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Edgarbaileyite, $Hg_6Si_2O_7$: The crystal structure of the first mercury silicate

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ABSTRACT

Edgarbaileyite is the first reported structure to contain both Hg and Si. It is monoclinic, with cell parameters $a = 11.755(3)$ Å, $b = 7.678(2)$ Å, $c = 5.991(2)$ Å, $\beta = 111.73(3)°$, $V_{cell} = 502.3(3)$ Å^3. The diffraction pattern shows systematic absences corresponding to diffraction symbol $2/mC$—possible space groups are $C2/m$, Cm, and $C2$. The structure was determined by Patterson synthesis followed by Fourier syntheses, and refined using single-crystal data collected by a four-circle diffractometer. The presence of polysynthetic twinning, poor crystal quality, and high absorption precluded the absolute determination of the correct space group, but the topology of the structure is the same for all three possible space groups. The stoichiometry determined by structure solution is $Hg_6Si_2O_7$, with the unit-cell contents given by $Z = 2$. All of the Hg atoms occur as two sets of symmetrically independent pairs separated by 2.522(3) Å and 2.524(2) Å, typical of $(Hg_2)^{2+}$ in other compounds. In addition, each Hg atom is coordinated by three O atoms at distances between 2.12 and 2.86 Å. These O atoms also provide tetrahedral coordination for the Si atoms; the SiO_4 tetrahedra share one O atom to form Si_2O_7 groups, which provide cross-links between the pairs of Hg atoms.

INTRODUCTION

Edgarbaileyite was first described by Roberts et al. (1990) as a mercury silicate mineral from a number of localities in California and Texas. Early discussions among these authors concerning the stoichiometry of edgarbaileyite included the possibility of mixed valence Hg in Hg_3SiO_4. However, because Hg has such a large atomic mass (200.6) it is not possible to determine reliably the correct oxidation state of the Hg atoms from microprobe data; the various models for the charge on the Hg atoms differ only in the number of O atoms, whose low atomic mass (16) makes little difference in the element weight percent totals. The correct stoichiometry can therefore only be determined from knowledge of the crystal structure. Although Roberts et al. (1990) were able to take a number of single-crystal precession photographs, the type material from the Socrates mine, California, was of insufficient quality to allow data measurement for the purpose of single-crystal structure determination. Instead, material from Terlingua, Brewster County, Texas, now in the Mineral collection of the Natural History Museum, London [formerly BM(NH)], was used in this single-crystal study to determine the structure and chemistry of this first occurrence of a mercury silicate compound.

The presence of Hg in the material presented a number of major experimental problems in addition to those associated with the interpretation of electron microprobe data. The measurement of quantitative X-ray diffraction intensities was hampered by the extremely high absorption coefficient (916 cm^{-1}) for the material, a problem which could not be avoided by grinding spherical crystals because of the small quantity of sample available and the dominant {100} cleavage. Structure determination was also complicated by the presence of multiple twinning and the distribution of Hg atoms within the unit cell. Together these difficulties precluded the absolute determination of the symmetry of the structure, but the structure solutions in all three possible space groups, $C2/m$, $C2$, and Cm, possess the same structural topology and stoichiometry. Edgarbaileyite is found to contain only monovalent Hg and has the formula $Hg_6Si_2O_7$.

EXPERIMENTAL

For the X-ray diffraction studies, two apparent single crystals of edgarbaileyite were chosen from the specimen from Terlingua, Brewster County, Texas (BM1906,190) described by Roberts et al. (1990). Although these particular crystals were not quantitatively analyzed by electron microprobe, it was assumed that they had the same composition as the other edgarbaileyite grains analyzed from this specimen. Analysis was carried out with a Cambridge Instruments Microscan IX electron microprobe operated at 20 kV with a beam current of 2.50×10^{-8} A as measured on a Faraday cup. The material was found to be sensitive to beam damage, so a defocused beam of 20 μm diameter was used for analysis. Standards used

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were cinnabar for Hg and wollastonite for Si; no other elements were detected in the specimens. The average results of five analyses indicate an atomic ratio of Hg to Si of 3:1 (Table 1). Recalculation on the basis of three possible models for the valence state of Hg in the compound indicates that the model with all of the Hg present as Hg^{2+} is unlikely to apply for edgarbaileyite on the basis of these microprobe data.

