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The structure of malayaite, $CaSnOSiO_4$, a tin analog of titanite

JOHN B. HIGGINS AND PAUL H. RIBBE

Department of Geological Sciences
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Abstract

The crystal structure of malayaite, $CaSn_{0.95}Ti_{0.05}OSiO_4$ ($A2/a$; a = 7.149, b = 8.906, c = 6.667 A; β = 113.3°; Z = 4) has been refined to R = 0.047, using 872 non-equivalent reflections. Malayaite is topologically identical to $P2_1/a$ titanite ($CaTiOSiO_4$) and a number of rare arsenate and phosphate minerals, but it is truly isostructural only with the high-temperature (>220°C) form of chemically pure titanite. Kinked chains of vertex-sharing $[SnO_6]$ octahedra run parallel to a; these are bridged by $[SiO_4]$ tetrahedra in such a way as to form an $[SnOSiO_4]^{-2}$ framework with large cavities containing the Ca atoms in irregular 7-fold coordination.

The steric details of the malayaite structure are predictable in terms of classical Pauling principles. The mean bond lengths are Si–O = 1.641 A, Sn–O = 2.042 A, and Ca–O = 2.483 A.

Introduction

Malayaite, $CaSnOSiO_4$, is a rare tin silicate usually found in skarns. An excellent review of its occurrences and paragenesis was presented by Takenouchi (1971). He also demonstrated the existence of a high-temperature solid-solution between titanite and malayaite, and delineated an asymmetric solvus in the system which crests at 615 ± 15°C and a composition of $Ti_{0.75}Sn_{0.25}$. A preliminary report of the crystal structure of malayaite (Higgins and Ross, 1977) confirmed its isomorphism with $A2/a$ titanite and other 7 A vertex-sharing octahedral chain structures described by Higgins and Ribbe (in preparation). This paper describes the structure of malayaite, comparing it with titanite.

Experimental methods

A specimen of malayaite associated with wollastonite from Red-a-Ven Mine, Meldon, Devonshire, England, was supplied to us by Dr. Peter G. Embrey of the British Museum (Natural History). Conventional electron microprobe analysis gave a composition of $Ca_{0.98}Sn_{0.94}Ti_{0.05}OSi_{1.02}O_4$, which within analytical error is presumed to be stoichiometric $CaSn_{0.95}Ti_{0.05}OSiO_4$. Long-exposure precession photographs showed no diffuse streaks in $k + l$ odd positions (as sometimes observed in titanite) and confirmed the space group $A2/a$. Lattice parameters were determined both by powder diffractometry using a BaF_2 (a = 6.1971A) internal standard and by centering 15 reflections on a Picker four-circle diffractometer. They are recorded in Table 1 along with those reported by Takenouchi (1971). A least-squares refinement of Takenouchi's measured d spacings (from his Table 2) gave c = 6.688 A, rather than the value recorded twice in his paper (6.888 A) which we assume is a stenographic error.

Intensity data for 872 unique reflections were collected on a four-circle diffractometer using Nb-filtered Mo radiation. The data was corrected for Lorentz and polarization effects and for absorption (μ = 78.45 cm^{-1}). Starting parameters were modified from the $P2_1/a$ refinement of synthetic titanite by Speer and Gibbs (1976) to give atomic coordinates appropriate to the higher-symmetry $A2/a$ space-group of malayaite. Specifically, the pairs of oxygen atoms O2,O4 and O3,O5 are pseudo-A related in the Speer and Gibbs structure. These correspond to O2A,O2B and O3A,O3B respectively in Taylor and Brown's (1976) refinement of titanite. In malayaite, the O2 oxygen is equivalent to the O2,O4 or O2A,O2B pair and O3 is equivalent to the O3,O5 or O3A,O3B pair.

