NEW DATA ON THE STRUCTURE OF NORBERGITE: LOCATION OF HYDROGEN BY X-RAY DIFFRACTION

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ABSTRACT

Two crystals of OH-rich norbergite from the Alpujarride Complex (Betic Cordilleras) have been analyzed, and their structure refined by single-crystal X-ray-diffraction analysis. The new data confirm the earlier refinement on a composition near the F end-member, and add new insight to the crystal chemistry of this humite-group mineral. In particular, hydrogen atoms were located on the difference-Fourier map. Their position and the consequent structural constraints to the $(OH)F_{-1}$ substitution suggest that OH-rich norbergite requires very high pressure to crystallize, thus explaining the normal occurrence of the fluorine-dominant compositions.

Keywords: norbergite, humite group, structure refinement, electron-microprobe data, hydrogen.

SOMMAIRE

Deux cristaux de norbergite relativement riches en OH, provenant du complexe de Alpujarride, dans les Cordillères bétiques d'Espagne, ont été analysés, et leur structure a été affinée par diffraction X sur cristal unique. Les données nouvelles confirment les résultats de l'affinement antérieur, obtenu sur un cristal proche du pôle fluoré, et ajoutent des nouveaux renseignements au sujet de la cristallochimie de ce membre du groupe de la humite. En particulier, les atomes d'hydrogène ont été repérés sur une projection de Fourier par différence. D'après leur position et les contraintes structurales qui en découlent concernant la substitution $(OH)F_{-1}$, la formation de la norbergite riche en OH requiert une pression assez élevée, ce qui rend compte de la présence courante de compositions à dominance de fluor.

(Traduit par la Rédaction)

Mots-clés: norbergite, groupe de la humite, affinement de la structure, données de microsonde électronique, hydrogène.

INTRODUCTION

Norbergite usually occurs in nature with compositions near the F (fluorine) end-member composition, and in fact is defined as a F-dominant species ($Mg_2SiO_4 \cdot MgF_2$). Experimental studies on norbergite have concentrated on the F end-member because of the instability of OH-rich compositions in the common range of temperature and pressure. This has prevented the location of H atoms and, thus, a study of the structural constraints concerning the crystal chemistry of this substitution. This paper contributes to the study of $(OH)F_{-1}$ substitution in humite-group minerals.

The structure of norbergite was first determined by Taylor & West (1929), who found it to be orthorhombic, space group *Pbnm*, and described it as being formed of alternating layers of olivine (Mg_2SiO_4) and brucite [$Mg(F,OH)_2$]. They used this scheme to explain the chemistry of all the humite-group minerals following the hypothesis of Penfield & Howe (1894), who described them as morphotropic, with the general formula $nMg_2SiO_4 \cdot Mg(F,OH)_2$, where $n = 1$ for norbergite.

Gibbs & Ribbe (1969) refined the structure of norbergite with a crystal near the F end-member composition. They also revised the crystal chemistry of the humite-group minerals (Ribbe *et al.* 1968, Gibbs & Ribbe 1969, Jones *et al.* 1969, Gibbs *et al.* 1970), in which they modeled the various structures using combinations of alternating layers of olivine and brucite. They concluded that the model of Taylor & West (1929) was misleading, as the real composition of the two layers was $Mg_2SiO_3(OH,F)$ and $Mg(OH,F)O$, respectively. They also proposed that the key structural unit for the humite minerals is (as in olivine) the zig-zag chain of octahedra, and that the $^{[6]}Fe^{[6]}Mg_{-1}$ substitution mainly controls the unit-cell parameters and, thus, the unit-cell volume. In addition, they

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obtained a correlation between the cell volume and the ratio F:OH, which was anticipated on the basis of the ionic radii involved.