TABLE 1. Compositional data for edgarbaileyite

Hg valence	Hg^{2+}	Hg^{1+}	⅔Hg^{1+}, ⅓Hg^{2+}
Element			
Hg	87.65	87.65	87.65
Si	3.80	3.80	3.80
O	11.32	7.82	8.99
Total	102.77	99.27	100.44
Formula	Hg_3SiO_5	$Hg_6Si_2O_7$	Hg_3SiO_4

Note: All values in wt%. Hg and Si as measured by microprobe, O as required for charge balance.

Edgarbaileyite crystals exhibit a platy habit, flattened on {100}, and have a well-developed {100} cleavage. X-ray precession photographs and preliminary investigation by four-circle diffractometry indicated that the crystals chosen for study consisted of a number of twinned crystals, each of which was growth-misoriented with respect to small rotations about the **a*** axis. On breaking one of the specimens for diffractometer work, the misorientation in the composite was eliminated, but crystallites related by a twin law remained. A plate flattened on {100} about 25 μm thick and 70 μm in diameter was selected for data measurement with a Picker four-circle diffractometer equipped with a Mo X-ray source. Diffractions from both twin components were located and centered by the method of King and Finger (1979). The unit-cell dimensions determined from each twin component using the positions of 14 reflections with $7° < 2\theta < 26°$ were identical within the esd. Both unit cells displayed $\alpha = \gamma = 90°$ within the experimental uncertainties. Constrained-vector least squares yielded cell parameters for the larger twin component of $a = 11.755(3)$ Å, $b = 7.678(2)$ Å, $c = 5.991(2)$ Å, $\beta = 111.73(3)°$, $V_{cell} = 502.3(3)$ Å^3. The twin matrix determined from the two UB matrices was [−1.0, 0.0, −1.455/0.0, −1.0, 0.0/0.0, 0.0, 1.0], which corresponds to a two-fold rotation about the **c** axis. This twin law was confirmed by X-ray precession photography. This crystal appeared optically homogeneous when viewed perpendicular to the plate, suggesting that the composition plane of the twin is {100}. Subsequent determination of the structure supports this hypothesis. The ratio of volumes of the two components in the crystal was estimated to be approximately 2:1 from observations of diffraction intensities. Because previous SEM observations on the multiple crystals did not reveal evidence of any macroscopic twinning, we surmise that the twinning is polysynthetic and coherent, with individual twins being of the order of ~1 μm thick. Allowing for the twinning, which causes apparent *C*-lattice violations, observations from both the diffractometer and precession photography confirm that the diffraction pattern exhibits absences $h + k$ odd for all *hkl*, and that the unit cell thus has a *C* lattice. No other systematic absence rules were detected, and the diffraction symbol is thus $2/mC$.

Diffractions from the larger twin component were selected for data measurement. Periodic monitoring of the intensities of two peaks throughout the data measurement indicated that their intensity did not deteriorate because of exposure to either light or X-rays. A full sphere of data (four asymmetric units) to $2\theta = 60°$ was collected with ω step scans, using a Nb filter to exclude Mo$K\beta$ radiation. The outer 10% of steps at each end of each scan were considered to be background, and they were used to calculate intensities from the inner 80% of each scan. Reflections whose two backgrounds differed by more than three times their combined esd, as deduced from counting statistics, were deleted at this stage (545 of 2536 reflections). The remaining intensities were corrected for the Lp factor and absorption effects and reduced to structure factors with the program of Burnham (1966). The extremely large value of the absorption coefficient, $\mu_l = 916$ cm^{-1}, means that the numerical integration method used by this program to determine the path lengths for the absorption correction is likely to be inaccurate. Calculated transmission factors for the 1641 nonzero intensities ranged from 0.019–0.137. The data were averaged in point group $2/m$ to give 690 symmetry independent data with an internal *R* value of 0.073 (0.065 for the 492 data with $F > 6\sigma_F$).

