the natural samples is uniformly small (less than about two micrometers in diameter), and therefore structural studies have been carried out using powder diffraction methods.

A model for the huntite structure was proposed by Graf and Bradley (1962) on the basis of similarity of the X-ray powder diffraction pattern of huntite with that of the common rhombohedral carbonates, such as calcite, which in turn is related to the NaCl structure. From the relationship of the unit cells, and using a NaCl-like arrangement of metal atoms and CO$_3$ groups, these authors adjusted the variable positional parameters to give interatomic distances appropriate for the chemical species involved. This model was then tested by comparing calculated X-ray intensities with 41 low-angle observed X-ray powder diffraction intensities. The reasonable residual, $R(F) = 11\%$, attested to the essential correctness of their model.

The present study of the huntite structure was undertaken to: (1) confirm and refine the huntite model using a more extensive data set, (2) determine the degree of Ca/Mg ordering, and (3) provide a test case for some recently developed crystal structure analysis methods for use with X-ray powder diffraction data showing overlapped peaks and/or preferred orientation effects.

Experimental methods

The sample from Tea Tree Gully, Australia (Skinner, 1958), was lightly crushed, loaded into 25 × 12 × 1 mm recess of plastic holder, moistened, compacted and smoothed with a spatula. Data collection used a Picker horizontal powder diffractometer, CuK$\alpha_{1,2}$ radiation, 40 kV, 20 mA, 4° take off angle, collimation by 4° Soller slits, 1° divergence and antiscatter slits, 0.005 inch receiving aperture; exit beam monochromator and scintillation detector. Intensities were measured for 10 seconds at each 0.01° step from $2\theta = 122°$ to 15°.

Integrated intensities were obtained by least-squares peak fitting of step-scanned intensity measurements using starting parameters obtained from second derivatives of background corrected, smoothed, $K\alpha_2$ stripped intensities (Snyder, 1983). Peak-shape function is the sum of Lorentzian and Gaussian terms with 50% Lorentzian for $2\theta = 15–30°$, 60% Lorentzian for $2\theta = 30–75°$, and 75% Lorentzian for $2\theta = 75–120°$. Fitted peak widths varied, but generally increased from 0.16° to 0.34° FWHM from lowest to highest 2θ. Weights were assigned as $1/I_0$. The goodness of fit, defined as: rms $[I_0 - I_c]^2/I_0$, is 1.19. 86 peaks were fitted ranging over three orders of magnitude in intensity, and were corrected for Lorentz and polarization factors and for a monochromator polarization ratio of 0.80.

Table 1. Comparison of observed and calculated (Lorentz-polarization corrected) intensities for huntite in order of increasing diffraction angle. An ampersand indicates that the several preceding reflections are overlapped and contribute to one observed peak

hkil	I(o)	I(c)	hkil	I(o)	I(c)	hkil	I(o)	I(c)
101̄1	8	4	156̄2	64	70	549̄1	93	92
112̄0	4	3	066̄0	141	142	369̄0	17	27
022̄1	16	13	325̄4	63	66	358̄4	-	17
011̄2	5	6	336̄3	87	110	707̄4	-	252
213̄1	202	209	437̄1	55	59	338̄6	-	256
202̄2	1403	1397	257̄0	185	189	178̄3	-	173
033̄0	30	26	000̄6	307	349	718̄3	-	188
000̄3	145	142	314̄5	29	52	134̄7	-	33
123̄2	168	155	347̄2	69	85	&	957	921
224̄0	149	161	055̄4	88	101	808̄2	34	28
112̄3	108	121	044̄5	110	145	628̄4	43	40
134̄1	152	141	167̄1	144	160	404̄7	32	30
404̄1	237	192	246̄4	101	109	617̄5	139	139
314̄2	714	678	235̄5	33	49	729̄2	311	269
101̄4	32	33	617̄2	26	31	369̄3	-	31
033̄3	-	16	516̄4	-	42	639̄3	-	22
303̄3	-	29	033̄6	-	15	&	64	53
&	51	45	303̄6	-	8	325̄7	34	41
325̄1	109	103	527̄3	-	27	819̄1	38	38
044̄2	78	76	257̄3	-	33	202̄8	234	202
145̄0	98	100	&	106	126	066̄6	-	66
022̄4	632	622	358̄1	-	145	606̄6	-	63
224̄3	577	567	707̄1	-	9	&	123	129
235̄2	109	118	&	148	154	538̄5	-	85
213̄4	25	31	224̄6	135	149	077̄5	-	4
055̄1	16	16	505̄5	48	43	&	117	90
336̄0	405	395	538̄2	-	29	460̄1	41	35
011̄5	10	14	077̄2	-	293	123̄8	30	36
246̄1	112	118	&	326	323	549̄4	-	39
505̄2	54	52	437̄4	23	26	257̄6	-	88
134̄4	265	309	426̄5	74	79	527̄6	-	131
145̄3	-	114	268̄2	63	64	&	272	258
415̄3	-	166	448̄3	-	68	730̄1	58	41
&	270	280	022̄7	-	26	640̄2	46	57
202̄5	22	16	&	76	94	099̄0	195	164
515̄1	139	150	156̄5	77	93	088̄4	14	15
426̄2	162	159	145̄6	-	32	246̄7	38	54
404̄4	137	137	415̄6	-	32	314̄8	107	110
123̄5	148	177	&	74	64	279̄4	174	181
						550̄3	198	117