Several syntheses of phases in the humite group have been reported, mainly of norbergite and chondrodite (Rankama 1947, Van Valkenburg 1955, 1961, Christie 1965, Duffy & Greenwood 1979, Irwin 1993). Most of them involve norbergite with different octahedrally coordinated cations (Mg, Ca, Zn, Fe). The norbergite end-member has also been synthesized (Irwin 1993). No OH equivalent has yet been synthetized and studied by means of X-ray diffraction.

There is another important substitution involving the OH site in humite-group minerals: $^{[6]}Ti^{4+}O^{2-}_{2}$ $^{[6]}Mg_{-1}(OH)^{-}_{-2}$. This substitution occurs at the $M3$ octahedron in clinohumite and in chondrodite, in which the increase of local charge at $M3$ can be balanced by the loss of the H atoms, $i.e.$, dehydrogenation (Fujino & Takéuchi 1978).

MATERIAL

The norbergite crystals used for this work (HV–47 N1, $0.59 \times 0.43 \times 0.39$ mm and HV–43 N4, $0.39 \times 0.36 \times 0.29$ mm) were extracted from two samples of metamorphosed and metasomatized limestone (HV–47 and HV–43) from Huerta del Vinagre, a small scheelite mine in the Guadaiza Unit of the Upper Alpujarride series, in the Betic Cordilleras. These samples belong to a magnesian skarn formed by the interaction between dolomitic marble and magmatic fluids issued from the surrounding granites (J. Currás, pers. commun.). In particular, the samples are representative of an exoskarn composed almost entirely of monomineralic metasomatic veins of calcite and humite-group minerals, with rare fluoborite and minor serpentine (from the alteration of humite-group minerals). The humite-group minerals in these samples have very low Fe and Ti contents. In norbergite, the $^{[6]}Ti^{4+}O^{2-}_{2}{}^{[6]}Mg_{-1}(OH)^{-}_{-2}$ substitution is negligible ($TiO_2 < 0.02$ wt%), whereas the extent of $(OH)F_{-1}$ substitution is significant.

EXPERIMENTAL PROCEDURES

The crystals were extracted directly from pieces of rock. X-ray data were collected with an automatic 4-circle Philips PW1100 diffractometer, using graphite-monocromatized Mo$K\alpha$ radiation. The space group was determined to be $Pbnm$; the unit-cell parameters were calculated from a least-squares refinement of d calculated for 56 rows of the reciprocal lattice by measuring the reflections in the range $-35 < \theta < 35°$; they are reported in Table 1 for the two crystals studied. Two equivalent orthorhombic reflections (hkl and $\bar{h}kl$) were collected in the θ range 2–40°. The profiles were integrated following the method of Lehmann & Larsen (1974), as modified by Blessing $et\ al.$ (1974).

TABLE 1. OH-RICH NORBERGITE: UNIT-CELL PARAMETERS AND SELECTED SREF RESULTS

	HV47 N1	HV43 N4
size (mm)	$0.59 \times 0.43 \times 0.39$	$0.39 \times 0.36 \times 0.29$
a (Å)	4.711(1)	4.710(1)
b (Å)	10.275(3)	10.279(3)
c (Å)	8.805(3)	8.807(3)
V (Å^3)	426.2(2)	426.4(2)
Z	4	4
R_{sym}	1.4	1.4
Extinction coef.	1.83E-02	4.36E-03
wR2	3.47(1378)	3.38(1377)
GooF	1.084	0.986
$R1_{4\sigma}$	1.43(1237)	1.42(1212)

Intensities were corrected for Lorentz-polarization and absorption following North $et\ al.$ (1968), and the equivalent pairs were merged, giving $R_{eq} = 1.4\%$.

Weighted full-matrix least-squares refinements were carried out using SHELXL-93 (Sheldrick 1993). The positional and atomic displacement parameters of Gibbs & Ribbe (1969) were used as a starting model. Scattering factors were taken from $International\ Tables$ $for\ Crystallography$: in particular, neutral $versus$ ionized scattering-factors were used for the Si and O1, O2, O3 sites; F$^-$ $versus$ O$^-$ for the O5 site, and Mg^{2+} was refined against Fe^{2+} in the $M2$ and $M3$ octahedral sites according to what was suggested by Ungaretti et $al.$ (1983). The oxygen atom involved in OH-rich norbergite is called O5 and not F, in accordance with the usage of Abbott $et\ al.$ (1989).