No significant difference was observed in the intensities of *hkl* and $\bar{h}\bar{k}\bar{l}$ pairs, whereas statistical tests of the normalized structure factors exhibited behavior intermediate between that predicted for centric and acentric distributions of otherwise randomly distributed equal atoms. The breakdown of such tests is to be expected in the presence of twinning and when the structure is known to contain heavy-atom scatterers that are nonrandomly distributed. Possible space groups for the structure were therefore $C2/m$ (centric), $C2$ or Cm (acentric). The first stages of structure solution were carried out in space group $C1$ to avoid biasing the result toward one particular space group. Hg atoms were located from analysis of the Patterson function, and the lighter Si and O atoms by difference-Fourier synthesis. The resulting structure was at least approximately centric, and subsequent refinement proceeded in space group $C2/m$. Refinements were carried out with the program RFINE88, a development version of RFINE4 (Finger and Prince, 1975). The robust-resistant method of weighting reflections was used to overcome problems in the data caused by the limitations of the absorption correction discussed above. Complex neutral-atom form factors were taken from *International Tables for X-ray Crystallography* (1974). A correction for isotropic Type I extinction (Becker and Coppens, 1974) and the twin fraction were refined in addition to positional parameters, scale factor, anisotropic thermal parameters

TABLE 2. Positional and thermal parameters for $Hg_6Si_2O_7$ refined in space group *C*2/*m*

Site	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq}
Hg1	0.1140(1)	0	0.0490(3)	0.0015(1)	0.0102(3)	0.0128(4)	0	0.0019(1)	0	1.56
Hg2	0.1155(1)	0.2423(2)	0.5789(2)	0.0016(1)	0.0072(2)	0.0135(3)	0.0002(1)	0.0011(1)	0.0010(3)	1.42
Si	0.6491(7)	0	0.105(2)							1.2(2)
O1	0.303(2)	0	0.113(4)							1.8(4)
O2	0.311(1)	0.168(3)	0.728(3)							1.7(3)
O3	½	0	0							0.1(4)

Note: For Tables 2 and 4, numbers in parentheses represent esd in the last decimal place quoted.

for the Hg atoms, and isotropic thermal parameters for Si and O atoms. Final values of the agreement indices were $R = 0.095$, $R_w = 0.047$ for all 690 data, $R = 0.058$, $R_w = 0.034$ for 490 unrejected data, with a goodness of fit of 1.41 for a total of 29 refined parameters. Final values of these parameters are reported in Table 2, observed and calculated structure factors in Table 3,[1] and bond lengths and angles in Table 4.

Subsequent refinements were also carried out in the two possible acentric space groups, *C*2 and *Cm*. These space groups allow the same topology of the structure but relax certain constraints upon either the positions of some sites or the equivalence of certain atom positions. Both of these refinements gave improved *R* values, with the solution in space group *Cm* being statistically favored over that in *C*2. Although both refinements resulted in statistically significant displacements of atoms from their positions in space group *C*2/*m*, they also both resulted in unusual Si-O bond lengths (up to 1.7 Å in *Cm*) and negative values for the isotropic temperature factors of some O sites. Furthermore, no difference in *R* values could be detected between refinements of the enantiomorphs in each of these two space groups, which is unusual in the light of the strong anomalous scattering of MoKα radiation by Hg atoms.

DISCUSSION

It is clear that the inconsistencies in the refinements arise, at least in part, from the difficulties associated with correcting the data for absorption and from the presence of twinning. It is possible, for instance, that the structure is truly acentric, but that the twin is enantiomorphic. Because the general features of the structure are similar in all three space groups, however, we will restrict our subsequent discussion to the results from the refinement in *C*2/*m*, with the understanding that this may represent an average structure of some kind.

