

## Poldervaartite, $\text{Ca}(\text{Ca}_{0.5}\text{Mn}_{0.5})(\text{SiO}_3\text{OH})(\text{OH})$ , a new acid nesosilicate from the Kalahari manganese field, South Africa: Crystal structure and description

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### ABSTRACT

Poldervaartite,  $\text{Ca}(\text{Ca}_{0.5}\text{Mn}_{0.5})(\text{SiO}_3\text{OH})(\text{OH})$ , space group *Pbca*,  $a = 9.398(1)$ ,  $b = 9.139(2)$ ,  $c = 10.535(2)$  Å,  $V = 904.8(3)$  Å<sup>3</sup>, is a new mineral from the Wessels mine in the Kalahari manganese field of northwest Kuruman Hill, Republic of South Africa. It occurs as wheat-sheaf polycrystals to euhedral crystals associated with bultfonteinite, braunite, hausmannite, henritermierite, calcite, and hematite. Poldervaartite is colorless to milky white, has a density of 2.91(2) g/cm<sup>3</sup> and a hardness (Mohs) of 5. Optically it is biaxial (+) with  $\alpha = 1.634(2)$ ,  $\beta = 1.640(4)$ , and  $\gamma = 1.656(2)$ , and with pleochroic color:  $\eta_\gamma$  = bluish gray,  $\eta_\beta$  = light gray, and  $\eta_\alpha$  = colorless. The five strongest powder diffraction lines are [ $d_i(hkl)$ ] 3.231<sub>x</sub>(122), 4.18<sub>s</sub>(210), 2.846<sub>d</sub>(311), 2.391<sub>d</sub>(223), and 2.789<sub>d</sub>(131) Å.

The structure was solved by direct methods and refined to  $R = 0.024$  using X-ray diffractometer data (1028 independent reflections). The structure is a hydroxyl nesosilicate with a single isolated Si tetrahedron and two  $\text{M}^{2+}$  sites. Ca is accommodated in M1, and both Ca and Mn share M2. OH groups are strongly bonded in the structure, preventing H<sub>2</sub>O loss at temperatures below 460 °C. One OH group is bound to Si, making poldervaartite an acid silicate. The SiO<sub>3</sub>OH tetrahedron is externally regular but internally distorted. Poldervaartite is probably isostructural with dicalcium silicate  $\alpha$  hydrate, a common phase in steam-cured Portland cement.

### INTRODUCTION

Poldervaartite, ideally  $\text{Ca}(\text{Ca}_{0.5}\text{Mn}_{0.5})(\text{SiO}_3\text{OH})(\text{OH})$ , occurs in the Wessels mine of the famous Kalahari manganese field in northwest Cape Province, South Africa (Wilson and Dunn, 1978; Von Bezing et al., 1991). We take great pleasure in naming this new mineral in honor of Arie Poldervaart (1918–1964), professor of petrology at Columbia University, who made great contributions to understanding the South African Karoo dolerites and Archean rocks in the Kakamas area of northwest Cape Province. The new mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA. Type material is preserved in the American Museum of Natural History under catalogue number T100728.

### DESCRIPTION

#### Occurrence and paragenesis

Poldervaartite was found in a pocket at the Wessels mine in the Kalahari manganese field of northwest Ku-

ruman Hill, northwest Cape Province, Republic of South Africa (Von Bezing et al., 1991). The pocket occurred in massive braunite and hausmannite, in which poldervaartite is intimately associated with henritermierite and calcite and is coated by bultfonteinite and hematite. The observed mineral assemblage suggests that the minerals were formed by modification of low-grade Mn-rich meta-sediments by hydrothermal fluids rich in Ca, SiO<sub>2</sub>, and CO<sub>2</sub>.

#### Mineral data

Poldervaartite crystals have colorless and transparent cores and milky white and translucent rims and have a distinct deep red fluorescent color under short-wavelength ultraviolet radiation. However, electron microprobe analyses do not show any compositional variation correlated with the aforementioned zonation. Luster is vitreous on fractured surfaces and subvitreous on crystal faces. Other physical and optical data for poldervaartite are presented in Table 1.