At convergence, a difference-Fourier map showed some residual maxima. Some of the highest were ascribed to bonding electrons in the middle of the covalent Si–O bond. The second maximum was set at 1.02 Å from O5, and had a peak height of 0.35 e/Å^3. It was inserted in the model as H, and refined without any constraints ($i.e.$, occupancy, isotropic atomic displacement parameter and fractional coordinates were allowed to vary). Both the wR^2 factor and the estimated standard deviations (e.s.d.) of the refined parameters improved significantly, and further residual peaks with peak height greater than 0.2 e/Å^3 were not observed in a subsequent map. Selected indices of the refinement are reported in Table 1. Final atomic parameters are listed in Table 2, and selected interatomic distances are reported in Table 3. A list of the observed structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A OS2.

Both crystals were mounted in epoxy and polished. They were analyzed for Si, Mg, Fe, Mn, Ti, Ca, Cr, K, F and Cl with an ARL electron microprobe (EMP)

TABLE 2. SITE SCATTERING, FRACTIONAL ATOMIC COORDINATES, AND
ATOMIC DISPLACEMENT PARAMETERS FOR THE
CRYSTALS OF OH-RICH NORBERGITE REFINED

Atom	s.s.†	x/a	y/b	z/c	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
HV43 N4											
M2	12.24(1)	0.99139(5)	0.90594(2)	1/4	7.06(7)	5.95(11)	5.49(1)	9.75(12)	0	0	0.27(7)
M3	12.20(1)	0.98973(4)	0.63316(2)	0.43062(2)	5.93(5)	6.13(8)	5.87(7)	0.58(8)	0.21(5)	0.59(5)	-0.21(5)
SI		0.41998(4)	0.71964(2)	1/4	4.24(4)	3.51(7)	4.63(7)	4.58(12)	0	0	0.00(5)
O1		0.76216(11)	0.72124(4)	1/4	5.65(8)	3.69(16)	6.54(17)	6.72(17)	0	0	0.31(14)
O2		0.27767(11)	0.57417(4)	1/4	5.94(8)	5.73(18)	4.60(16)	7.49(17)	0	0	-0.04(13)
O3		0.27011(7)	0.79107(3)	0.10415(4)	5.55(6)	5.01(12)	6.44(11)	5.20(11)	1.27(1)	-0.19(1)	-0.05(9)
O5	8.86(1)	0.73471(7)	0.96786(3)	0.08157(3)	8.87(7)	9.88(13)	7.38(12)	9.34(12)	-0.16(9)	-2.79(1)	0.87(1)
H	0.23(3)	0.881(9)	0.996(4)	0.011(6)	43.7(19.1)						
HV47 N1											
M2	12.17(1)	0.99135(5)	0.90588(2)	1/4	6.97(7)	5.95(11)	5.57(10)	9.38(11)	0	0	0.35(7)
M3	12.14(1)	0.98980(3)	0.63318(2)	0.43066(2)	5.93(5)	6.06(7)	6.13(7)	5.60(7)	0.23(4)	0.56(5)	-0.29(5)
SI		0.42001(4)	0.71963(2)	1/4	4.39(4)	3.56(7)	5.00(6)	4.60(7)	0	0	0.07(5)
O1		0.76194(10)	0.72125(4)	1/4	5.69(7)	3.62(15)	7.14(16)	6.32(15)	0	0	-0.08(12)
O2		0.27753(10)	0.57414(4)	1/4	6.26(7)	6.07(16)	5.17(15)	7.53(16)	0	0	0.05(12)
O3		0.27010(7)	0.79103(3)	0.10426(4)	5.80(5)	5.42(11)	6.75(11)	5.24(10)	1.16(9)	-0.19(10)	-0.14(9)
O5	8.84(1)	0.73479(6)	0.96787(3)	0.08149(3)	8.89(6)	9.99(12)	7.45(11)	9.24(12)	-0.27(9)	-2.87(10)	0.86(9)
H	0.21(2)	0.890(10)	0.989(4)	-0.013(7)	42.48(21)						

