Department of Geology and Applied Geology,
University of Glasgow,
Glasgow, G12 8QQ, UK

J. W. HARRIS

Department of Geology and Geophysics,
University of Edinburgh,
West Mains Road,
Edinburgh, EH9 3JW, UK

B. HARTE

Institute de Physique du Globe,
4, Place Jussieu,
University of Paris VI,
Paris, France

S. R. BOYD

A high-precision crystal structure refinement of daqingshanite-(Ce) from the Nkombwa Hill carbonatite, Zambia

DAQINGSHANITE-(CE) was only recently recognized as a new mineral species, although it is a common mineral at several major rare earth element (*REE*) deposits (Chao and Baker, 1979; Horvath and Gault, 1990; Ren *et al.*, 1983). Its occurrence at the Nkombwa Hill carbonatite was recently described in this journal (Appleton *et al.*, 1992), and that work provided several new mineralogical data for the phase.

The crystal structure of daqingshanite-(Ce) was described by Ximen and Peng (1985) using Bayan Obo material. The crystal structure study, however, lacked precision and yielded a large residual value (R = 7.9%), and thus structural details are lacking. This fact, coupled with the similarity to the huntite atomic arrangement despite the non-parallel formulae and different space groups, invited refinement of the daqingshanite-(Ce) atomic arrangement and comparison to that of huntite. This work profers a high-precision structure study of daqingshanite-(Ce) and elucidates the huntite–daqingshanite structure relationship.

Experimental

The procedures for X-ray data collection and structure refinement are given in Ni *et al.* (1993);

TABLE 1. Crystal data and results of Daqingshanite-(Ce) structure refinement

Dimensions	0.12 × 0.13 × 0.14 mm
Cell Parameters (*R3m*)	
a(Å)	10.073(10)
c	9.234(5)
Theta limits	0–30°
Scan time (seconds)	⩽ 50
Data collected	1664, $\pm h$, $\pm k$, $+l$
R_{merge} (%)	3.1
# unique data	321
# data > 3 σ_I	276
R(%)	1.7
R_w(%)	2.0
Peaks on difference map (e/Å³), (+,−)	1.08, 1.76

TABLE 2. Atomic positions and equivalent isotropic displacement factors in daqingshanite-(Ce)

Atom	x	y	z	$B_{eq}(\text{Å}^2)$
Ce	0	0	0	0.845(8)
Sr	0.48294(4)	−0.48294	0.0431(1)	0.897(8)
P	⅓	⅔	0.2448(4)	1.30(5)
C	0.3307(9)	0.165	0.2325(8)	1.2(2)
O(1)	⅓	⅔	0.407(1)	4.8(3)
O(2)	0.2503(4)	0.501	0.1897(7)	1.8(1)
O(3)	0.1900(7)	0.095	0.2071(7)	1.4(1)
O(4)	0.4046(5)	0.0938(4)	0.2521(5)	1.73(9)

details of data collection and structure refinement specific to this study are given in Table 1. The crystal studied was obtained from the material described by Appleton et al. (1992), who gave the formula $(Sr_{2.69}Ca_{0.11}Ba_{0.20})_{\Sigma3.0}(La,Ce,Nd,Pr)_{1.02}$-$(PO_4)_{0.99}$ $(CO_3)_{3-x}(OH,F)_x$, with x indeterminate. For the crystal structure refinement, Sr and Ce were used to represent the occupants of the divalent metal and REE sites, respectively.

The final R-value obtained in this study indicates a superior refinement. Although structural parameters differ by up to 19 σ and bond lengths by up to 0.10 Å between this work and the earlier results of Ximen and Peng (1985), the structural principals put forth in the earlier work are essentially confirmed.

Table 2 contains atomic coordinates and equivalent isotropic thermal parameters for daqingshanite-(Ce), and Table 3 lists selected bond lengths for the structure. Copies of structure factors and anisotropic thermal parameters may be obtained from this journal upon request.