The unit-cell contents determined by structure solution correspond to a formula for edgarbaileyite of $Hg_6Si_2O_7$, with $Z = 2$. Thus, all of the Hg within the structure is in the +1 oxidation state. This is confirmed by the central feature of this crystal structure (Fig. 1), the occurrence of all of the Hg atoms as pairs separated by 2.522(3) Å (Hg1) or 2.524(2) Å (Hg2), a configuration diagnostic of Hg (I) compounds. Reported examples, with Hg-Hg distances, include $(Hg_2)_3(AsO_4)_2$, 2.535 Å (Kamenar and Kaitner, 1973), Hg_2SO_4, 2.500 Å and Hg_2SeO_4, 2.51 Å (both Dorm, 1969). The calculated density of 9.1 g cm^{-3} is also consistent with the value of 9.4(3) g/cm^{-3} measured by Roberts et al. (1990). It is interesting to note in the structure of edgarbaileyite that both of the symmetrically-distinct Hg_2 pairs have an almost identical separation and that all six Hg_2 pairs within the unit cell are aligned almost parallel to one another. Both Hg sites are also coordinated by three O atoms in addition to the single close Hg neighbor. Again, in common with previously reported structures of Hg (I) compounds, there is one very short Hg-O

TABLE 4. Bond lengths and angles for $Hg_6Si_2O_7$ in space group *C*2/*m*

Hg1-Hg1	2.522(3) Å	Hg2-Hg2	2.524(2)	Si-O1	1.60(3)	
-O1	2.12(2)	-O2	2.21(1)	-O2 [2]	1.59(2)	
-O2 [2]	2.86(2)	-O2	2.41(2)	-O3	1.629(8)	
Mean Hg-O	2.61	-O1	2.63(2)	Mean Si-O	1.60	
Hg1-Hg1-O1		Mean Hg-O	2.42			
Hg1-Hg1-O2 [2]		177.2(7)		Hg2-Hg2-O2		164.9(5)
O1-Hg1-O2 [2]		103.1(3)		Hg2-Hg2-O2		108.8(4)
O2-Hg1-O2		78.0(4)		Hg2-Hg2-O1		110.9(3)
		125.9(7)		O2-Hg2-O2		76.6(6)
				O2-Hg2-O1		100.5(7)
				O1-Hg2-O2		81.8(6)
O1-Si-O2 [2]		113.6(8)				
O1-Si-O3		109.6(9)				
O2-Si-O2		108.2(1.3)				
O2-Si-O3 [2]		105.6(7)				

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[1] A copy of Table 3 may be ordered as Document AM-90-441 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.

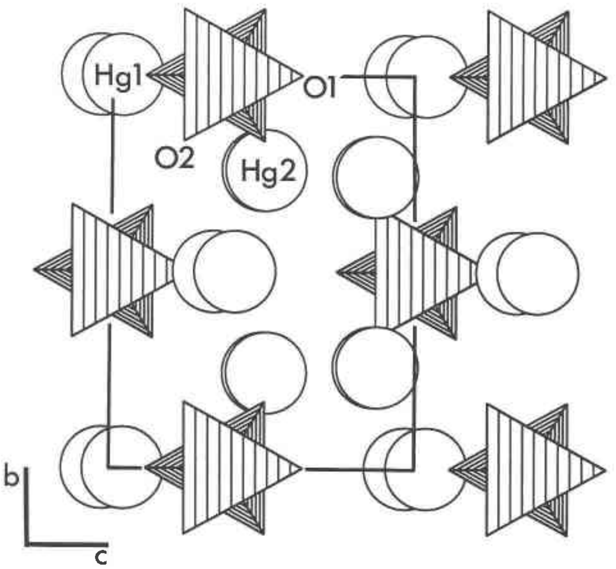

Fig. 1. A polyhedral representation (Fischer, 1985) of the crystal structure of edgarbaileyite viewed approximately down [100]. The unit cell is outlined.

