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Uptake and release of arsenic and antimony in alunite-jarosite and beudantite group minerals

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Abstract
Arsenic and antimony are highly toxic to humans, animals, and plants. Incorporation in alunite, jarosite, and beudantite group minerals can immobilize these elements and restrict their bioavailability in acidic, oxidizing environments. This paper reviews research on the magnitude and mechanisms of incorporation of As and Sb in, and release from, alunite, jarosite, and beudantite group minerals in mostly abiotic systems. Arsenate-for-sulfate substitution is observed for all three mineral groups, with the magnitude of incorporation being beudantite (3–8.5 wt% As) > alunite (3.6 wt% As) > natroalunite (2.8 wt%) > jarosite (1.6 wt% As) > natroalunite (1.5 wt% As) > hydroniumalunite (0.034 wt% As). Arsenate substitution is limited by the charge differences between sulfate (–2) and arsenate (–3), deficiencies in B-cations in octahedral sites, and for hydroniumalunite, difficulty in substituting protonated H2O-for-OH groups. Substitution of arsenate causes increases in the c-axis for alunite and natroalunite, and in the c- and a-axes for jarosite. The degree of uptake depends on, but limited by, the AsO4/TO4 ratio. Aerobic and abiotic As release from alunite and natroalunite is limited, especially between pH 5 and 8. Release of As is also very limited in As-bearing jarosite, natrojarosite, and ammoniumjarosite at pH 8 due to the formation of secondary maghemite, goethite, hematite, and Fe arsenates that resorb the liberated As. Abiotic reductive dissolution of As-bearing jarosite at pH 4, 5.5, and 7 is likewise restricted by the formation of secondary green rust sulfate, goethite, and lepidocrocite that take up the As. Similar processes have been observed for the aerobic dissolution of Pb-As-jarosite (beudantite analog), with secondary Fe oxyhydroxides resorbing the released As at pH 8. Higher amounts of As are released, however, during microbial-driven jarosite dissolution. Natural jarosite has been found to contain up to 5.9 wt% Sb5+ substituting for Fe3+ in the B-site of the mineral structure. Sb(V) is not released from jarosite at pH 4 during abiotic reductive dissolution, but at pH 5.5 and 7, up to 75% of the mobilized Sb can be structurally incorporated into secondary green rust sulfate, lepidocrocite, or goethite. Further research is needed on the co-incorporation of As, Sb, and other ions in, and the uptake and release of Sb from, alunite, jarosite, and beudantite group minerals, the influence of microbes on these processes and the long-term (>1 yr) stability of these minerals.

Keywords: Arsenic, antimony, alunite, jarosite, beudantite; Invited Centennial article

Introduction
Arsenic (As) and antimony (Sb) are two of the most toxic elements to humans and many biota (Sundar and Chakravarty 2010; Feng et al. 2013; Abdul et al. 2015). The risks posed by exposure to As and Sb can be mitigated by the precipitation of minerals and especially those that are relatively insoluble and have low bioaccessibility. Alunite, jarosite, and beudantite-group minerals form in oxidizing, low-pH conditions in a wide variety of environments, including mine wastes (Hudson-Edwards et al. 1999; Nieto et al. 2003; Kocourková et al. 2011), acid sulfate soils (Nordstrom 1982; Welch et al. 2007), saline lakes (Alpers et al. 1992), and sulfuric acid caves (D’Angeli et al. 2018). A significant body of work has been carried out to understand the capacity and mechanisms of uptake of As and Sb in, and release from, alunite, jarosite, and beudantite group minerals formed in these environments. The aim of this paper is to synthesize and review research and to outline research gaps that should be filled by future work.

Minerals of the Alunite, Jarosite, and Beudantite Groups
Minerals of the alunite supergroup have a general formula of AB2(TO4)2(OH)6. In the formula, A represents cations with a coordination number greater than or equal to 9, B represents cations in a slightly distorted octahedral coordination, and T represents cations with tetrahedral coordination (Kubisz 1964, 1970; Jambor 1999; Hawthorne et al. 2000; Fig. 1). Within the supergroup, the alunite group minerals contain more Al3+ than Fe3+, and jarosite group minerals contain more Fe3+ than Al3+, in the B-site (Table 1). The A-site can be filled by univalent or divalent cations such as K+, Na+, H2O+, Ca2+, Sr2+, Ba2+, and Pb2+, but the most common substitutions are K+ (giving alunite and jarosite), Na+ (giving natroalunite and natrojarosite), and H2O+...