Conventional full-matrix least-squares refinement of the six atoms with anisotropic temperature factors

Table 1. Lattice parameters of malayaite and titanite

	a(Å)	*b*(Å)	*c*(Å)	β(°)
Malayaite - this study (powder diffractometer)	7.156(6)*	8.895(9)	6.668(4)	113.4(1)
Malayaite - this study (4-circle diffractometer)	7.149	8.906	6.667	113.3
Malayaite (Takenouchi, 1971)	7.173(9)	8.876(5)	6.688(8)**	113.7(1)
synthetic titanite (Speer and Gibbs, 1976)	7.069(2)	8.722(5)	6.566(8)	113.86(2)

* *Estimated standard deviation (in parentheses) refers to the last decimal place; e.s.d.'s not calculated for second data set.*

** *The value reported by Takenouchi (1971) is* 6.888 Å, *but this is in error (see text for explanation).*

produced an R-factor of 0.047. Atomic coordinates, anisotropic temperature factors and their isotropic equivalents are given in Table 2. The orientations of the thermal ellipsoids are listed in Table 3, and selected interatomic distances and angles appear in Table 4.

Discussion

The crystal structure of malayaite is discussed most significantly in the context of recent refinements of the crystal structure of titanite (Speer and Gibbs, 1976; Taylor and Brown, 1976). In titanite and malayaite $[MO_5]^\infty$ chains of vertex-sharing octahedra (M = Ti and Sn respectively) extend parallel to [100]. In Moore's (1970) topologic scheme, the octahedral chains and associated tetrahedra are Type I isomers with two tilted octahedra per unit repeat, sharing in common the O1 oxygen atom (Fig. 1). The O1–O1–O1 angle of 141° in titanite and 133° in malayaite is a measure of the kinking of the chains.

In chemically pure $P2_1/a$ titanite the small Ti atom is displaced from the center of the fairly regular $[TiO_6]$ octahedron so that alternate Ti–O1 bond lengths along the chain are 1.77 and 1.97 A. Two chains per unit cell are related by a center of symmetry. "These chains are cross-linked by silicate tetrahedra sharing the remaining four oxygens in such a way as to produce a $[TiOSiO_4]^{-2}$ framework with large cavities containing calcium atoms in irregular 7-coordination polyhedra" (Speer and Gibbs, p. 240, and their Fig. 3, p. 244. Also see Fig. 3, p. 440 in Taylor and Brown for a polyhedral drawing of the structure). Except for the fact that malayaite has Sn *centered* in the octahedron, its topology may be described in similar terms.

Domain formation in heated and chemically impure titanites

Discussions of domains in titanite have recently flooded the literature (Speer and Gibbs, 1976, p. 242-246; Taylor and Brown, 1976, p. 439-446; Higgins and Ribbe, 1976, p. 885-888); these are briefly summarized here in two categories.

1. Temperature dependence of the $P2_1/a \rightarrow A2/a$ *transformation.* The primitive structure of pure $CaTiOSiO_4$ is most simply characterized by the displacement of the Ti atom from the geometrical center of the $[TiO_6]$ octahedron and concomitant slight dis-

Table 2. Atomic parameters with standard deviations

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	0.25	0.9117(4)	0.75	0.0136(8)	0.0008(2)	0.0044(6)	-	-0.0015(5)	-
Sn	0.50	0.75	0.25	0.0021(1)	0.0014(1)	0.0037(1)	-0.0002(2)	0.0008(1)	-0.0001(2)
Si	0.75	0.9335(4)	0.75	0.0032(6)	0.0002(3)	0.0029(7)	-	0.0010(5)	-
O(1)	0.75	0.8367(8)	0.25	0.0028(10)	0.0009(6)	0.0075(15)	-	0.0025(10)	-
O(2)	0.9125(7)	0.8171(6)	0.9255(8)	0.0034(8)	0.0024(5)	0.0038(9)	0.0007(5)	0.0007(7)	0.0004(5)
O(3)	0.3724(8)	0.9614(6)	0.1414(8)	0.0039(8)	0.0018(4)	0.0046(9)	0.0010(5)	0.0026(7)	-0.0002(5)

Table 3. Magnitude and orientation of the principal axes of the thermal ellipsoids for malayaite