#### Chemical composition

Chemical analysis was performed on an ARL SEMQ mine-spectrometer electron microprobe, and data were

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**TABLE 1.** Physical and optical properties of poldervaartite

Habit:	wheat-sheaf to euhedral prismatic
Forms:	{110}, {100}, {010}, {001}
Hardness:	5 (Mohs scale)
Tenacity:	very brittle
Density:	
Measured:	2.91(2) g/cm <sup>3</sup> (Berman balance, toluene at 25 °C)
Calculated:	2.90 g/cm <sup>3</sup>
Optics:	biaxial positive
2V:	65 (± 5) <sup>o</sup> (meas), 63 <sup>o</sup> (calc)
α = 1.634(2)	X = b
β = 1.640(4)	Y = a
γ = 1.656(2)	Z = c
Dispersion:	weak; r < ν
Pleochroism:	weak
η <sub>γ</sub> :	bluish gray
η <sub>β</sub> :	light gray
η <sub>α</sub> :	colorless

corrected for ZAF effects using Magic-IV (Colby, 1968). H<sub>2</sub>O content was determined using a DuPont 951 ThermoGravimetric Analyzer (TGA), and, up to 1000 °C, H<sub>2</sub>O was the only component recorded by the attached VG Micromass 300D mass spectrometer. TGA showed no observable H<sub>2</sub>O loss at temperatures lower than 460 °C, indicating strong bonding of the H<sub>2</sub>O components and high thermal stability of the hydrated phase. The analyses yield a general formula of (Ca<sub>2-x</sub>Mn<sub>x</sub>)SiO<sub>4</sub> · H<sub>2</sub>O, with x values ranging from 0.28 to 0.52. Results in weight percent (range in parentheses) for a relatively homogeneous grain are SiO<sub>2</sub> 29.8 (28.1–28.9); CaO 41.5 (40.7–41.9); MnO 18.7 (17.9–19.8); FeO 0.1 (0.0–0.1); MgO 0.0 (0.0–0.1); and H<sub>2</sub>O 9.4 (average of TGA), with the average formula being Ca<sub>1.47</sub>Mn<sub>0.53</sub>Si<sub>0.99</sub>O<sub>3.96</sub> · 1.04H<sub>2</sub>O. The composition of the crystal used in the structure determination was estimated by site refinement (see below); mounting the crystal for probe analysis was not practical.

The Gladstone-Dale relationship for optical and compositional data yields a superior compatibility index. (Mandarino, 1981).

#### X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE DETERMINATION

The space group of poldervaartite was established from both overexposed precession photographs and three-dimensional structure data from a crystal measuring 0.07 × 0.07 × 0.10 mm. X-ray powder diffraction data from an automated Philips PW1710 diffractometer (graphite-monochromatized CuKα radiation) are given in Table 2. Indexing of the powder diffractions is conformable with the single-crystal diffraction intensity data. The least-squares refined unit-cell parameters are a = 9.398(1), b = 9.139(2), c = 10.535(2) Å, and V = 904.8(3) Å<sup>3</sup> (Z = 8), with axes defined to conform with space group *Pbca*.

X-ray intensity data from a quadrant of reciprocal space were measured on a Kriese-automated Picker FACS-I four-circle diffractometer utilizing Zr-filtered MoKα radiation. Details of the data measurement and reduction are given in Table 3. Absorption corrections employed an empirical ψ scan technique, utilizing intensity data obtained from ±180° ψ scans at 10° intervals for one reflection (006). Symmetry equivalent reflections were averaged, and only the reflections with F<sub>o</sub> > 3σ<sub>F</sub> were used in the structure determination and refinement.

