The joesmithite enigma: Note on the 6s² Pb²⁺ lone pair

PAUL BRIAN MOORE

Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, U.S.A.

ABSTRACT

Joesmithite, end-member composition PbCa₂Mg₂Fe⁴⁺⁺(OH)₆(Si₂Be₂O₆)₂, 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 6s² Pb²⁺ at the “A” site in clinoamphibole conserves only the inversion centers at (½ ½ 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 Pb²⁺. 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 (Pb₀.₄ Ca₀.₆)₂⁺⁺(Mg₀.₄Fe₀.₆)⁺⁺⁺(Si₂Be₂O₆)₆(OH)₆[Z = 2], is highly peculiar, it being a beryllosilicate with (Pb, Ca) in the large “A” site that is vacant in most clinoamphiboles. The “A” site is centered at (0 ½ 0) for C2/m clinoamphiboles. The species was first reported in detail by Moore (1968) and after assembling 1604 independent F’s, 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 PbCa₂Mg₂Fe⁴⁺⁺(OH)₆(Si₂Be₂O₆)₂. But neither this composition nor any additional site occupancy would degrade the symmetry group from C2/m to P2/a, a simple “same cell” relationship decomposed by suppressing the inversion center at (0 0 0). In other words P2/a C C2/m.

The space group P2/a is peculiar among the reported clinoamphibole 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 clinoamphibole 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 6s² Pb²⁺ at purported (0 ½ 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 Pb²⁺ into two symmetrically disposed halves. Since all other sites in the joesmithite structure involve ions that are not stereoactive, Pb²⁺ 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 (½ ½ 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 Pb²⁺ 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 Pb²⁺ centroid from the purported inversion center of the first kind. This is |½ ½ 0|-(½ 0.2836 0)|b = 17.875 Å| = 0.601 Å, a typical lone pair displacement for 6s² Pb²⁺ 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 (Pb²⁺) in solution with a cation stripped of all its valence electrons (Ca⁺⁺). This is analogous to the Pb-K segregation in synthetic KPS, PbO(Pb,K)₂Si₄O₁₂ (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 Pb²⁺ 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...
20 × 0.60 = 12 electrons for Ca. This would require careful re-examination of the entire chemical crystallography of joessmithite, 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*, Na*, and Ca2+ pathways in living organisms that may explain in part T1+, Pb2+, Bi3+, Sb3+, As3+, 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 Pb2+ 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.

ACKNOWLEDGMENTS

A portion of this work was supported by National Science Foundation EAR-84-08164.

REFERENCES CITED


MANUSCRIPT RECEIVED DECEMBER 14, 1987
MANUSCRIPT ACCEPTED MARCH 21, 1988