

SHORT COMMUNICATIONS

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Crystal structure refinement of Mg- and Zn-rich sonolite from Franklin and Sterling Hill, New Jersey

In a study on manganese humites and leucophoenicites from Franklin and Sterling Hill, New Jersey, Dunn (1985) noted that numerous sonolite chemical analyses showed three clusters, apparently due to limitations in the Mg and Zn contents. The first chemical cluster is almost end-member sonolite, $Mn_9(SiO_4)_4(OH)_2$, with some substitution of Zn (c. 3 wt.% ZnO); the second chemical cluster has approximately the same amount of ZnO and a significant amount of Mg (c. 7 wt.% MgO); the third chemical cluster has major amounts of both Mg and Zn (c. 16 wt.% MgO and c. 10 wt.% ZnO). In order to determine the crystal-chemical role of Mg and Zn in sonolite, samples of the second and third clusters were chosen for crystal-structure analyses. Chemical analyses of the crystals used in the structure analysis, ignoring minor amounts of CaO, yield the following empirical formulae calculated on the basis of Si = 4 for Z = 2: $(Mn_{7.04}Mg_{1.83}Zn_{0.44}Fe_{0.05})_{\Sigma 9.36}[SiO_4]_4(OH_{1.56}F_{0.46})$ for sample NMNH#143755 from Sterling Hill and $(Mn_{4.71}Mg_{3.39}Zn_{1.15}Fe_{0.15})_{\Sigma 9.40}[SiO_4]_4(OH_{1.20}F_{0.78})$ for sample NMNH#12965 from Franklin or Sterling Hill. It was not necessary to refine the sonolite structure for a sample from the first chemical cluster as it would replicate the structure determination of Kato *et al.* (1989).

Details of the intensity data collection are given in Table 1. Intensity measurements on each spherical crystal were made on a fully automated, Nicolet R3m four-circle diffractometer

operated at 50 kV and 35 mA with graphite-monochromated Mo- $K\alpha$ radiation. A set of 25 reflections was used to orient each crystal and refine the cell parameters (Table 1). Unique sets of intensity data up to $2\theta = 60^\circ$ were collected. Reduction of the intensity data and refinement of the structure were done by the SHELXTL package of programs (Sheldrick, 1990). Data reduction included background, scaling, Lorentz and polarization and absorption corrections using 11 ψ -diffraction-vector scans after the method of North *et al.* (1968). Scattering curves for neutral atoms

TABLE 1. Crystal data for sonolite structures.

Sample No.	143755	129965
Space Group	$P2_1/b$	$P2_1/b$
a Å	4.849 (1)	4.811 (1)
b Å	10.611 (2)	10.544 (2)
c Å	14.162 (3)	14.022 (2)
α°	100.61 (3)	100.77 (1)
V (Å ³)	716.2 (2)	698.8 (2)
Z	2	2
$D_{(calc)}$ g/cm ³	4.03	3.89
Crystal diam. (mm)	0.20	0.15
μ (Mo- $K\alpha$) (mm ⁻¹)	7.24	6.56
Total no. $ F_o $	2100	2053
No. $ F_o > 4\sigma$ (obs)	1685	1832
Final R (obs) (%)	3.4	4.9
Final wR (obs) (%)	3.7	4.8

TABLE 2. Atomic coordinates, equivalent isotropic temperature factors ($\text{\AA} \times 10^2$) and occupancy factors for sonolite samples.