Crystallographic calculations were undertaken using an XTAL3.0 package [both UNIX and PC versions (Hall and Stewart, 1990; Grossie, 1991)]. Interpolated form factors of neutral atoms, including terms for anomalous dispersion (Davenport and Hall, 1990); were used in all calculations, and all reflections were weighted equally in the least-squares refinements. Direct methods were used

**TABLE 2.** X-ray powder diffraction data for poldervaartite

hkl	d <sub>meas</sub> (Å)	d <sub>calc</sub> (Å)	hkl	d <sub>meas</sub> (Å)	d <sub>calc</sub> (Å)	hkl	
11	5.24	5.27	002	10	2.229	2.233	041
45	4.18	4.18	210	13	2.215	2.217	124
11	4.09	4.11	112	11	2.137	2.139	331
18	3.87	3.88	211	13	2.091	2.096	042
11	3.82	3.83	121	13	2.085	2.089	420
24	3.50	3.51	202	15	2.063	2.067	233
11	3.44	3.45	022	28	2.042	2.046	142
26	3.27	3.28, 3.27	220, 212	9	2.019	2.017, 2.017	332, 241
100	3.231	3.240	122	12	1.939	1.942	422
14	3.091	3.095	113	20	1.911	1.914, 1.910	242, 413
42	2.846	2.853	311	12	1.871	1.875	125
35	2.789	2.794, 2.784	131, 023	12	1.829	1.834, 1.832	234, 431
16	2.685	2.688, 2.692	213, 302	20	1.770	1.773, 1.772	243, 225
17	2.665	2.67	123	11	1.748	1.753	404
26	2.624	2.634	004	12	1.723	1.722	414
26	2.576	2.583	312	14	1.713	1.717	315
23	2.554	2.556	230	20	1.696	1.697	144
12	2.531	2.536	104	14	1.647	1.644	433
25	2.504	2.509	321	21	1.634	1.633	325
11	2.478	2.484	231	12	1.613	1.620	244
11	2.436	2.444	114	20	1.559	1.564	442
42	2.391	2.395	223	13	1.522	1.520	434
12	2.296	2.297	204	13	1.481	1.484, 1.484	425, 443
13	2.276	2.282, 2.276	024, 410	13	1.467	1.471	245

Note: scan rate = 0.6 °/min, step size = 0.01°, and Si as internal standard.

TABLE 3. Experimental details for poldervaartite

2θ limit:	1–60
Scan type:	θ/2θ
Scan width (2θ°):	2.0° + 0.70 tan θ
Scan duration:	≤180 s
Intensity standards:	3 per 5 h
Total reflections:	3052
Unique reflections:	1330
$R_{\text{merge}}$	0.02
No. data ( $F_o > 3\sigma_f$ ):	1028
$R$	0.024
$R_w$	0.026
Residual on difference maps (max e/Å <sup>3</sup> ):	
(+)	0.7
(-)	0.7

for phase determination, and a relative scale factor for the structure factor and an overall displacement factor were calculated, based on Wilson statistics.

All atoms reside in the general positions, including two divalent cations ( $M1$ ,  $M2$ ), one Si, five O, and two H atoms. On the basis of residual peaks at M sites in difference maps and the results of refinements with different Mn occupancies (vs. Ca occupancies) for M sites, Mn was determined to reside only at M2. The refined occupancy, constrained to unity sum, of the M2 site is 0.67(1) Ca and 0.33 Mn and, thus, defines the chemical formula of this crystal: Ca<sub>1.67</sub>Mn<sub>0.33</sub>(SiO<sub>3</sub>OH)(OH). Two H atoms were located from difference-Fourier maps. All positional parameters, a single scale factor, a secondary extinction factor, and anisotropic displacement factors of all atoms except for isotropic H sites were varied in the final cycle of refinement. Selected parameters of the final cycle of refinement are recorded in Table 3. Table 4 contains final positional and displacement parameters, Table 5 gives the selected interatomic distances and angles, and Table 6<sup>1</sup> contains a list of the observed and calculated structure factors.