Atom, axis	rms displacement (Å)	Angle (°) with respect to: +a	+b	+c
Ca, r_1	0.058(7)	90	0	90
r_2	0.083(6)	102(2)	90	145(2)
r_3	0.203(6)	12(2)	90	125(2)
Sn, r_1	0.066(2)	35(2)	69(14)	85(4)
r_2	0.076(2)	70(8)	158(13)	92(15)
r_3	0.088(1)	117(12)	94(15)	5(8)
Si, r_1	0.030(20)	90	0	90
r_2	0.074(9)	95(37)	90	152(37)
r_3	0.086(11)	5(37)	90	118(37)
O1, r_1	0.061(18)	90	0	90
r_2	0.071(22)	177(16)	90	70(16)
r_3	0.119(12)	93(16)	90	20(16)
O2, r_1	0.072(10)	57(17)	114(13)	63(20)
r_2	0.096(14)	56(42)	117(47)	149(30)
r_3	0.106(11)	52(38)	38(40)	105(47)
O3, r_1	0.055(24)	137(11)	52(15)	55(16)
r_2	0.093(11)	84(24)	58(29)	144(20)
r_3	0.105(8)	48(12)	54(22)	81(31)

placements of the equatorial oxygens (O2,O3; O4,O5 in Speer and Gibbs notation, O2A,O2B; O3A,O3B in Taylor and Brown notation) to pseudo-*A*-related positions. At elevated temperatures Taylor and Brown (p. 441) report what is probably a second-order "distortional transformation" (terminology of Buerger, 1971) from the $P2_1/a$ to the $A2/a$ structure, in which at ~220°C the Ti atom has moved to the center of the [TiO_6] octahedron and the oxygen pairs in the octahedron have become related by a center of symmetry. The *k* + *l* odd reflections become gradually weaker (but not streaked or diffuse) between 25 and 220°C. The mean Ti–O bond lengths in the octahedron do not change from room temperature to 270°C, so that one cannot argue that the cause of the increase in symmetry is an effective increase in cation

Table 4. Interatomic distances (A) and angles (°) in malayaite

		M–O distance			O–O distance	O–*M*–O angle
SiO_4 tetrahedron						
Si–O(1)	[2]*	1.649(5)**	O(2)–O(2)		*2.564(9)*	102.1(4)
–O(2)	[2]	1.633(6)	–O(3)	[2]	2.670(8)***	108.9(3)
			–O(3)	[2]	2.742(8)	113.4(3)
			O(3)–O(3)		2.677(13)	110.1(4)
Mean		1.641			2.678	109.5
SnO_6 octahedron						
Sn–O(1)	[2]	1.947(3)	O(1)–O(2)	[2]	2.837(6)	89.3(2)
–O(2)	[2]	2.088(5)	–O(2)	[2]	2.872(7)	90.7(2)
–O(3)	[2]	2.092(5)	–O(3)	[2]	*2.738(6)*	85.3(2)
			–O(3)	[2]	2.973(9)	94.7(2)
			O(2)–O(3)	[2]	*2.938(8)*	89.3(3)
			–O(3)	[2]	2.973(7)	90.7(2)
Mean		2.042			2.888	90.0
CaO_7 polyhedron						
Ca–O(1)		2.241(8)				
–O(2)	[2]	2.401(6)				
–O(3)	[2]	2.422(5)				
–O(3)	[2]	2.746(5)				
Mean		2.483				

* *Multiplicity indicated in brackets.*

** *e.s.d.'s, given in parentheses, refer to last decimal place.*

*** *Italics indicate shared polyhedral edge.*

size with temperature (as for example in the $C\bar{1} \rightarrow C2/m$ transformation in disordered albite, $NaAlSi_3O_8$).

2. Composition dependence of the apparent symmetry of titanites. J. A. Speer (personal communication, 1973) examined a natural titanite, and noted diffuse streaks in place of the $k + l$ odd reflections which distinguish the primitive from the centered lattice type. As a result, Speer and Gibbs (1976) modified Robbins' (1968) domain theory for natural titanites, proposing that those which exhibit diffuse or no visible $k + l$ odd reflections consist of multiple $P2_1/a$ domains related by half-turns parallel to b. Higgins and Ribbe (1976) found that the primary substituents for Ti are trivalent Al and Fe, and that at levels greater than ~5 mole percent (Al + Fe) natural titanites have diffuse $k + l$ odd reflections which become undetectable at levels greater than 15–20 mole percent (Al + Fe). Apparently, octahedral sites containing Al or Fe serve as boundaries on either side of which linear domains of octahedra contain Ti atoms displaced in opposite directions along the chain. The greater the substituent level, the more abundant the oppositely oriented domains and the more diffuse the $k + l$ odd reflections. At a high frequency of domains the positional parameters of the oppositely oriented octahedra are "averaged" by X-rays, the (Ti,Al,Fe) atom appears equidistant from the O1 oxygens, and the space group for the average structure becomes $A2/a$. Although a careful study of the structure of an $A2/a$ titanite containing high levels of Al + Fe for Ti has not been done, it is expected