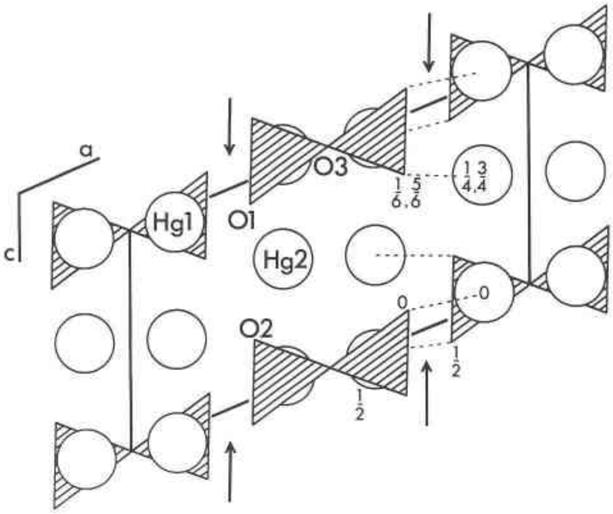

Fig. 2. The structure of edgarbaileyite viewed down the **b** axis. Figures indicate fractional y coordinates of atoms, and the arrows indicate the planes of low bonding density believed to be responsible for the {100} cleavage. Broken lines indicate the short Hg-O bonds.

bond that forms an almost linear O-Hg-Hg-O group and two longer Hg-O bonds (Table 4). Together with the other Hg atom the three O atoms form a very distorted tetrahedral coordination polyhedron for each Hg site.

The three O atoms bonded to each Hg atom belong to three different Si_2O_7 groups. In space group $C2/m$ there is only a single symmetrically independent SiO_4 tetrahedron, and these are paired by the shared atom O3 that occupies the symmetry center at ½,0,0. This necessitates a Si-O3-Si bond angle of 180°, a configuration often regarded with suspicion in many structure determinations, although a number of genuine cases have been confirmed (see, for example, Table 3.1 in Liebau, 1985). The constraint on this bond angle would obviously be relaxed in either acentric space group. However, the linear Si-O-Si configuration arising from the assumption that the true symmetry is $C2/m$ is supported by the following three points: first, in cases of misassignment of bridging O atoms to centers of symmetry, the site tends to display extremely large refined thermal parameters (see discussion by Shannon and Katz, 1970). In contrast, the O3 site in the refined structure of edgarbaileyite displays an anomalously small value of B_{iso}, although this may be due in part to problems associated with the absorption correction. Second, the geometry of the SiO_4 tetrahedron is very similar to tetrahedra in other structures confirmed to possess linear Si-O-Si linkages. These structures possess relatively regular tetrahedra, in constrast to nonlinear Si_2O_7 groups in which the bond to the bridging O is usually considerably longer than those to the nonbridging O atoms (Liebau, 1985). The reason for this distinctive behavior appears to be related to the fact that the bridging O atoms of linear Si-O-Si linkages tend not to be coordinated to any other cation, as is the case in edgarbaileyite. Third, the Si-Si distance within the Si_2O_7 group is 3.26(2) Å and remains ~3.2 Å in the refinements in $C2$ and Cm, in comparison with typical Si-Si distances for normal, nonlinear, Si-O-Si linkages of 3.10 Å or less.

When its structure is viewed down the **b** axis (Fig. 2), it is immediately apparent why edgarbaileyite displays such dominant {100} cleavage, and also why it is likely that this is the twin composition plane. The traces of the {100} planes indicated in Figure 2 are traversed by only a single Hg-O bond from each Hg_2 group, in contrast to the strong bonding between the Hg_2 groups and Si_2O_7 groups within {100} layers (Fig. 1). Twinning could also occur across this same plane within the unit cell (Fig. 3), but even if a twin operation of 180° rotation about [001] is accompanied by the optimum translation parallel to [001], there is considerable disruption of the shorter Hg-O bonds across the twin plane. An alternative position for the twin boundary within the unit cell is also presented in Figure 3. In this configuration a m_x operator is chosen to pass through the bridging O position of the Si_2O_7 group. Although this twin operation would change the point symmetry of the Si_2O_7 group from $2/m$ to $mm2$, it allows even the nearest neighbor coordination of the Si and both of the Hg sites to be maintained. The excess energy associated with the formation of such twin boundaries is expected therefore to be extremely small, a situation which would favor the formation of polysynthetic twins.