<sup>1</sup> A copy of Table 6 may be ordered as Document AM-93-537 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 4. Positional and displacement parameters of poldervaartite

	x	y	z	$U_{\text{eq}}^*$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
M1	0.15406(5)	0.49326(6)	0.39021(5)	0.0091(1)	0.0090(2)	0.0101(2)	0.0084(2)	-0.0004(2)	0.0007(2)	0.0003(2)
M2	0.51266(5)	0.33390(5)	0.43048(5)	0.0101(1)	0.0101(2)	0.0104(2)	0.0098(2)	-0.0022(2)	-0.0003(2)	-0.0004(2)
Si	0.32973(8)	0.21515(7)	0.65939(7)	0.0073(2)	0.0076(3)	0.0075(3)	0.0069(3)	0.0002(2)	-0.0002(2)	-0.0004(2)
O1	0.2518(3)	0.3502(2)	0.5735(2)	0.0175(5)	0.028(1)	0.0104(8)	0.0140(9)	0.0046(8)	-0.0084(9)	-0.0005(8)
O2	-0.0559(2)	0.3590(2)	0.4368(2)	0.0118(5)	0.0092(8)	0.0145(9)	0.0117(8)	-0.0019(7)	-0.0002(7)	-0.0042(7)
O3	0.1020(2)	0.7101(2)	0.2829(2)	0.0127(5)	0.0160(9)	0.0134(9)	0.0087(8)	0.0022(7)	0.0045(7)	0.0043(7)
O4	0.3965(2)	0.5492(2)	0.3980(2)	0.0158(5)	0.0118(9)	0.019(1)	0.016(1)	-0.0012(8)	-0.0002(8)	0.0063(8)
O5	0.2019(2)	0.3986(2)	0.1893(2)	0.0140(5)	0.0146(9)	0.0145(9)	0.0129(9)	0.0044(7)	0.0018(7)	-0.0016(7)
H1	0.257(5)	0.074(5)	0.117(4)	0.03(1)						
H2	-0.084(5)	0.588(5)	0.173(4)	0.03(1)						

\*  $U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3$ .

TABLE 5. Selected bond lengths (Å) and O-Si-O angles (°) of poldervaartite

M1 <sup>a</sup> -O1 <sup>a</sup>	2.506(2)	M2 <sup>a</sup> -O1 <sup>c</sup>	2.807(2)
-O2 <sup>a</sup>	2.374(2)	-O1 <sup>a</sup>	2.881(2)
-O3 <sup>a</sup>	2.333(2)	-O2 <sup>c</sup>	2.340(2)
-O4 <sup>a</sup>	2.336(2)	-O3 <sup>f</sup>	2.204(2)
-O5 <sup>a</sup>	2.330(2)	-O4 <sup>d</sup>	2.265(2)
-O2 <sup>b</sup>	2.447(2)	-O4 <sup>a</sup>	2.275(2)
		-O5 <sup>e</sup>	2.259(2)
Si <sup>a</sup> -O1 <sup>a</sup>	1.696(2)	O1 <sup>a</sup> -Si <sup>a</sup> -O3 <sup>g</sup>	107.2(1)
-O3 <sup>g</sup>	1.603(2)	O1 <sup>a</sup> -Si <sup>a</sup> -O2 <sup>c</sup>	104.8(1)
-O2 <sup>c</sup>	1.625(2)	O1 <sup>a</sup> -Si <sup>a</sup> -O5 <sup>h</sup>	104.5(1)
-O5 <sup>h</sup>	1.619(2)	O3 <sup>g</sup> -Si <sup>a</sup> -O2 <sup>c</sup>	114.8(1)
Mean	1.636	O3 <sup>g</sup> -Si <sup>a</sup> -O5 <sup>h</sup>	114.4(1)
$\sigma$	0.04	O2 <sup>c</sup> -Si <sup>a</sup> -O5 <sup>h</sup>	110.1(1)
H1 <sup>h</sup> -O1 <sup>a</sup>	0.84(4)	H1 <sup>h</sup> ...O5 <sup>g</sup>	1.81(4)
H2 <sup>a</sup> -O4 <sup>a</sup>	0.84(4)	H2 <sup>a</sup> ...O3 <sup>a</sup>	2.38(4)

\* The superscripts denote the symmetry and translation operations applied: a = x, y, z (as listed in Table 4); b = -x, 1 - y, 1 - z; c = 1/2 + x, 1/2 - y, 1 - z; d = 1 - x, 1 - y, 1 - z; e = 1/2 + x, y, 1/2 - z; f = 1/2 - x, y - 1/2, z; g = 1/2 - x, 1 - y, 1/2 + z; h = x, 1/2 - y, 1/2 + z.

