

## Elucidating the natural–synthetic mismatch of $\text{Pb}^{2+}\text{Te}^{4+}\text{O}_3$ : The redefinition of fairbankite to $\text{Pb}_{12}^{2+}(\text{Te}^{4+}\text{O}_3)_{11}(\text{SO}_4)$

OWEN P. MISSEN<sup>1,2,\*</sup>, MICHAEL S. RUMSEY<sup>3</sup>, STUART J. MILLS<sup>1</sup>, MATTHIAS WEIL<sup>4,†</sup>, JENS NAJORKA<sup>5</sup>, JOHN SPRATT<sup>5</sup>, AND UWE KOLITSCH<sup>6,7</sup>

<sup>1</sup>Geosciences, Museums Victoria, GPO Box 666, Melbourne 3001, Victoria, Australia

<sup>2</sup>School of Earth, Atmosphere and Environment, Monash University, Clayton 3800, Victoria, Australia

<sup>3</sup>Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, England, U.K.

<sup>4</sup>Institute for Chemical Technologies and Analytics, Division of Structural Chemistry, TU Vienna, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria

<sup>5</sup>Department of Core Research Laboratories, Natural History Museum, Cromwell Road, London SW7 5BD, England, U.K.

<sup>6</sup>Department of Mineralogy and Petrography, Natural History Museum, Burgring 7, A-1010 Vienna, Austria

<sup>7</sup>Institute of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria

### ABSTRACT

For four decades fairbankite was reported to have the formula  $\text{Pb}^{2+}(\text{Te}^{4+}\text{O}_3)$ , but repeated attempts to isolate fairbankite crystals for structural determination found only the visually similar cerussite and, more rarely, anglesite. The crystal-structure determination of fairbankite using single-crystal X-ray diffraction, supported by electron microprobe analysis and X-ray powder diffraction on the type specimen, has shown that fairbankite contains essential S, along with Pb, Te, and O. The chemical formula of fairbankite has been revised to  $\text{Pb}_{12}^{2+}(\text{Te}^{4+}\text{O}_3)_{11}(\text{SO}_4)$ . This change has been accepted by the IMA–CNMNC, Proposal 19-I. The crystal structure of fairbankite [space group  $P1$  (no. 1); revised cell:  $a = 7.0205(3)$  Å,  $b = 10.6828(6)$  Å,  $c = 14.4916(8)$  Å,  $\alpha = 75.161(5)^\circ$ ,  $\beta = 81.571(4)^\circ$ ,  $\gamma = 83.744(4)^\circ$ ,  $V = 1036.35(9)$  Å<sup>3</sup>, and  $Z = 1$ ] is the first atomic arrangement known to contain a  $\text{Te}_3^{4+}\text{O}_6^{2-}$  non-cyclic, finite building unit. Fairbankite has an average structure, formed from a 3D framework of  $\text{Pb}^{2+}\text{O}_n$  polyhedra,  $\text{Te}^{4+}\text{O}_n$  polyhedra, and  $\text{SO}_4$  tetrahedra in a 12:11:1 ratio. The stereoactive lone pairs of the  $\text{Pb}^{2+}$  and  $\text{Te}^{4+}$  cations are oriented into void space within the structure. Fairbankite contains two mixed sites statistically occupied by  $\text{Te}^{4+}$  and  $\text{S}^{6+}$  in approximately 4:1 and 1:4 ratios. These two sites possess  $\text{Te}^{4+}$  in trigonal-pyramidal environment and  $\text{S}^{6+}$  in tetrahedral environment (with an additional O site to create tetrahedral  $\text{SO}_4$  shape for the S-dominant site). Six of the 10 fully occupied  $\text{Te}^{4+}$  sites have  $\text{Te}^{4+}$  in trigonal-pyramidal environment, while four have  $\text{Te}^{4+}$  at the center of highly distorted  $\text{Te}^{4+}\text{O}_4$  disphenoids. The disphenoids allow for the creation of two dimeric  $\text{Te}_2^{4+}\text{O}_8^{2-}$  units in addition to the  $\text{Te}_3^{4+}\text{O}_6^{2-}$  trimeric unit, which contains two disphenoids. All linkage between disphenoids and trigonal pyramids is via corner-linking. Secondary connectivity is via long Te–O and Pb–O bonds.

**Keywords:** Lead tellurite, fairbankite, redefinition, crystal structure, tellurium oxysalt, average structure; Tombstone, Arizona, U.S.A.