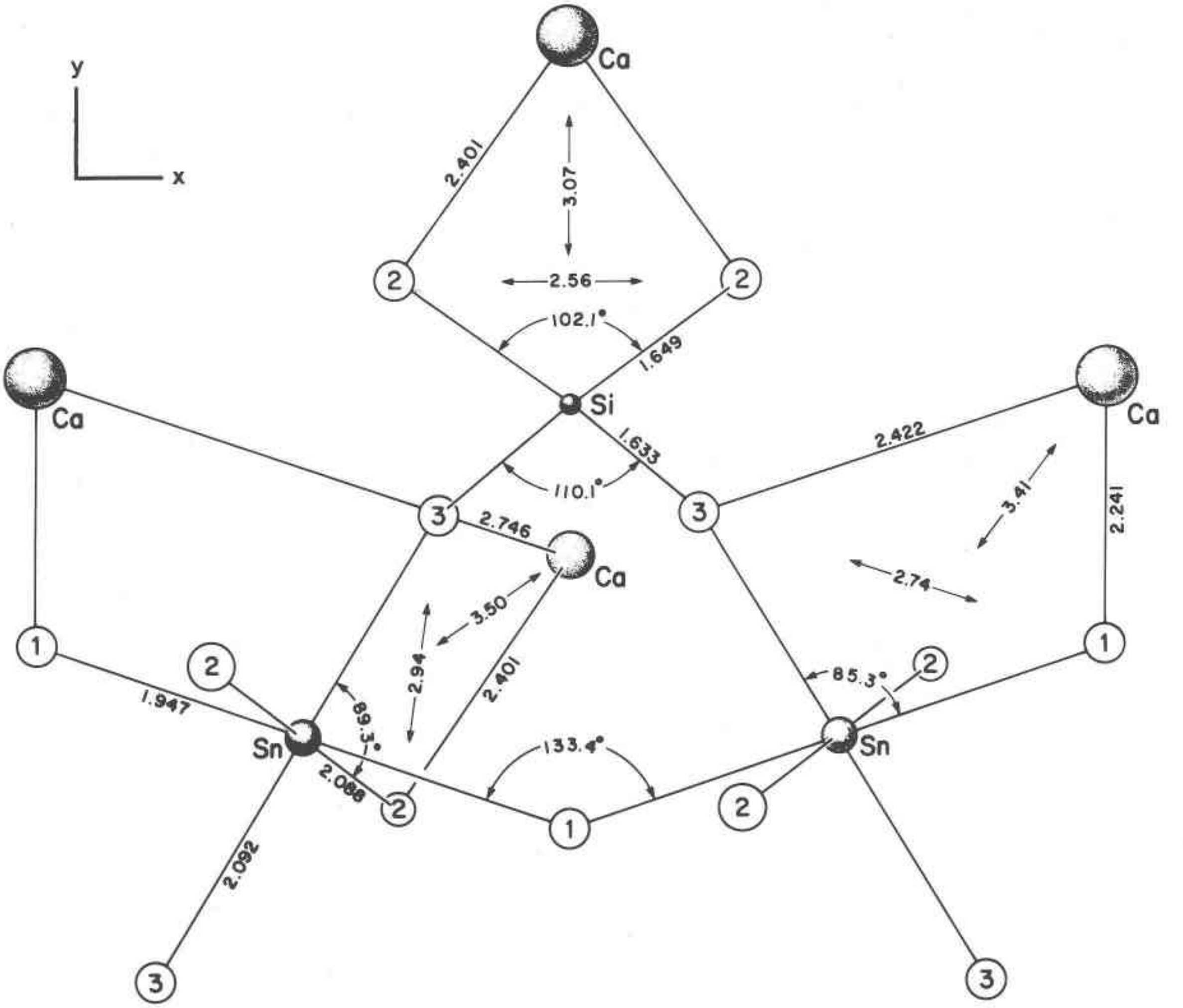

Fig. 1. Projection of a portion of the malayaite structure onto (001) showing the linkage of two $[SnO_6]$ octahedra along [100]. The bridging $[SiO_4]$ tetrahedron and the edges shared between $[CaO_7]$ polyhedra and the $[SiO_4]$ tetrahedron and the $[SnO_6]$ octahedron are also illustrated. The oxygen atoms are shown as unshaded, labelled circles. All bond lengths and interatomic distances are in Angströms.