## DISCUSSION OF THE STRUCTURE

### Structure description

The poldervaartite structure contains three distinct cation polyhedra (Fig. 1). The M1 site is coordinated by four O atoms and two OH groups in a cis-relationship to form a slightly distorted octahedron. The M2 site coordination resembles a very distorted trigonal dipyramid with two additional distant O1 atoms capping the opposing trigonal faces. M2 is thus fivefold- (or sevenfold-) coordinated to two (or four) OH groups and three O<sup>2-</sup> ions. The Si atom is fourfold-coordinated to three O atoms and one OH group at O1, forming an acid unit of [SiO<sub>3</sub>OH]<sup>3-</sup>, which is an uncommon feature of nesosilicates. The structure can be described as a stacking of alternating poorly defined polyhedral layers parallel to (010). One layer contains M2 + Si polyhedra at  $y \sim 1/4$  and  $3/4$ , and the other contains M1 octahedra at  $y \sim 0$  and  $1/2$ . Figure 2a shows the layer at  $y \sim 1/4$ , in which each M2 polyhedron shares opposite edges with adjacent edges of the Si tetrahedra, forming a chain along [100]. The chains are corner linked (O3) between Si and M2 polyhedra to form a sheet. In the other layer (Fig. 2b), edge-sharing pairs of M1 octahedra are interconnected by H bonds. The Si-M2 layers are coupled through the M1 layer: two octahedral

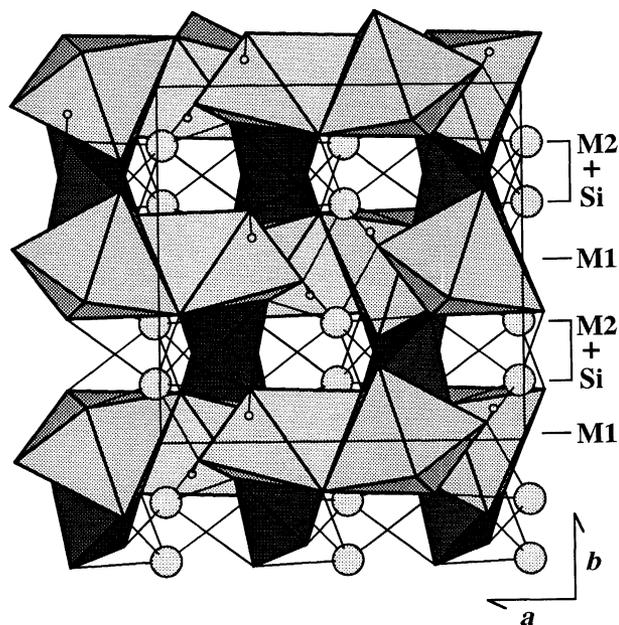


Fig. 1. The poldervaartite structure projected onto the (001) plane with cell boundary shown. Shaded polyhedra are used for Si tetrahedra (dark), and Ca M1 octahedra (light), and shaded spheres are used for M2 (large) and H (small) atoms. Bonds from O atoms to H and M2 atoms are shown as solid lines.

corners (on one M1 edge) are linked to Si tetrahedra in opposing layers, and two octahedral edges are shared with an M2 polyhedron in one layer and one octahedral edge with an M2 polyhedron in the opposite layer. In addition, each M2 polyhedron shares an OH-OH edge with another M2 polyhedron through the intervening M1 layer. The result is a strongly bonded polyhedral network, which accounts for the lack of cleavage in poldervaartite.

#### Bonding of H

A bond valence calculation (less H, Table 7; constants from Brese and O'Keeffe, 1991) shows that O1 and O4 are substantially under-bonded, consistent with the assignment of adjacent H atoms. However, as is typical with X-ray diffraction results, the observed O-H bond lengths (Table 5) in poldervaartite are short, probably unrealistically, compared with the O-H bond length ( $\sim 0.95$  Å) observed for OH groups by neutron diffraction. Thus, calculated bond valences for O-H are high ( $\sim 1.35$  vu) and not meaningful for Table 7. The H bonding in the structure,  $\text{H1} \cdots \text{O5}$  and  $\text{H2} \cdots \text{O3}$ , may satisfy the minor undersaturation of bonding to these O atoms (Table 7). The fact that H is completely bonded as OH groups in the polyhedral network of poldervaartite explains the lack of  $\text{H}_2\text{O}$  loss at temperatures below  $460^\circ\text{C}$ .

