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The Crystal Structure of Gillespite II at 26 Kilobars: Correction and Addendum

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Correction

In the conclusion of our recent paper on "The Crystal Structure of Gillespite I and II: A Structure Determination at High Pressure" (Hazen and Burnham, 1974) we stated that "until recently high-pressure single-crystal X-ray diffraction techniques were unknown." We then continued with the misleading statement: "With the introduction of the Bassett miniature pressure cell, X-ray diffraction experiments at elevated pressures are now possible." In fact, National Bureau of Standards researchers, who have introduced a variety of high pressure experimental techniques, were the first to study successfully single crystals at high pressures with X-rays.

A major advance in the study of single crystals at high pressures was Van Valkenburg's (1965) development of a metal foil gasketing technique by which a crystal, surrounded by a pressure transmitting fluid, could be compressed between the flat parallel faces of a diamond anvil. This procedure was adapted to single crystal X-ray diffraction by the National Bureau of Standards Crystallography Section in their high pressure crystal structure studies of ice VI and ice VII (Block, Weir, and Piermarini, 1965; Weir, Block, and Piermarini, 1965), and has been employed in additional studies of several simple compounds (including C_6H_6, CS_2, CCl_4, KNO_3), and elements (cesium, gallium, and bromine) (Weir *et al,* 1969a; Block *et al,* 1970; Weir *et al,* 1971; Piermarini and Braun, 1973). The workers at the National Bureau of Standards were also the first to fabricate components of the pressure apparatus from beryllium to minimize X-ray absorption (Weir *et al,* 1969b), and they developed procedures to correct for the complex X-ray absorption of this equipment (Santoro *et al.*, 1968). The pioneer work of the National Bureau of Standards was further advanced by Merrill and Bassett (1974) who developed a smaller form of the NBS pressure cell that can be attached easily to standard goniometer heads. Thus, high-pressure X-ray experiments can now be carried out with precession cameras and single-crystal diffractometers without the goniometer head modification which the NBS cell requires.

We wish to thank Dr. Stanley Block, Chief of the National Bureau of Standards Crystallography Section, and Dr. Alvin Van Valkenburg, Bureau of Mines, for calling to our attention this matter, and we apologize to Dr. Block and his co-workers for our unintentional error.

Addendum

In our reported study of gillespite II at 26 kilobars, absorption corrections for the diamond and beryllium components of the pressure cell were not included. The uncorrected systematic errors caused large uncertainties in atom positions as well as abnormally large isotropic temperature factors for the high-pressure phase. We have now developed a computation procedure to correct for these absorption effects (Hazen, 1975), and the gillespite II structure has been re-refined. Transmission factors including absorption by both the crystal and the pressure cell varied from 10 to 19 percent. Six cycles of least-squares refinement using isotropic temperature factors reduced the *R* value to 6.3 percent, compared with the minimum of 10.5 percent before the improved absorption correction was applied.

Revised values of atomic coordinates, isotropic temperature factors, bond distances, and bond angles appear in Tables 1 and 2. No major changes in atomic positions are observed, and isotropic temperature factors are significantly lower than before. Bond angles are generally little changed, but one significant revision should be noted. The original determinations of square planar O–Fe–O (opposite) angles were 167° for both O3*A*–Fe–O3*A* and O3*B*–Fe–O3*B* (Figure 5b, Hazen and Burnham, 1974). Changes in the *z* coordinates of O3*A*, O3*B*, and Fe lead to new values of 158° ± 2° for O3*A*–Fe–O3*A* and 175° ± 2° for O3*B*–Fe–O3*B*. Thus O3*B* and Fe are close to the same *c*-axis level,

TABLE 1. Gillespite II. Revised Atomic Coordinates, Isotropic Temperature Factors

Atom	x	y	z	B (Å^2)
Ba	0	0	-.017(1)[a]	1.64(8)
Fe	0	1/2	0.159(3)	1.60(17)
SiA	0.689(2)	0.224(2)	0.322(4)	1.0(3)
SiB	0.261(2)	0.188(2)	0.297(4)	1.4(2)
O1	0.208(3)	0.267(3)	0.479(9)	0.6(6)
O2A	0.474(3)	0.221(3)	0.255(7)	1.4(6)
O2B	0.236(3)	0.978(5)	0.285(7)	4.2(8)
O3A	0.232(3)	0.625(3)	0.207(6)	0.4(5)
O3B	0.143(3)	0.282(3)	0.148(6)	0.4(5)

a) Parenthesized figures represent the estimated standard deviation in terms of least units cited for the value to the immediate left.

TABLE 2. Gillespite II. Revised Interatomic Distances and Bond Angles

Bond	Distance (Å)	Atoms	Angle (°)
SiA-O1	1.58(8)[a]	O1-SiA-O2A	113(3)
SiA-O2A	1.66(3)	O1-SiA-O2B	101(2)
SiA-O2B	1.64(4)	O1-SiA-O3A	120(2)
SiA-O3A	1.57(4)	O2A-SiA-O2B	105(2)
mean	1.61	O2A-SiA-O3A	100(2)
		O2B-SiA-O3A	116(2)
SiB-O1	1.60(7)		
SiB-O2A	1.62(3)	O1-SiB-O2A	111(2)
SiB-O2B	1.59(4)	O1-SiB-O2B	113(3)
SiB-O3B	1.62(5)	O1-SiB-O3B	111(2)
mean	1.61	O2A-SiB-O2B	105(2)
		O2A-SiB-O3B	108(2)
SiA-SiB	3.16(2)	O2B-SiB-O3B	109(2)
SiA-SiB	3.12(2)		
SiA-SiB	3.12(4)	SiA-O1-SiB	158(2)
		SiA-O2A-SiB	149(4)
		SiA-O2B-SiB	150(2)
Fe-O3A [2][b]	1.98(2)		
Fe-O3B [2]	1.95(2)	O3A-Fe-O3A	158(2)
		O3A-Fe-O3B	87(1)
mean	1.965	O3A-Fe-O3B	94(1)
		O3B-Fe-O3B	175(2)
Ba-O2A [2]	2.82(4)		
Ba-O2B [2]	2.95(5)		
Ba-O3A [2]	2.65(3)		
Ba-O3B [2]	2.70(3)		
mean	2.78		

a) Parenthesized figures represent the estimated standard deviation in terms of least units cited for the value to the immediate left.

b) Bracketed figures represent bond multiplicities.

while O3*A* is distorted out of the ideal square (001) plane. Revision of the Fe–O distances downward to a new mean of 1.965 Å indicates that compression of these bonds is slightly greater than originally reported. Recent studies on the crystal structure of fayalite at high pressure (Hazen, 1975) indicate a similar relative shortening for octahedral Fe–O bonds at about 25 kilobars. Thus a high-spin to low-spin iron transition in gillespite is not indicated by these data.

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