† Refined site scattering in electrons.
*isotropic equivalent atomic displacement parameters (a.d.p.) (x10^3); a.d.p. are of the form: $\exp[2p^2(a^{*2}U_{11}h^2....+2a^*b^*U_{12}hk...)]$

equipped with four spectrometers (RAP, PET, LiF200 and ADP) at the Dipartimento di Mineralogia e Petrografia, Università di Modena (only elements with concentrations more than 2σ above background are reported in Table 4). Natural mineral standards were used for calibration. Fluorite from the Carrara marble was used as the standard for F. The concentration of fluorine was determined with the RAP crystal (rubidium acid phthalate, $hkl = 100$, $2d = 26.121$ Å). Analytical conditions were 15 kV and 20 nA. A defocused beam of 30 µm was used. Counting time was 20 s on the peak and 4 s on background, measured at both sides of the peak and approximated with a linear function. Results of analyses were processed with the program PROBE v3.52 (Donovan & Rivers 1990) The Phi-Rho-Z correction of Armstrong (1988) was applied. The counting errors reported in Table 4 are the calculated detection-limit (CDL) = [3 × (ZAF) × (100 × I_B/t)$^{1/2}$]/I_S, where ZAF is the correction factor for the sample matrix, I_S is the count rate on the analytical standard, I_B is the background count-rate on the unknown sample, and t is the counting time on the unknown sample.

Discussion

This study provided an accurate refinement of norbergite having a composition richer in OH than that reported by Gibbs & Ribbe (1969); it also allowed the H atom to be located, and information to be gained on the crystal chemistry of norbergite.

The position of the H atom is shown in Figure 1, which is a projection on (100) of the structure of norbergite. The H atom points toward the center of symmetry, at the center of a cavity surrounded by two $M2$ octahedra, four $M3$ octahedra and two Si tetrahedra (Fig. 2). Thus there are two centrosymmetric positions available for H; the same situation was found by Fujino & Takéuchi (1978) in the case of titanian clinohumite. The refined distance between the two centrosymmetric H atoms is 1.085 and 1.141 Å for samples HV–47 and HV–43, respectively; the refined site-occupancy of the H atom is rather low (Table 2), and is in reasonable agreement with that independently obtained for F. The latter in also consistent with EMP data (Table 4).

The local configuration prevents H occupancy in norbergite to be higher than 0.5 (corresponding to 1.0 atom per formula unit, $apfu$). Owing to the cationic arrangement around the cavity (Fig. 2), the strong repulsion between two H atoms at ~1.0 Å cannot in fact be avoided by bending the O–H bonds. Yamamoto (1977, Fig. 4) found two independent positions (H1 and H2) in hydroxyl-dominant chondrodite, another mineral of the humite group; he proposed a "parity rule": two H atoms in the same cavity must occupy positions not related by the center of symmetry. Thus, where present, the H atoms should occupy two slightly different positions; he found them in a hydroxyl-dominant chondrodite and named them H1 and H2. The coordinate of H refined in this work agrees with those of H1 of Yamamoto. Subsequent structure-energy calculations by Abbott et $al.$ (1989) confirmed the Yamamoto parity