#### Tetrahedral distortion and acid silicate character

The acid character of the Si tetrahedron in poldervaartite creates interesting bonding asymmetry, which is otherwise uncommon in nesosilicates. Internal distortions

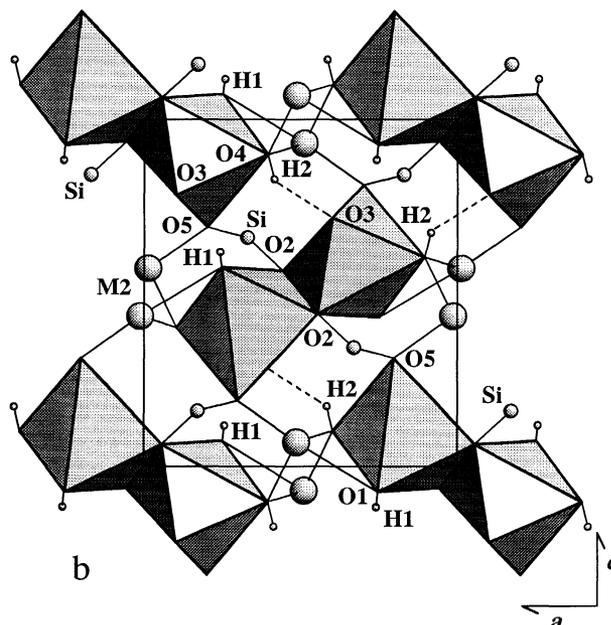
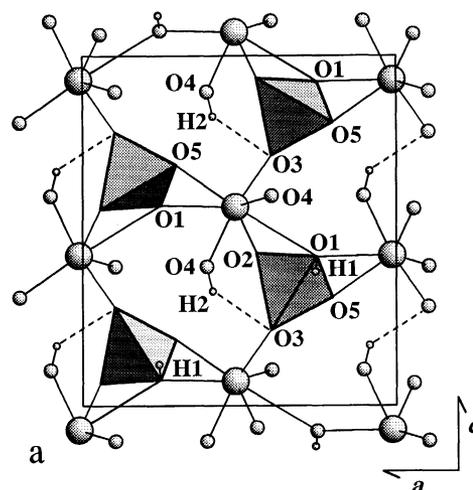


Fig. 2. Two polyhedral layers parallel to (010) are projected onto the (010) plane with cation-ligand bonds indicated by solid lines (dashed lines represent H bonds). (a) Layer with M2 cations (large spheres) and Si (shaded) tetrahedra at  $y \sim 1/4$ . O atoms bonded to M2 (but not to Si) are shown as intermediate-sized spheres and H atoms as small spheres. (b) Layer of M1 (shaded) octahedra at  $y \sim 1/2$  showing ligands to adjacent M2 (large spheres) and Si (intermediate-sized spheres).

are characterized by the short Si-O distances (av. =  $1.616$  Å) and the long Si-OH distance ( $1.696$  Å); however, the overall average Si-O distance of  $1.636$  Å is not unusual for a nesosilicate (Smyth and Bish, 1988). The three OH-Si-O angles (av. =  $105.5^\circ$ ) are significantly smaller than the O-Si-O angles (av. =  $113.1^\circ$ ), manifesting the accommodation of the long Si-OH distance by an internal displacement of Si but an externally regular tetrahedron. The parameter  $s_{00}$  for the external geometric distortion of a

TABLE 7. Bond valences in poldervaartite

	O1	O2	O3	O4	O5	Total
M1	0.23	0.33	0.37	0.37	0.38	1.95
M2*	0.07	0.32	0.46	0.39	0.39	2.10
	0.09			0.38		
Si	0.82	1.00	1.06	—	1.01	3.89
Total	1.21	1.92	1.89	1.14	1.78	

Note: measurements are in valence units.