Site*	x	y	z	K	Ueq
M(1) _C	$\frac{1}{2}$	0	$\frac{1}{2}$	0.433(2)	0.87(3)
	$\frac{1}{2}$	0	$\frac{1}{2}$	0.407(3)	0.73(4)
M(1) _N	0.4962(2)	0.9478(1)	0.2730(1)	0.930(4)	0.94(2)
	0.4988(2)	0.9466(1)	0.2722(1)	0.865(5)	0.78(3)
M(2) _s	0.0094(2)	0.1398(1)	0.1711(1)	0.963(4)	0.88(2)
	0.0099(2)	0.1392(1)	0.1696(1)	0.891(5)	0.67(2)
M(2) ₆	0.5129(2)	0.2537(1)	0.3878(1)	0.982(5)	0.77(2)
	0.5151(2)	0.2523(1)	0.3876(1)	0.950(5)	0.65(2)
M(3)	0.4860(2)	0.8738(1)	0.0410(1)	0.749(4)	1.02(3)
	0.4899(3)	0.8760(1)	0.0412(1)	0.605(5)	0.92(4)
Si(1)	0.0734(3)	0.0677(1)	0.3897(1)	1	0.69(3)
	0.0767(3)	0.0651(1)	0.3890(1)	1	0.57(3)
Si(2)	0.0771(3)	0.1748(1)	0.8366(1)	1	0.72(3)
	0.0756(3)	0.1758(1)	0.8382(1)	1	0.58(3)
O(1,1)	0.7403(7)	0.0655(3)	0.3886(2)	1	1.02(9)
	0.7427(8)	0.0612(4)	0.3873(3)	1	1.1 (1)
O(1,2)	0.2839(7)	0.4260(3)	0.3877(2)	1	0.90(8)
	0.2759(8)	0.4232(3)	0.3877(3)	1	0.75(9)
O(1,3)	0.2144(7)	0.1148(3)	0.2970(2)	1	0.98(8)
	0.2156(8)	0.1112(4)	0.2949(3)	1	1.0(1)
O(1,4)	0.2150(7)	0.1564(3)	0.4837(2)	1	1.02(8)
	0.2176(8)	0.1549(4)	0.4836(3)	1	0.96(9)
O(2,1)	0.2441(7)	0.3245(3)	0.1611(2)	1	1.03(9)
	0.2383(8)	0.3253(3)	0.1597(2)	1	0.69(9)
O(2,2)	0.7820(7)	0.9654(3)	0.1615(2)	1	1.00(8)
	0.7762(8)	0.9657(3)	0.1607(3)	1	0.79(9)
O(2,3)	0.7139(7)	0.2808(3)	0.2578(2)	1	1.00(8)
	0.7176(8)	0.2809(3)	0.2570(2)	1	0.78(9)
O(2,4)	0.7199(7)	0.2316(3)	0.0713(2)	1	0.98(8)
	0.7213(8)	0.2305(3)	0.0684(2)	1	0.74(9)
(OH,F)	0.2604(8)	0.0444(3)	0.0532(3)	1	1.67(9)
	0.2619(8)	0.0425(3)	0.0511(2)	1	0.64(9)

* sample 143755 listed above sample 12965

from Cromer and Mann (1968) and anomalous dispersion coefficients from Cromer and Liberman (1970) were used in conjunction with the weighting scheme $w = [\delta^2(F_o)]^{-1}$. For the structure refinements the initial set of atomic positions are those determined for the Mn end-membered-sonolite of Kato *et al.* (1989). The nomenclature of the atomic positions is that used by Ribbe (1982) in his review of the crystal chemistry for the humite group. The final atomic positions and isotropic thermal parameters are given in Table 2. Anisotropic temperature factors, bond lengths and a listing of observed and calculated structure factors are given in an Appendix*.

The crystal structure of sonolite is described in detail by Kato *et al.* (1989) and our refinements are consistent with their results. The split H position in their structure was not detected in either of the sonolite samples reported here, probably due to the significant replacement of F for OH. The occupancy factors listed in Table 3 are based on the refinement of the Mn scattering curve in each of the octahedral sites [$M(1)_C$, $M(1)_N$, $M(2)_s$, $M(2)_6$ and $M(3)$]. For the Mg-rich, Zn-poor sample (#143755) it is evident that the majority of the Mg goes into the smallest octahedral site $M(3)$. Refining the Mg/Mn ratio in the $M(3)$ site yielded 1.72(3) Mg atoms of the

* Available on request from the editor

TABLE 3. Octahedral site occupancies and mean M-O distances for sonolite samples.

Site	Sample # 143755				Sample # 12965			
	Mn	Mg	Zn	<M-O>	Mn	Mg	Zn	<M-O>
M(1) _C	0.55	0.31	0.14	2.173(3)	0.26	0.46	0.28	2.144(4)
M(1) _N	0.74	0.17	0.09	2.193(3)	0.38	0.36	0.26	2.157(4)
M(2) ₅	0.95	0.07	-0.01	2.214(3)	0.84	0.20	-0.03	2.201(4)
M(2) ₆	1.03	0.02	-0.05	2.222(3)	1.02	0.06	-0.08	2.220(4)
M(3)	0.34	0.53	0.13	2.150(3)	-0.05	0.84	0.21	2.109(4)
Σ _{calc}	6.67	1.89	0.46		4.64	3.38	1.00	
Σ _{chem}	7.04	1.83	0.44		4.71	3.39	1.15	