TABLE 3. OH-RICH NORBERGITE:
SELECTED GEOMETRICAL
PARAMETERS

	HV43 N4	HV47 N1
Si-O1	1.612 (1)	1.611 (1)
Si-O2	1.639 (1)	1.639 (1)
Si-O3	1.639 (1)	1.638 (1)
Si-O3	1.639 (1)	1.638 (1)
<Si-O>	1.632	1.631
Vol	2.201	2.198
TQE	1.0092	1.0093
TAV	41.18	41.63
M2-O1	2.184 (1)	2.183 (1)
M2-O2	2.043 (1)	2.043 (1)
M2-O3 [x2]	2.183 (1)	2.183 (1)
M2-O5 [x2]	2.017 (1)	2.017 (1)
<M2-O>	2.105	2.104
Vol	12.074	12.069
OQE	1.0209	1.0209
OAV	68.34	68.28
O5-O5 [M2]	2.967	2.968
M3-O1	2.121 (1)	2.122 (1)
M3-O2	2.177 (1)	2.176 (1)
M3-O3	2.003 (1)	2.004 (1)
M3-O3	2.115 (1)	2.114 (1)
M3-O5	2.004 (1)	2.004 (1)
M3-O5	2.044 (1)	2.043 (1)
<M3-O>	2.077	2.077
Vol	11.662	11.659
OQE	1.0173	1.0173
OAV	57.11	57.12
O5-O5 [M3]	2.718 (1)	2.718 (1)
H-H	1.141 (1)	1.085 (1)
O5-H	0.972 (1)	1.129 (1)

are very similar to the refined ones, except for the value of the x coordinate. The refined x coordinates are nearer to the center of symmetry; this is reasonable because of the low observed H occupancy. Therefore, at maximum, only one single H is present in each cavity and can approach the center to minimize repulsion. No evidence for the alternative positions in models 2 and 3 of Abbott *et al.* (1989) has been found on the difference-Fourier map, thus confirming the predictions made by energy calculations. In addition, Abbott *et al.* (1989) calculated O–H distances (from 1.08 to 1.16 Å), somewhat longer than usually expected for an O–H bond, which is also observed in the crystals studied (Table 3).

TABLE 4. CHEMICAL COMPOSITION OF
OH-RICH NORBERGITE (wt%):
RESULTS OF ELECTRON-MICROPROBE
ANALYSES

SAMPLE	HV-43		HV-47	
	mean	dev	mean	dev
no. points		5		6
SiO_2	29.17 (2)	0.02	29.24 (2)	0.31
B_2O_3†	0.24	0.00	0.24	0.00
TiO_2	0.09 (1)	0.01	0.10 (1)	0.01
FeO	0.66 (3)	0.07	0.70 (3)	0.02
MgO	59.46 (1)	0.32	59.52 (1)	0.37
F	14.40 (31)	0.36	14.20 (34)	0.31
(H_2O)*	2.02	0.17	2.13	0.15
O=F	6.06	0.15	5.98	0.13
TOTAL	100.63	0.40	100.84	0.71
Si	0.985	0.003	0.985	0.005
B	0.014	0.000	0.014	0.000
Σ tet	0.999	0.003	0.999	0.005
Ti	0.002	0.000	0.002	0.000
Fe^{2+}	0.019	0.002	0.020	0.000
Mg	2.991	0.006	2.989	0.010
Σ oct	3.012	0.006	3.011	0.010
F	1.537	0.037	1.513	0.032
OH	0.454	0.037	0.478	0.033
$O^=$	0.009	0.001	0.009	0.001
Σ Cations	4.011	0.003	4.010	0.005
X(F)	0.768	0.019	0.757	0.016
$X(O^{2-})$	0.005	0.000	0.004	0.000
X(OH)	0.227	0.019	0.239	0.016

