

# Crystal chemistry of the alunite-jarosite solid solution series: Insights from atomistic modelling and EXAFS experiments

K. A. HUDSON-EDWARDS<sup>1\*</sup>, K. WRIGHT<sup>2</sup>, G. CIBIN<sup>3</sup> AND D. KOSSOFF<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Birkbeck, University of London, Malet St., London WC1E 7HX, UK. (\*correspondence: k.hudson-edwards@bbk.ac.uk, jkoss02@mail.bbk.ac.uk)

<sup>2</sup>Office of Research and Development, Curtin University, GPO Box U 1987, Perth, Western Australia 6845. (Kate.Wright@curtin.edu.au)

<sup>3</sup>Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 ODE, UK. (giannantonio.cibin@diamond.ac.uk)

Minerals of the alunite supergroup occur in a wide variety of weathering, lacustrine and hydrothermal environments on Earth and Mars, where they preserve information about the fluids and bacteria that formed them [1] [2]. The alunite supergroup consists of more than 40 minerals with the general formula  $AB_3(TO_4)_2(OH)_6$ , and in ideal alunite  $[KAl_3(SO_4)_2(OH)_6]$  and jarosite  $[KFe_3(SO_4)_2(OH)_6]$ , the B site cations are  $Al^{3+}$  and  $Fe^{3+}$ , respectively, the A site is occupied by  $K^+$  in 12-fold coordination, and the T site is filled with  $S^{2-}$  leading to the formation of the sulfate anion ( $SO_4^{2-}$ ) [3] [4]. Chemical and crystallographic information on the complete alunite-jarosite solid solution series is lacking, however, because natural and synthetic samples do not cover the whole series, and in particular, samples of intermediate composition are scarce.

To fill this knowledge gap, we have conducted classical atomistic computer simulations and EXAFS experiments on synthetic analogues to determine the energetics of substitution of  $Fe^{3+}$  in alunite, and  $Al^{3+}$  in jarosite, the cell parameters arising from bulk substitution of  $Fe^{3+}$  and  $Al^{3+}$  in alunite and jarosite, respectively, and the likely atomic configurations that these substitutions might produce. The most favorable structures are those in which  $Al^{3+}$  and  $Fe^{3+}$  are dispersed evenly within the alunite-jarosite structure, and the least favorable when the  $Al^{3+}$  and  $Fe^{3+}$  segregate into layers that are separated evenly within the structure.

[1] Alpers *et al.* (1992) *Sci. Géol. Bull.* **42**, 281-298. [2] Klingelhofer *et al.* (2004) *Science* **306**, 1740-1745. [3] Dutrizac & Kaiman (1976) *Can. Min.* **14**, 151-158. [4] Hawthorne *et al.* (2000) *Rev. Min. Geochem.* **40**, pp. 1-112.