total 2.60 indicated in the chemical analysis. The remainder being disordered over the other M^{2+} sites. Similarly for the Mg- and Zn-rich sample (#12965), Mg is concentrated at the $M(3)$ site. In this sample Mg is actually dominant as the site with a refined Mg/Mn occupancy of 2.96(2) atoms of Mg and 1.04(2) atoms of Mn. Remembering these refinements are based on scattering power it should be realized that the Mg content might be higher if some of the site is actually occupied by Zn. For both samples the number of electrons calculated from the chemical analysis agrees very well with those determined from the crystal structure for the 9 atoms possible in the M site refinements: sample #143755, 204 e^- from chemical composition vs. 203(1) e^- from structure and sample #12965, 188 e^- from chemical composition vs. 186(1) e^- from structure. The excellent agreement between the two sets of experimental results establishes confidence in the results.

The role of Zn in the sonolite structure is less evident. It has an ionic radius similar to that of Mg^{2+} but it has an atomic number of 30 which is considerably higher than that of Mg (12) and somewhat higher than that of Mn (25). In the Zn-rich sample (#12965) there is no obvious octahedral site with an occupancy factor significantly higher than the others (Table 2). In order to obtain useful information about the ordering of Zn in the sonolite structure a set of linear equations with three unknowns was derived. The first equation given below is the trivial relationship for which the site populations of each atomic site totals 1; the second equation relates the ionic radii of the site populations to the mean bond length for the octahedron; and the third equation relates the site populations mean atomic number to the scattering power (number of electrons determined by the least squares structure refinement). The

cationic radii in equation (2) are those of Shannon (1976) and the anionic radius of O^{2-} (1.39 Å) is that derived empirically for these two crystal structure refinements so that no large negative site populations appeared in the solutions of the linear equations:

$$x^{Mn} + x^{Mg} + x^{Zn} = 1 \quad (1)$$

$$(x^{Mn} \times 0.830) + (x^{Mg} \times 0.720) + (x^{Zn} \times 0.740) = <M-O> - 1.39 \quad (2)$$

$$(x^{Mn} \times 25) + (x^{Mg} \times 12) + (x^{Zn} \times 30) = K \times 25 \quad (3)$$

Table 3 lists the mean bond lengths and the calculated site populations for each of the five octahedral sites in the two crystal structure refinements. Table 3 also includes a comparison of the total number of cations derived by electron microprobe analysis vs. the total number of cations derived from the solution of the linear equations.

It is evident that the measured and calculated number of cations agree quite well, thus giving us information on the portioning of Mg and Zn in the sonolite structure. Mg shows a preference for the $M(3)$ and $M(1)_C$ sites. This is consistent with the findings of: Kato *et al.* (1989) who determined there was minor Mg in the $M(3)$ site for their crystal; Francis (1985) who determined there was Mg dominant in $M(3)$ and lesser Mg in $M(1)$ for structure-related magnesian alleghanyite; and Francis and Ribbe (1978) who determined there was Mg dominant in $M(3)$ and lesser Mg in $M(1)$ in structure-related magnesian manganhumite. Sample NMNS#12965 can be considered a magnesian sonolite with Mg dominant in the $M(3)$ site. Zinc shows a preference for sites $M(1)_C$, $M(1)_N$ and $M(3)$ in almost equal proportions. It would be expected that a sample would have to contain almost twice as much Zn as sample

NMNS#12965 before an atomic site became dominant in Zn (i.e. c. 20 wt.% ZnO). The distribution of Zn in these sonolite samples could not have been determined without the linear equation solutions.

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Lead oxychlorides at Elura, western NSW, Australia

SEVERAL different Pb oxychloride minerals are known to form under saline conditions, the most common being laurionite [Pb(OH)Cl] and mendipite [Pb₃O₂Cl₂]. Several others, penfieldite

[Pb₂Cl₃(OH)] and fiedlerite [Pb₃Cl₄(OH)₂] are known mainly as marine corrosion products of ancient Pb objects or slags (Edwards *et al.*, 1992). The rare minerals, blixite [Pb₂Cl(O,OH)_{2-x} where