that the positional disorder of the M cation in the $[MO_6]$ octahedron would be observable in electron density maps. This contrasts with chemically pure titanite above the $P2_1/a \rightarrow A2/a$ transition (~220°C), in which no evidence of positional disorder was found at the Ti site (Taylor and Brown, 1976, p. 441).

Comparison of malayaite with titanites

Natural titanites contain (Al + Fe) as substituents for Ti, and since Al, which is ~0.075 A smaller than Ti, usually predominates, most natural titanites have smaller lattice parameters than pure $CaTiOSiO_4$ (see Fig. 3, p. 884 in Higgins and Ribbe, 1976). Tin, on the other hand, is ~0.085 A larger than Ti, and as expected, the unit cell of malayaite is proportionately larger than that of titanite (Table 1). The 0.085 A difference in effective ionic radii is almost exactly reflected in the 0.083 A difference in mean Sn–O and mean Ti–O bond lengths in the octahedra of malayaite and titanite.[1]

But of greater interest is the fact that in titanite the concentration of a cation *smaller* than Ti (*e.g.*, Al) is correlated to the frequency of domain formation which ultimately leads to an "average" structure with $A2/a$ symmetry, whereas in malayaite the substitution of a cation *larger* than Ti also ultimately leads to a structure with $A2/a$ symmetry. Presumably the structural explanation for the latter phenomenon need not involve domain formation, for one might expect that the larger tin atom is more likely to occupy the center of the octahedron than is titanium. In that regard, however, it would be interesting to examine single crystals of titanite containing small amounts of Sn to determine whether or not diffuse streaks were evident in the $k + l$ odd reflection positions. Takenouchi (1971) reports very limited solid solution of Sn in $CaTiOSiO_4$ and an asymmetric solvus in the system $CaTiOSiO_4$-$CaSnOSiO_4$. Apparently it is the size difference in Ti and Sn that is responsible for titanite-malayaite immiscibility at temperatures below ~615°C.

Inasmuch as the three-coordinated O1 oxygen is highly underbonded in malayaite (Pauling bond-strength sum = 1.62), the Ca–O1 distance is the shortest in the $[CaO_7]$ polyhedron and the Sn–O1 bond length is 0.143 A shorter than the Sn–O2,3 bonds, which are nearly equal in length at 2.09 A (Table 4 and Fig. 1). As in titanite, the largest deviation of the octahedral O–M–O angle from 90° is ~5°, so that the $[SnO_6]$ polyhedron may be described as a tetragonally-compressed octahedron.

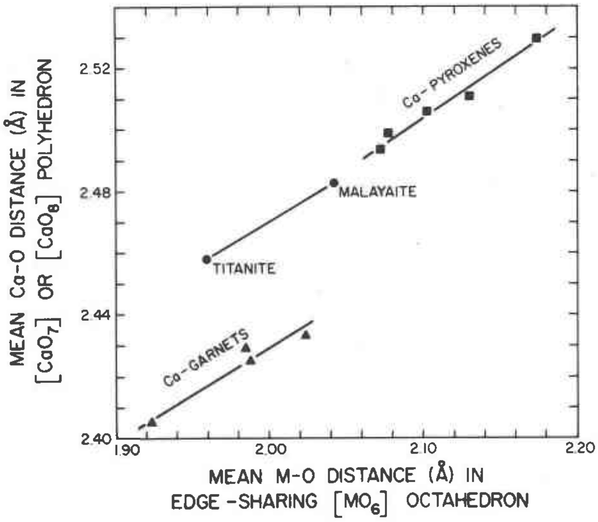

Fig. 2. The mean M–O distances in edge-sharing $[MO_6]$ octahedra plotted against the mean Ca–O distances in $[CaO_7]$ or $[CaO_8]$ polyhedra for Ca-garnets (Novak and Gibbs, 1971), Ca-pyroxenes (Ribbe and Prunier, 1977), titanite (Speer and Gibbs, 1976), and malayaite (Table 4).