\* The bond valence for the M2 site is calculated based on the occupancies of 67% Ca and 33% Mn at the M2 site from the structure data.

polyhedron has been defined by Horiuchi and Sawamoto (1981) as  $s_{oo} = [\sum(x_i/x - 1)^2/(n - 1)] \cdot 10^4$  where  $x_i$  is the length of the  $i$ th O-O edge and  $x$  is the mean value of  $n$  (O-O) edge lengths. A larger value of  $s_{oo}$  implies a greater distortion of the polyhedron.

A comparison of distortion parameters of Si tetrahedra in several structures is given in Table 8. The value of  $s_{oo}$  of the SiO<sub>3</sub>OH tetrahedron in poldervaartite is small, representing little external distortion, but the variance in bond lengths and angles indicates, as discussed above, considerable internal distortion from regular tetrahedral coordination. The tetrahedral geometry in poldervaartite is comparable to that in awillite, another acid silicate, Ca<sub>3</sub>(SiO<sub>3</sub>OH)<sub>2</sub>·2H<sub>2</sub>O (Malik and Jeffery, 1976), and in the sorosilicate forms of olivine-like compositions formed at high pressure, β-Mg<sub>2</sub>SiO<sub>4</sub> (Horiuchi and Sawamoto, 1981) and β-Co<sub>2</sub>SiO<sub>4</sub> (Morimoto et al., 1974). The tetrahedral geometry in the olivine structures, on the other hand, is distinctly different, with much larger  $s_{oo}$  and bond angle variance and much smaller bond length variance. The data suggest that H<sup>+</sup> operates analogously to Si<sup>4+</sup> in the polymerization of silica tetrahedra; the repulsive force between Si<sup>4+</sup> and H<sup>+</sup> ions (or overbonding of O1) may displace Si from the center of the tetrahedron and reduce the effect of edge-sharing by other cations with lower field strength.

#### Relationship of poldervaartite to cement compounds

Reaction of calcium silicates to form calcium silicate hydrates and hydroxides occurs during consolidation of Portland cement (Liu et al., 1992; Taylor, 1990; Fujii and Kondo, 1974; Lea, 1970), but because of the poor crystallinity of many of the compounds so formed, the reaction mechanisms and compound structures are poorly known. Dicalcium silicate α hydrate [Ca<sub>2</sub>(SiO<sub>3</sub>OH)(OH): Heller, 1952], a common component in steam-cured cements, crystallizes in space group *Pbca*,  $a = 9.34$ ,  $b = 9.22$ ,  $c = 10.61$ ,  $Z = 8$ . The similarity in space group and cell parameters and the very similar powder diffraction patterns imply that poldervaartite and dicalcium α hydrate are possibly isostructural, despite Heller's different structure model. Thus dicalcium silicate α hydrate may represent the Ca end-member of poldervaartite, which makes it a good departure point for examining cement compounds.

TABLE 8. Tetrahedral distortion parameters for selected silicate structures

Phase	Site	Bond length variance (σ)	Bond angle variance (σ)	$s_{oo}$ *	References
Poldervaartite	Si	0.041	20.7	2.2	this work
Afwillite	Si1	0.034	13.7	2.5	1
	Si2	0.029	11.7	3.7	
β-Mg <sub>2</sub> SiO <sub>4</sub>	Si	0.034	14.7	3.1	2
β-Co <sub>2</sub> SiO <sub>4</sub>	Si	0.036	11.6	2.2	3
Forsterite	Si	0.017	49.5	14.9	4
Fayalite	Si	0.012	36.5	11.5	4
Tephroite	Si	0.016	36.2	10.6	4
Glaucochroite	Si	0.015	33.1	10.6	5

Note: references are as follows: 1 = Malik and Jeffery, 1976; 2 = Horiuchi and Sawamoto, 1981; 3 = Morimoto et al., 1974; 4 = Fujino et al., 1981; 5 = Lager and Meagher, 1978.

\* See text for definition of  $s_{oo}$ .

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