* calculated by stoichiometry; † from SIMS analysis
dev = variation within the sample calculated as the
standard deviation of no. of point analysis

rule, and allowed the calculation of H coordinates for norbergite. They considered either a cavity with one F and one O in the O5 position (model 1), or two atoms of O in the O5 position; in the latter case, two possible configurations were assumed: one with both H pointing toward the center of the cavity (model 2), and the other with one H pointing toward the center and the other pointing in the opposite sense, *i.e.*, toward the next cavity (model 3). Since the H content in the refined structures of this work is <<1.0 *apfu*, its position should be that predicted by model 1 of Abbott *et al.* (1989) (0.2153, –0.0409, –0.0109). The latter values
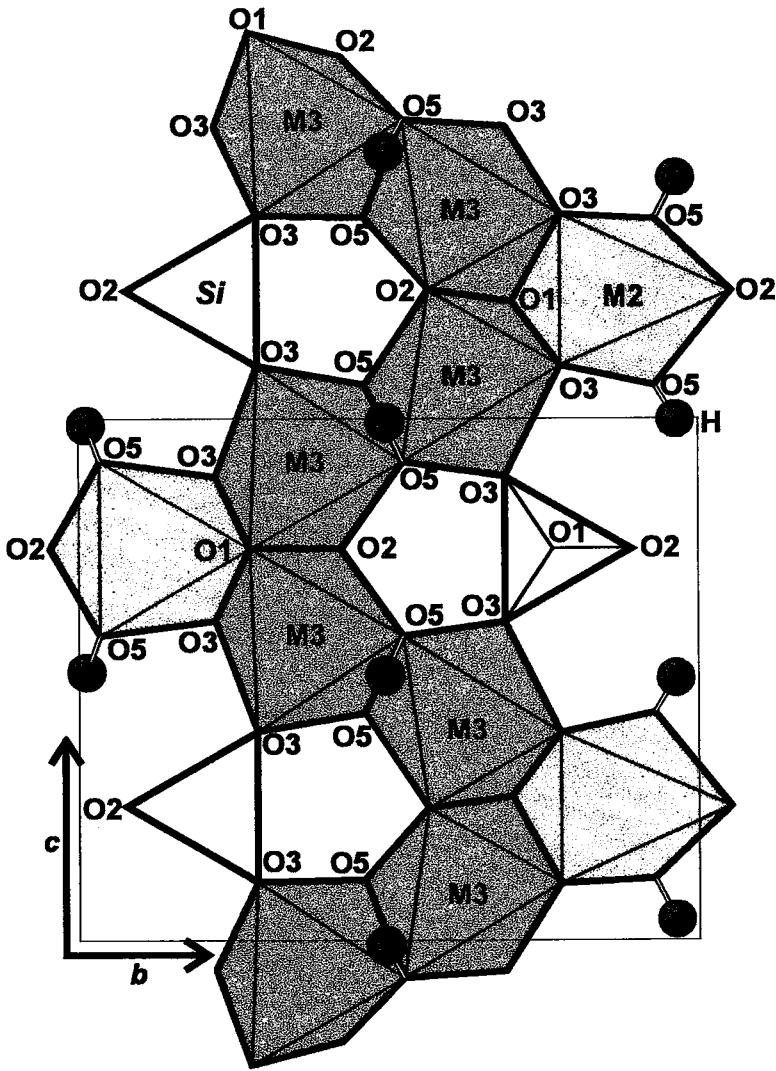
Fig. 1. A projection of the norbergite structure on (100).

There are few published chemical data on norbergite in the literature, and it has to be considered a rare mineral. In particular, no OH-dominant norbergite has been described until now, all the published information pertaining to F-rich (>1.7 *apfu* F) material. In principle, this could be related only to incomplete sampling; however, the discussion above suggests that a stable structure of norbergite should contain at least 1.0 F *apfu*. For OH content greater than 1.0 H *apfu*, both the H1 and H2 positions would have to be simultaneously present, as is the case for the OH-dominant chondrodite synthesized and refined by Yamamoto (1977), resulting in strong H–H repulsion. This structural constraint can be overcome by high

pressure. In fact, Yamamoto's chondrodite was synthesized at 77 kbar and 1125°C, and synthesis of OH-dominant norbergite would most probably require still higher pressures. Ribbe (1979) suggested that OH-dominant norbergite is not expected to be stable except to very high pressures (>150 kbar) since "proton–proton interactions serve to expand the structures of OH-rich humites considerably more than is indicated by comparing M–O,F,OH bond lengths". Such conditions for the crystallization of norbergite are not common in nature, thus explaining the usual occurrence of fluorine-dominant norbergite.