Figure 1 is a projection of part of the malayaite structure onto (001), illustrating the linkage of two $[SnO_6]$ octahedra along [100] with the bridging $[SiO_4]$ tetrahedron in the center, causing the octahedral chain to be kinked (the O1–O1–O1 angle is 133.4°). Edges shared between the $[CaO_7]$ coordination group and $[SnO_6]$ and $[SiO_4]$ polyhedra are shown with O · · · O distances specified. The O1 · · · O3 shared edge (2.738 A) is the shortest in the $[SnO_6]$ octahedron, and it is opposite the smallest O–Sn–O angle (85.3°). The Sn · · · Ca distance across this edge is 3.41 A. The other edge shared between $[CaO_7]$ and $[SnO_6]$ polyhedra is the 2.938 A O2 · · · O3 edge opposite an angle of 89.3° (Sn · · · Ca = 3.50 A).

The $[SiO_4]$ tetrahedra in malayaite and titanite are very similar indeed: the largest difference in O–Si–O angle is 1.4° for a range in observed angles of 102.1–113.4°; the mean Si–O distance is 1.641 A in malayaite, and is statistically identical in the Speer and Gibbs refinement of titanite and all five refinements of Taylor and Brown, including those at temperatures up to 740°C. Curiously, it is the Si–O bonds to the 3-coordinated, slightly underbonded O2 oxygens that are ~0.016 A longer than those to the 4-coordinated, formally overbonded O3 oxygens in malayaite. (In titanite all Si–O bonds are statistically

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[1] Because of acknowledged difficulties associated with parameter interactions in the room temperature and 165°C refinements of titanite by Taylor and Brown (1976), we have chosen to compare structural details of malayaite with the room-temperature refinement of titanite by Speer and Gibbs (1976).

identical.[2]) But Figure 1 shows that the shortest tetrahedral edge (2.562 A) is the O2···O2 edge shared between the $[CaO_7]$ and $[SiO_4]$ polyhedra, and that it is opposite the smallest O–Si–O angle (102.1°). Classically interpreted, then, it is expected that the Si–O2 bonds be longer than the Si–O3 bonds. Furthermore, their relative lengths are consistent with the observations of Louisnathan and Gibbs (1972) for most silicates: the mean of the three O–Si–O angles opposite the longer Si–O2 bond is 110.8°, whereas the mean of those opposite the shorter Si–O3 bond is 108.1°.

The irregular $[CaO_7]$ polyhedron shares four edges with other $[CaO_7]$ polyhedra, one edge with the $[SiO_4]$ tetrahedron and two edges with the $[SnO_6]$ octahedron. The mean Ca–O distance in malayaite is 2.483 A, whereas that in titanite is 2.458 A. As in the $[CaO_8]$ dodecahedra in garnets (Novak and Gibbs, 1971) and the $[CaO_8]$ polyhedra in ordered Ca-pyroxenes (Ribbe and Prunier, 1977), this increase can be directly attributed to the increase in size of the cations in edge-sharing octahedra. In fact, Figure 2 shows that for all three isostructural groups the increase in the mean Ca–O distance is 0.3 A per A increase in the mean M–O distance of the edge-sharing $[MO_6]$ octahedron.

In conclusion it can be said that the steric details of the malayaite structure are predictable in terms of the classical Pauling principles, and that it is truly isostructural with high-temperature $A2/a$ titanite. It could be argued that it is not isostructural with chemically impure titanites whose $A2/a$ symmetry arises from domains of primitive structure related by half-turns parallel to b, because there is no evidence for positional disorder in $A2/a$ malayaite.

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[2] The 25° and 165°C refinements of Taylor and Brown (1976) are omitted from consideration for reasons given to footnote 1. Note that it was not possible to calculate the Brown and Shannon (1973) bond strengths to O2 and O3 because data are not available for tin.