Unit cell dimensions were obtained by a least-squares fit to all 86 d-values obtained from peak-fitting with 2θ calibration by external quartz standard, refined sample displacement from focussing circle 0.12(1) mm, unit weights, $a = 9.5027(6)$, $c = 7.8212(6)$ Å. Space group is $R32$ consistent with X-ray powder data and isomorphous borates (Hong and Dwight, 1974). TEM observations of grains on holey carbon film show diffraction symmetry consistent with this unit cell and space group; there were no indications seen of twinning, which might be expected, if the symmetry were lower. The inequant, platey grain shapes match previous SEM observations of Faust (1953).

The crystal structure was refined by least-squares fitting of 86 F^2, or, a sum of F^2 for peaks spaced less than 0.5 FWHM (Cooper et al., 1981). Weights were assigned as $1/(e^2 + s^2)$ where e is esd from peak fitting and s is an estimate of all other sources of measurement and model uncertainties. In this case, s was chosen as 1.0, a value less than about 85% of all e-values. Neutral atom scattering factors were taken from *International Tables* (1974) and there was a total of 11 variables (scale factor, 7 atomic

Table 2. Final refined positional and thermal parameters

atom	x	y	z	B(Å²)
Ca	0	0	0	0.94(7)
Mg	0.5443(7)	0	0	"
C(1)	0	0	1/2	"
C(2)	0.4535(20)	0	1/2	"
O(1)	0.8663(15)	0	1/2	"
O(2)	0.5895(13)	0	1/2	"
O(3)	0.4569(11)	0.1355(12)	0.5161(11)	"

Table 3. Cation-oxygen distances (in Ångstroms) for huntite and ordered dolomite after Reeder and Wenk (1983)

huntite	dolomite
Ca - O(3) = 2.409(11) 6X	Ca - O = 2.380
Ca - O(2) = 3.154(13) 6X	
Mg - O(1) = 2.108(16) 2X	Mg - O = 2.084
Mg - O(2) = 2.107(14) 2X	
Mg - O(3) = 2.031(13) 2X	
C(1) - O(1) = 1.270(15) 3X	C - O = 1.283
C(2) - O(2) = 1.292(22) 1X	
C(2) - O(3) = 1.278(21) 2X	

positional parameters, overall isotopic temperature factor, Ca-site occupancy and preferred orientation parameter). Without preferred orientation correction, $R(F) = 8\%$, and some C–O distances were as short as 1.24 Å. A preferred orientation correction similar to that of Rietveld (1969), except that a March function, $p(\alpha) = [P^{-\frac{2}{3}}\cos^2\alpha + P^{\frac{1}{3}}\sin^2\alpha]^{-3/2}$ (March, 1932), was substituted for Rietveld's exponential function, $p(\alpha) = \exp(-G\alpha^2)$, resulted in a lower R-factor. With the preferred orientation plane (101̄1), P refined to 2.00(11) resulting in correction factors ranging from 0.8 to 1.3. Final R-factors are: $R(F^2) = 0.080$, $R(F) = 0.053$, $wR(F) = 0.060$. All calculations used unpublished programs written by the authors.

Results and discussion

To test the ordering of Ca and Mg atoms between the alkaline-earth sites, the occupancy of the "Ca" site was treated as a least-squares variable and refined to 0.99(2) Ca per site. This occupancy, plus the near stoichiometric chemical formula reported for the Tea Tree Gully huntite (Skinner, 1958), indicates that the alkaline-earth sites are fully ordered within the accuracy of the data. Table 1 lists observed and calculated (Lp-corrected) intensities.

Table 2 lists the refined positional and thermal parameters. Cation-oxygen distances resulting from these parameters are given in Table 3 where they are compared with the corresponding distances found in the single-crystal refinement of dolomite by Reeder and Wenk (1983). The huntite bond lengths are not significantly different from those of dolomite.