Table 5 shows bond-valence calculations according to the procedure of Brown & Altermatt (1985), based
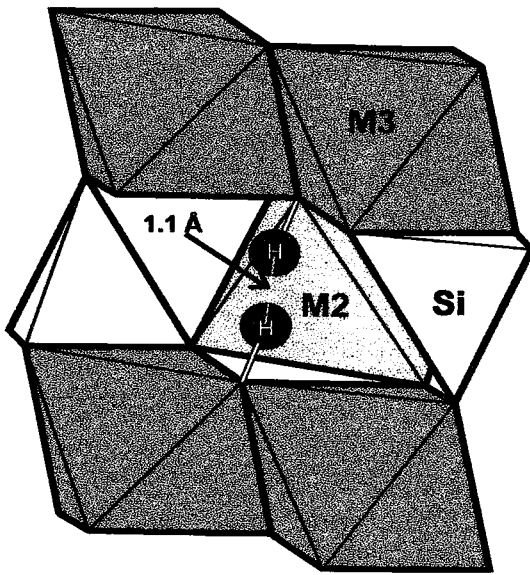
Fig. 2. The relative position of two centrosymmetric H atoms in norbergite.

on the mean bond-lengths of HV–43 refinement and: (a) the actual composition, (b) the ideal F-only end member, and (c) the OH-only end member. Among the two end-members, a lower charge imbalance is obtained for O5 if the site occupancy is near 1 *apfu* F. In the OH end-member norbergite, the positive charge imbalance at the O5 site may indicate that a longer *M*–O5 bond is required. This would further push the H atoms toward the center of the cavity.

A limited $^{[6]}Fe^{2+[6]}Mg_{-1}$ substitution is present in the samples examined here. The reluctance of Fe^{2+} to enter sites coordinating F anions is well known, and thus no high concentrations of Fe^{2+} are expected in the norbergite structure. Irwin (1993) managed to synthesize F-only norbergite with Fe^{2+} contents higher than those reported here, but they are still very low: $Fe/(Fe + Mg)$ = 0.07; in that instance, Fe^{2+} was found to be disordered over *M*2 and *M*3. The composition studied by Gibbs & Ribbe (1969) is intermediate between that of Irwin (1993) and those examined here.

The *M*3 site could be a better host to smaller but more highly charged cations, such as Ti or Fe^{3+}. This is the case for titanian clinohumite where, according to Fujino & Takeuchi (1978), Ti enters *M*3 following the substitution $^{[6]}Ti^{4+}O^{2-}_{-2}{}^{[6]}Mg_{-1}(OH)_{-2}$. The samples studied here present very low Ti^{4+} and very little, if any, Fe^{3+} content is expected in the norbergite structure, since Irwin (1993) synthetized the F end-member at conditions of high $f(O_2)$, and no Fe^{3+} was incorporated. The higher distortion of the *M*2 site [^{M2}OAV (Octahedral Angle Variance: Robinson *et al.* (1971)], ~68°

versus ^{M3}OAV, ~57°, should favor Fe^{2+} ordering at *M*2. Minor but significant differences in site scattering between *M*2 and *M*3 (Table 2) are in agreement with this hypothesis.