CONCLUSIONS

Although the crystal structure of edgarbaileyite has been solved to a reasonable degree, further work is required to overcome some of the experimental difficulties associated

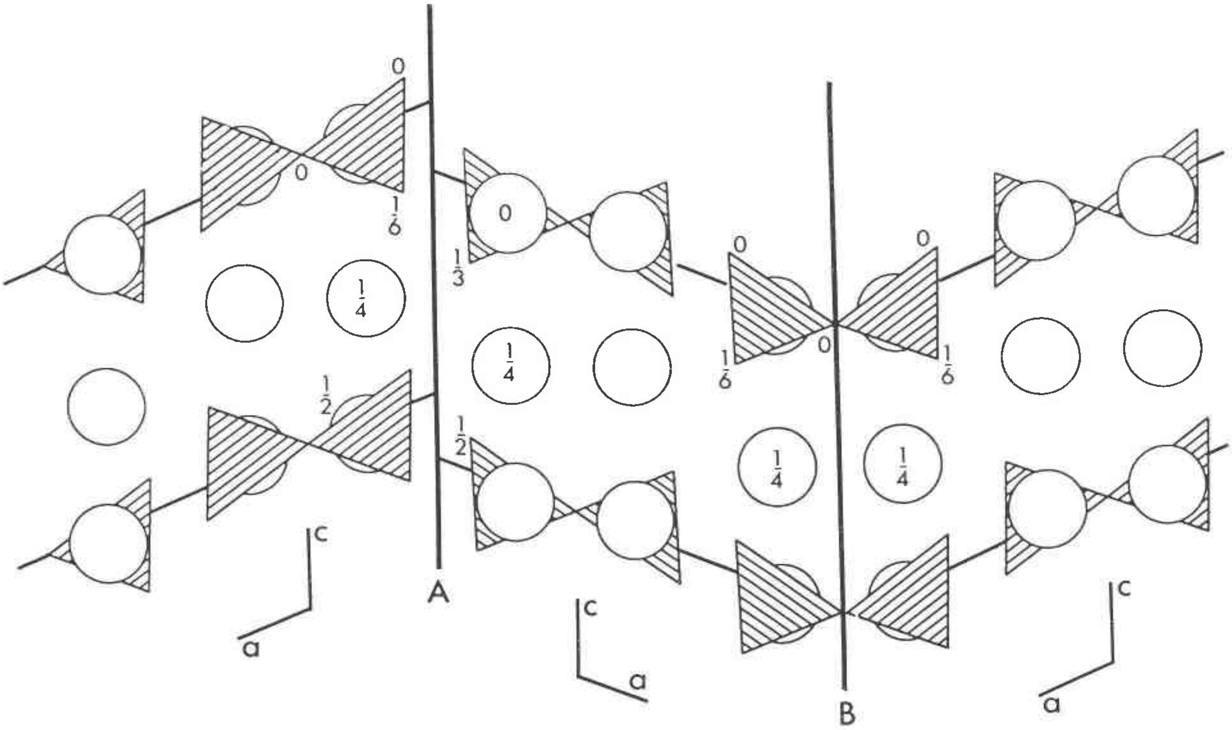

Fig. 3. Two possible structural configurations for the {100} twin planes in edgarbaileyite. Heavy lines indicate the traces of composition planes. The composition plane A, with a twin operator 2_z accompanied by a translation parallel to [001], leaves the Si_2O_7 group undisturbed at the expense of disrupting the shortest Hg-O bonds across the twin boundary. By contrast, the configuration shown at B, with a twin operation m_x, changes the point symmetry of the Si_2O_7 groups at the boundary to $mm2$, but maintains the nearest neighbor coordinations of all of the cation sites.

with X-ray diffraction. High-resolution transmission electron microscopy would be desirable to confirm our deductions about the nature and structure of the twin boundaries. A single-crystal neutron diffraction study of $Hg_6Si_2O_7$ would provide an obvious way around the problem of absorption of X-rays by the sample and would have the added advantage that the lighter atoms have neutron scattering lengths similar to those of the Hg atoms that dominate the diffracted X-ray intensities. Such a study would thereby allow a definitive conclusion to be drawn regarding the true symmetry and space group of edgarbaileyite. Unfortunately, neither of these techniques are currently feasible owing to the very small quantity of sample available for study (two crystals). Nevertheless, we have successfully demonstrated that edgarbaileyite, the first mercury silicate to be described, has the stoichiometry $Hg_6Si_2O_7$ with all of the Hg occurring within the structure as $(Hg_2)^{2+}$ dimers.

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