TABLE 3. Selected interatomic distances in daqing-shanite-(Ce)

Ce -	O(1)	2.398(13) Å	Sr -	O(2)	2.462(5)
	O(3)	2.531(6) (×3)		O(2)′	2.639(5) (×2)
	O(4)	2.642(4) (×6)		O(3)	2.771(4) (×2)
				O(4)	2.650(5) (×2)
Mean		2.584		O(4)′	2.763(4) (×2)
C-	O(3)	1.250(10)	Mean		2.679
	O(4)	1.282(6) (×2)			
			P-	O(1)	1.498(13)
Mean	1.271			O(2)	1.535(9) (×3)
			Mean		1.526

Discussion of the structure

Huntite and daqingshanite-(Ce) are formed of intervening layers of cations (Mg_3Ca_1 in huntite, Sr_3REE_1 in daqingshanite) and anionic complexes [$(CO_3)_4$ in huntite, [$(CO_3)_3(PO_4)_1$] in daqingshanite]. Although huntite and daqingshanite have been proposed as isostructures, the parallelism between the phases has not been elucidated. The formula of daqingshanite-(Ce) relates to that of huntite by the substitution $Sr_3REE_1(PO_4)_1$ ⇌ $Mg_3Ca_1(CO_3\square_1)_1$. As noted in Fig. 1, the substitution of the cations is straightforward, with the substituents occupying similar positions in each structure.

Of particular interest in the relationship between the daqingshanite and huntite atomic arrangements is the substitution of the daqing-shanite phosphate tetrahedron for the huntite C(1) trigonal planar carbonate group, (PO_4) ⇌ $(CO_3\square_1)$. The substitution is accomplished by addition of a phosphorus atom above the carbonate plane and an apical oxygen [O(1)] in the intervening cation layer between successive carbonate layers. The substitution occurs only for the huntite C(1)-O3 carbonate group, that group centered on the C atom in the 3b special position in the huntite structure (space group R32). The C(2) carbonate groups in the huntite structure are not substituted, and are related by a diad in huntite and a mirror plane in daqingshanite-(Ce) (Fig. 1).

The O(1) atom, that atom that is 'added' to the daqingshanite structure as compared to the huntite structure, deserves special comment. In the structure refinement described here and in the work of Ximen and Peng (1985), the thermal displacement factor of O(1) is unusually large (Table 2). It has been suggested (Ximen and Peng, 1985) that the phosphorous site is not fully occupied and that the (PO_4) tetrahedra may be partially replaced by carbonate groups, with
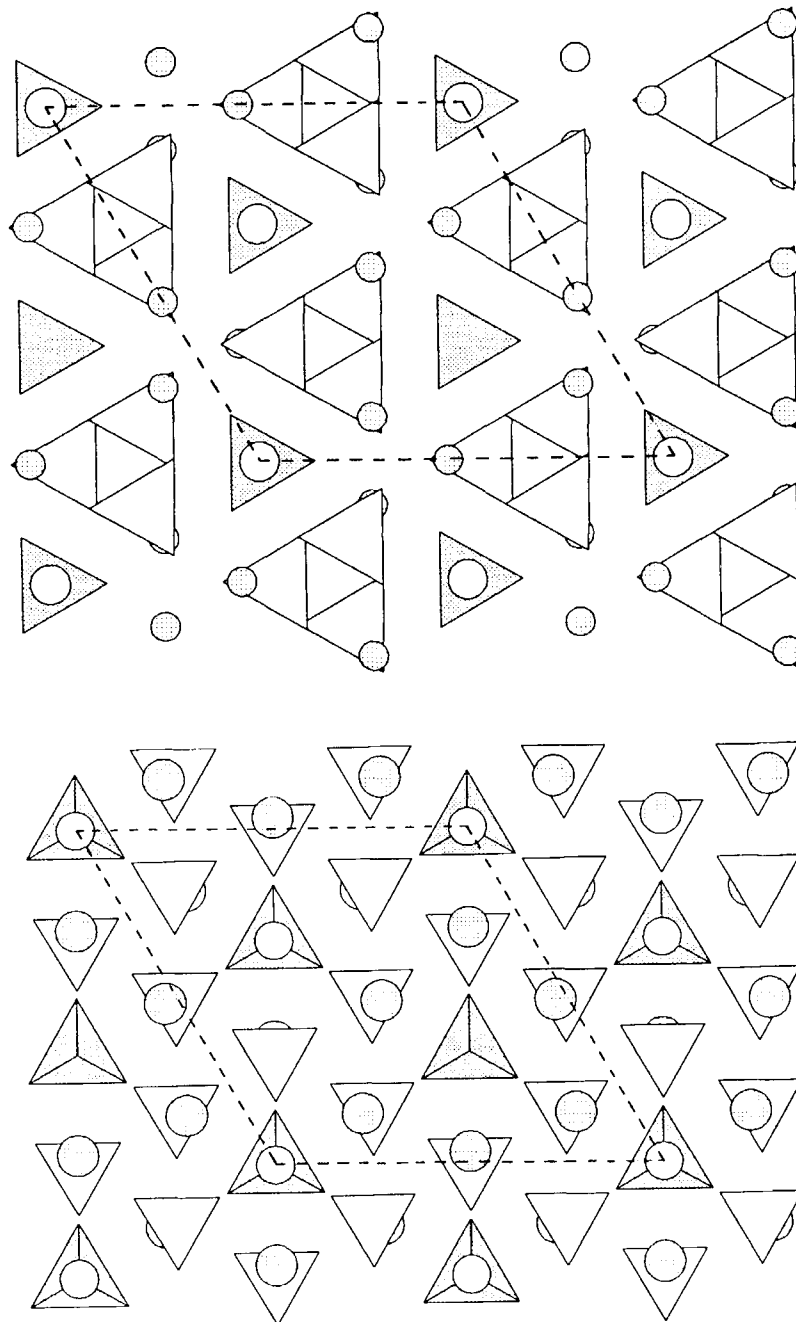
FIG. 1. Atomic arrangements of huntite (top) and daqingshanite-(Ce) (bottom) projected on (001); the unit cells are outlined. For huntite, large open atoms are Ca, smaller stippled atoms are Mg; for daqingshanite-(Ce), large open atoms are REE, smaller stippled atoms are Sr. Carbonate groups and phosphate tetrahedron are shown as polyhedra. The C(1) carbonate group in huntite and PO_4 tetrahedral group in daqingshanite-(Ce), the objects of the $(PO_4) \rightleftharpoons (CO_3\square_1)$ substitution, are stippled.