A major difference between huntite and dolomite is the shape of the Ca coordination polyhedron. In the more common rhombohedral carbonates the Ca polyhedron is a nearly regular octahedron, whereas in huntite this polyhedron is quite close to being a right trigonal prism. Though a trigonal prism is somewhat uncommon for VI-coordinated Ca, it is not unusual for the rare-earth elements, and is found in the series of borates isostructural with huntite (Ballman, 1962). As is sometimes found with trigonal prismatic coordination of rare-earth atoms, the trigonal prism ligands (at 2.37 Å for $NdAl_3(BO_3)_4$) occur along with a second, further set of ligands (six at 3.07 Å for the Nd compound). In huntite the Ca atom has a similar second set of further oxygen neighbors at 3.15 Å. If such remote contacts represent bonds, they must surely be so weak as to be of negligible structural importance, at least for Ca. This secondary set of neighbors may, how-
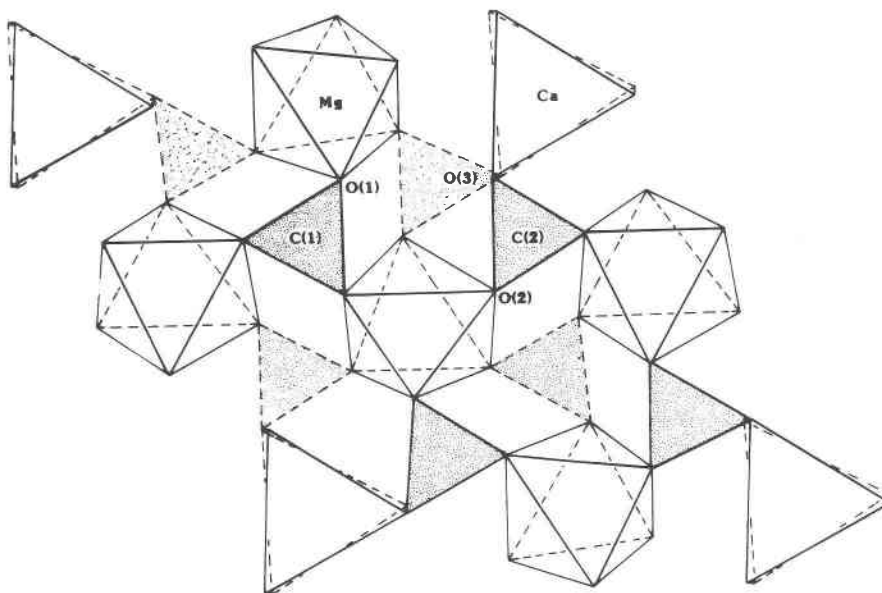
Fig. 1. Polyhedral drawing of a layer of the huntite structure viewed along the c axis. Solid lines represent polyhedral edges at $z = \frac{1}{6}$ to $\frac{1}{3}$ and dashed lines represent polyhedral edges at $z = \frac{1}{2}$.

ever, be of importance if the Ca atom is replaced by a larger divalent atom such as Eu(2+), Sr, or Ba. It is probable that the stability field (if any) and occurrence of huntite may well be expanded by such chemical substitutions. Shayan (1984) has recently reported nearly 2 wt.% SrO in several huntites. This strontium content, along with lower than ideal calcium content, suggests that Sr substitutes into the trigonal prismatic site, to the extent of about 7 mol.% in these particular samples.

A polyhedral representation of the huntite structure is shown in Figure 1. As in the calcite and dolomite structures, there are alkaline-earth polyhedra forming layers normal to the c-axis. These polyhedra are interconnected within the layers by corner sharing with CO_3 groups of two types. A quarter of these are the $C(1)O_3$ groups; these have symmetry 32 and are planar, equal-sided triangular groups oriented parallel to (0001). The other three-quarters are the $C(2)O_3$ groups; these have symmetry 2 and are planar but not quite equal-sided (sides = 2.21 and 2.24 Å) triangular groups which are tilted at 6 degrees to (0001). In huntite these layers contain both Ca trigonal prisms and Mg octahedra, which is in contrast to the (ordered) dolomite structure, in which each alkaline-earth layer contains only Ca octahedra or Mg octahedra.

Another difference between the huntite and more common rhombohedral carbonate structures occurs in the polyhedral connectivity between successive Ca, Mg layers. In the dolomite or calcite structures each Ca or Mg polyhedron shares three of its six corners with the Ca or Mg polyhedron in the layer above and the other three corners with Ca or Mg polyhedra in the layer below; there is no edge sharing. In huntite the alkaline-earth polyhedra share all corners with polyhedra in the layers directly above and below, but in such a way that each Mg octahedron shares

two edges, one in each neighboring layer. This edge sharing forms three-octahedron-repeat, infinite spiral chains running parallel to the c-axis. The shared octahedral edges, of length 2.63 Å, are substantially shorter than the 3.00 Å average length of the remaining, unshared edges.

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