The substitution $^{[4]}B^{[4]}Si_{-1}$ has previously been reported for chondrodite (Hinthorne & Ribbe 1974). Also BO_6Fe_3, structurally equivalent to norbergite, has been synthetized by White *et al.* (1965). Thus, a limited $^{[4]}B^{[4]}Si_{-1}$ substitution is possible in norbergite, as suggested by the slightly low SiO_2 content (Table 4). A SIMS (Secondary Ion Mass Spectrometry) analysis performed on the refined crystals at the CSCC-Pavia indicates a maximum B content of ~0.24 wt% B_2O_3, *i.e.*, ~0.014 *apfu*, which appears to be inversely correlated to SiO_2. I suggest that this substitution is present to a minor but significant extent. Since the Ti^{4+} is less than 0.005 *apfu*, the deficiency in charge at the tetrahedral sites needs to be compensated by means of either another high-charge octahedrally coordinated cation or a loss of H. The former would imply that all the Fe present might be Fe^{3+}, and that all the excess charge at the octahedral sites could be balanced with the $^{[4]}B^{[4]}Si_{-1}$ substitution in the absence of dehydrogenation. No direct data about the Fe^{3+} content are available; the R^{3+} at the tetrahedral sites has been compensated by dehydrogenation (OH + F + O must be 1), as assumed in the recalculation of the formula.

TABLE 5. BOND-VALENCE CALCULATIONS FOR OH-RICH NORBERGITE AND NORBERGITE†

a) HV43 N.4	M2	M3	Si	Σ
O1	0.265	0.314	1.037	1.931
O2	0.390	0.271	0.959	1.890
O3	0.266	0.433	0.957	
O3'		0.320		1.977
O5	0.332	0.343		
O5'		0.308		0.984
Σ	1.852	1.990	3.910	−0.257

b) norbergite				
O1	0.265	0.314	1.037	1.930
O2	0.389	0.271	0.959	1.889
O3	0.266	0.433	0.957	
O3'		0.320		1.976
O5	0.308	0.318		
O5'		0.286		0.913
Σ	1.802	1.942	3.910	−0.404

c) "OH-norbergite"				
O1	0.265	0.314	1.037	1.930
O2	0.389	0.271	0.959	1.889
O3	0.266	0.433	0.957	
O3'		0.320		1.976
O5	0.417	0.431		
O5'		0.387		1.235
Σ	2.020	2.156	3.910	0.242

† according to Brown & Altermatt (1985), and expressed in valence units.
' indicates the longer *M*3–(O3,O5) bond length. "OH-norbergite" refers to the hypothetical OH end-member.

Electron-microprobe analyses carried out on the refined crystals yielded F contents slightly lower than those obtained by structure refinement (1.53 *versus* 1.72 *apfu*). This could be due to analytical problems with EMP determination of fluorine concentrations. During the analyses, special care was taken to identify possible interference with Fe or Cr, for peaks and background. Owing to the high fluorine content of the studied samples (up to 14 wt%), a natural standard with a silicate matrix and comparable fluorine content could not be found; therefore matrix effects are possible and difficult to evaluate.

In a study on the synthesis of humite-group minerals, Duffy & Greenwood (1979) obtained by least-squares regression a number of equations relating unit-cell parameters and unit-cell volume to the F/(OH + F). However, they used the proportion of these anions in the reagent mixture to calibrate the F/(OH + F) ratio of the mineral products. The most sensitive and reliable of these equations is that concerning the *c* dimension, which is reasonable since the brucite bands alternate in the **b** direction, but there is also an alternation in the **c** direction. Calculation of F/(OH + F) as a function of *c* give = 0.74 *apfu*. This is slightly lower than the mole fraction (0.85) obtained by single-crystal structure refinement, but is nearly the same as found by EMP (Table 4). As noted earlier, EMP analyses may be affected by analytical problems at high F contents; however, site scattering of F may be affected by erroneous assumptions in the refined model, and the calculation according to Duffy & Greenwood (1979) may be hampered by the lack of analytical data on their products. This discrepancy can only be overcome by an independent estimate. A SIMS analysis for the independent evaluation of H and F in this matrix is in progress, but it requires accurate calibration curves for such an uncommon matrix.

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