charge balance being maintained by substitution of fluorine and/or hydroxyl for oxygen. If indeed this occurs, the O(1) site would be partly occupied, a fact consistent with a large thermal parameter. However, the infrared absorption spectrum and electron-microprobe analysis of the phase given by Appleton et al. (1992) suggest such substitution occurs only in very small amounts, if at all. To test this hypothesis, occupancy of the O(1) site was released. Although the occupancy of the site dropped to 0.93(4), the value is less than 2 sigma from full occupancy and there was no decrease in the R value. These results suggest that the site is essentially fully occupied, a result in accord with the chemical and infrared data of Appleton et al. (1992). The large thermal parameter may thus result from factors such as positional disorder, not uncommon in atoms occupying positions of high symmetry as O(1) in daqingshanite-(Ce) (site symmetry = $3m$).

The results of the high-precision crystal structure study described herein elucidate the huntite-daqingshanite-(Ce) relationship; the work also demonstrates that the ideal formula of Nkombwa Hill daqingshanite-(Ce) is $Sr_3(REE)_1(CO_3)_3(PO_4)_1$, and that there is little or no substitution of hydroxyl or fluorine in its atomic arrangement.

References

Appleton, J. D., Bland, D. J., Nancarrow, P. H., Styles, M. T., Mambwe, S. H. and Zambezi, P. (1992) Mineral. Mag., 56, 419–422.

Chao, G. Y. and Baker, J. (1979) Mineral. Record, 10, 99–101.

Dollase, W. A. and Reeder, R. J. (1986) Amer. Mineral., 71, 163–166.

Horvath, L. and Gault, R. A. (1990) Mineral. Record, 21, 281–359.

Ni, Y., Hughes, J. M. and Mariano, A. N. (1993) Amer. Mineral., 78, 415–418.

Ren, Y., Ximen, L. and Peng, Z. (1983) Geochemistry (China), 2, 180–184.

Ximen, L. and Peng, Z. (1985) Geochemistry (China), 4, 89–96.

KEYWORDS: daqingshanite-(Ce), crystal structure, Zambia, Nkombwa Hill

Department of Geology,
Miami University,
Oxford,
OH 45056, USA

J. M. HUGHES
N. YUNXIANG

Monticellite in the Gwena kimberlite (Shaba, Zaïre): evidence of late-magmatic crystallization

PRIOR to 1975 monticellite was considered a rare mineral in kimberlites but microprobe studies have now established it as a fine grained constituent in many kimberlite matrices (e.g. Clement et al., 1975; Mitchell, 1978; Skinner and Clement, 1979). This paper describes the mode of occurrence and chemical composition of well-developed monticellite in the Gwena kimberlite, Shaba, Zaïre.