

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

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Abstract

Peak-fitting of $\text{CuK}\alpha_{1,2}$ 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, $\text{CaMg}_3(\text{CO}_3)_4$, 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 platy, 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, $\text{CaMg}(\text{CO}_3)_2$.

Introduction

Huntite, $\text{CaMg}_3(\text{CO}_3)_4$, is a naturally occurring rhombohedral carbonate whose composition lies half way between dolomite, $\text{CaMg}(\text{CO}_3)_2$, 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 $25 \times 12 \times 1$ mm recess of plastic holder, moistened, compacted and smoothed with a spatula. Data collection used a Picker horizontal powder diffractometer, $\text{CuK}\alpha_{1,2}$ 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 $2\theta = 122^\circ$ 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: $\text{rms} [I_0 - I_c]^2/I_0$, 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

hkl	I(o)	I(c)	hkl	I(o)	I(c)	hkl	I(o)	I(c)
1011	8	4	1562	64	70	5491	93	92
1120	4	3	0660	141	142	3690	17	27
0221	16	13	3254	63	66	3584	-	17
0112	5	6	3363	87	110	7074	-	252
2131	202	209	4371	55	59	3366	-	256
2022	1403	1397	2570	185	189	1783	-	173
0330	30	26	0066	307	349	7183	-	188
0009	145	142	3145	29	52	1347	-	33
1232	168	155	3472	69	85	&	957	921
2240	149	161	0554	88	101	8082	34	28
1123	108	121	0445	110	145	6284	43	40
1341	152	141	1671	144	160	4047	32	30
4041	237	192	2464	101	109	6175	139	139
3142	714	678	2355	33	49	7252	311	269
1014	32	33	6172	26	31	3693	-	31
0333	-	16	5164	-	42	6393	-	22
3033	-	29	0336	-	15	&	64	53
&	51	45	3036	-	8	3257	34	41
3251	109	103	5273	-	27	8191	38	38
0442	78	76	2573	-	33	2028	234	202
1450	98	100	&	106	126	0666	-	66
0224	632	622	3581	-	145	6056	-	63
2243	577	567	7071	-	9	&	123	129
2352	109	118	&	148	154	5385	-	85
2134	25	31	2246	135	149	0775	-	4
0551	16	16	5055	48	43	&	117	90
3360	405	395	5382	-	29	4601	41	35
0115	10	14	0772	-	293	1238	30	36
2461	112	118	&	326	323	5494	-	39
5052	54	52	4374	23	26	2576	-	88
1344	265	309	4265	74	79	5276	-	131
1453	-	114	2682	63	64	&	272	258
4153	-	166	4483	-	68	7301	58	41
&	270	280	0227	-	26	6402	46	57
2025	22	16	&	76	94	0950	195	164
5161	139	150	1565	77	93	0884	14	15
4262	162	159	1456	-	32	2467	38	54
4044	137	137	4156	-	32	3148	107	110
1235	148	177	&	74	64	2794	174	181
						5503	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, platy 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 (Å ²)
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) = 2.107(14) 2X	Mg - O = 2.084
Mg - O(3) = 2.031(13) 2X	
C(1) - O(1) = 1.270(15) 3X	
C(2) - O(2) = 1.292(22) 1X	C - O = 1.283
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, $p(\alpha) = [P^{-2}\cos^2\alpha + P^2\sin^2\alpha]^{-3/2}$ (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 (1011), 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-

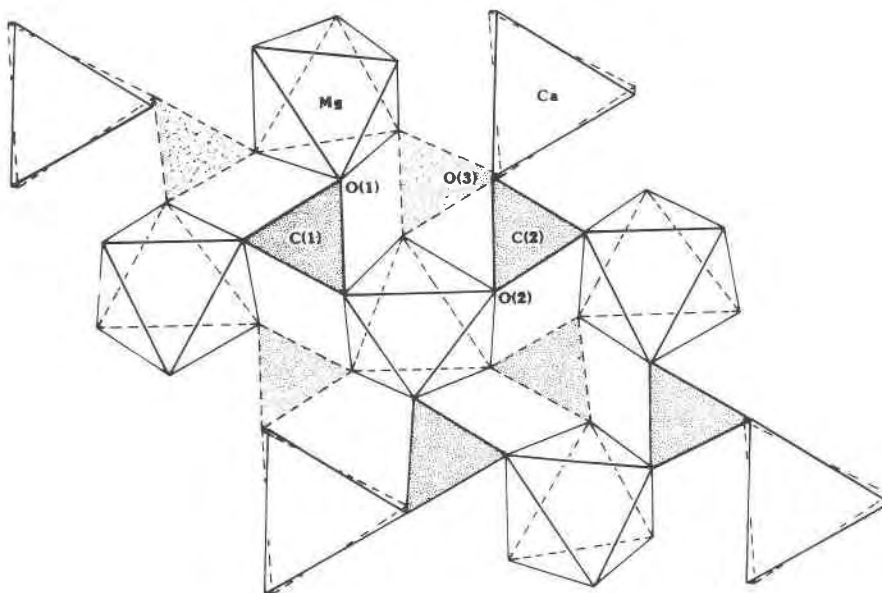


Fig. 1. Polyhedral drawing of a layer of the huntite structure viewed along the *c* axis. Solid lines represent polyhedral edges at $z = \frac{1}{6}$ to $\frac{1}{3}$ and dashed lines represent polyhedral edges at $z = \frac{1}{2}$.

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 CO₃ groups of two types. A quarter of these are the C(1)O₃ groups; these have symmetry 32 and are planar, equal-sided triangular groups oriented parallel to (0001). The other three-quarters are the C(2)O₃ 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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