The joesmithite enigma: Note on the $6s^2$ Pb$^{2+}$ lone pair

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ABSTRACT

Joesmithite, end-member composition PbCa$_{0.1}$Mg$_{0.1}$Fe$_{0.8}$($\text{OH})_2$[Si$_8$O$_{20}$], is unique among clinoamphiboles in possessing same-cell space group $P2/a$. Since $P2/a$ is a subgroup of $C2/m$ and can be generated by suppressing inversion centers at (0 0 0, etc.) in the larger group, it is believed the lone pair-bond pair interaction by $6s^2$ Pb$^{2+}$ at the “A” site in clinopyroxene conserves only the inversion centers at ($\frac{1}{4}$ 0 0, etc.) and subsequent cell translation to $P2/a$. The $\{Cn\}$ ($n = 2, 3, 4, 6$) rotations and $\{m\}$ reflections can accommodate the stereoactive lone pair but $\{1\}$ inversion cannot.

The Pb−“A” displacement is 0.601 Å, a typical displacement for Pb$^{2+}$. The Pb atomic position is well-ordered and not split, suggesting that the lone pair was stereochemically active during growth of joesmithite crystals.

INTRODUCTION

For all practical purposes, joesmithite is a rare clinoamphibole culled from its only reported locality in Långban, Sweden. Its composition (Pb$_{0.4}$Ca$_{0.6}$)$_2$($\text{OH})_2$[Si$_8$O$_{20}$], is highly peculiar, it being a berylliosilicate with (Pb,Ca) in the large “A” site that is vacant in most clinoamphiboles. The “A” site is centered at (0 $\frac{1}{2}$ 0) for $C2/m$ clinopyroxenes. The species was first reported in detail by Moore (1968) and after assembling 1604 independent $F_{\text{e}}$, the full structure was reported by Moore (1969). The $R = 0.128$ was an acceptable discrepancy factor for the state of the art at that time and bond distances, site populations, and isotropic thermal parameters suggested the end-member composition PbCa$_{0.1}$Mg$_{0.1}$Fe$_{0.8}$($\text{OH})_2$[Si$_8$O$_{20}$]. But neither this composition nor any additional site occupancy would degrade the symmetry group from $C2/m$ $P2/a$, a simple “same cell” relationship decomposed by suppressing the inversion center at (0 0 0). In other words $P2/a \subset C2/m$.

The space group $P2/a$ is peculiar among the reported clinopyroxene structures, and Hawthorne (1983) in a review on the subject made a point of declaring its uniqueness. Yet the structure was topochemically that of a classic clinopyroxene with the exception of the “A” site at the origin. Moderate to strong intensity distributions and centric morphology required $P2/a$. What happened?

DISCUSSION

Actually, joesmithite is no enigma. The lone pair associated with $6s^2$ Pb$^{2+}$ at purported (0 $\frac{1}{2}$ 0) forces a break in symmetry. Many tested examples in my laboratory show that the stereoactive lone pair at a special site need not break the symmetry of any point, allowing at least one degree of freedom such as $\{Cn\}$ ($n = 2, 3, 4, 6$) rotation or $\{m\}$ reflection. But residence on $\{1\}$ inversion automatically either destroys the symmetry or splits Pb$^{2+}$ into two symmetrically disposed halves. Since all other sites in the joesmithite structure involve ions that are not stereoactive, Pb$^{2+}$ is the most likely culprit for symmetry breaking. This remarkable group-subgroup relation was not earlier recognized because in Henry and Lonsdale (1969), the origin shift for $C2/m$ requires a translation of ($\frac{1}{4}$ $\frac{1}{4}$ 0) to the second kind of inversion centers. The entire relation is summarized in Figure 1, which outlines the desired translations. Figure 2 portrays the displacements in the anion envelope of Pb$^{2+}$ for joesmithite. All structural evidence indicates that the Pb atomic position is well-ordered and not split into two halves. This immediately suggests that the lone pair was stereochemically active at the onset of joesmithite’s creation. Indeed, Moore (1969) stated “The ‘A’-Be pair was coupled during incipient crystal growth, acting as a template and dictating the other cation distributions in the crystal.” One may inquire about the displacement of the Pb$^{2+}$ centroid from the purported inversion center of the first kind. This is $|\{0.2836 0\}|(b = 17.875 \text{ Å}) = 0.601 \text{ å},$ a typical lone pair displacement for $6s^2$ Pb$^{2+}$ due to interaction with the neighboring bond pairs. Such a displacement along with atomic number 82 for Pb leads to a pronounced appearance of $P2/a$ in lieu of $C2/m$.

An interesting feature concerns the “A” site itself. Chemical crystallographic evidence suggests mixing of (Pb,Ca) at this site, that is, a lone-pair cation (Pb$^{2+}$) in solution with a cation stripped of all its valence electrons (Ca$^{2+}$). This is analogous to the Pb-K segregation in synthetic KPS, Pb$_2$(Pb$_{0.1}$K$_{0.9})[Si$_8$O$_{20}$] (R = 0.034), where half-occupied Pb(2) and K have Pb(2)-K 0.59-Å separation (Moore et al., 1985). The driving mechanism for this separation can be attributed to lone pair–bond pair interactions for Pb$^{2+}$ but no such interactions for K$^+$. In joesmithite, a similar splitting may exist, but such proof will not be easy since 82 x 0.40 = 32.8 electrons for Pb and
MOORE: THE JOESMITHITE ENIGMA

Fig. 1. Symmetry breaking in joesmithite. Top left, the space group elements and symbols of equivalences in C2/m with dot denoting Pb\textsuperscript{2+} displaced off "A" (0 1/2 0) leading to equivalences compatible with displacement (lower left). Translation of cell by (1/4 1/4 0) gives the desired P2/a on right.

20 \times 0.60 = 12 electrons for Ca. This would require careful re-examination of the entire chemical crystallography of joesmithite, which is already chemically very complex. It is predicted that a Pb-Ca separation would occur in a manner similar to Pb-K in KPS. This lone-pair cation-inert-core cation splitting could have some remarkable consequences, e.g., in disruption of K\textsuperscript{+}, Na\textsuperscript{+}, and Ca\textsuperscript{2+} pathways in living organisms that may explain in part Tl\textsuperscript{+}, Pb\textsuperscript{2+}, Bi\textsuperscript{3+}, Sb\textsuperscript{3+}, As\textsuperscript{3+}, etc., "heavy metal" toxicities and ensuing neuropathies. This, of course, is highly speculative but may lead to potentially fruitful further investigation.

I suggest that this phenomenon will be found to be generally operative in crystals where Pb\textsuperscript{2+} occurs at purported {1} point symmetry. Examination of sulfosalt structure types with lone-pair cations should also reveal pleasant surprises and may explain some of their complex crystal structures, which also possess symmetry groups of low order.

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