LETTER

Terrestrial analogs of martian sulfates: Major and minor element systematics of alunite–jarosite from Goldfield, Nevada

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ABSTRACT

Alunite and jarosite from Goldfield, Nevada, show spectacular relationships between early alunite and later jarosite. In some cases, jarosite overgrows alunite with the same crystallographic orientation and sharp contacts. Electron microprobe analyses of these phases show that they fall in the alunite–jarosite quadrilateral defined by alunite, KAl₃(SO₄)₂(OH)₆; natroalunite, NaAl₃(SO₄)₂(OH)₆; jarosite, KFe₇⁺(SO₄)₃(OH); and natrojarosite, NaFe₇⁺(SO₄)₃(OH). A large compositional gap occurs between alunite-natroalunite and jarosite-natrojarosite. This gap has no crystal chemical basis because Al and Fe can readily substitute for each other in octahedral site coordination. We believe the “on-off switch” behavior between early alunite and later jarosite is caused by an oxidant entering the system, oxidizing Fe²⁺ in solution to Fe³⁺, raising the Eh and possibly oxidizing H₂S to lower the pH, and thus stabilizing jarosite relative to alunite. The activity of Fe (as Fe³⁺) increased in the solution because of prolonged alunite crystallization but could not readily enter the crystal structure until it was oxidized to Fe³⁺. The jarosite overgrowths show striking oscillatory zoning of Na- and K-rich bands. This reflects up to an order of magnitude change in the fluid K/Na ratio. These textures are interpreted to represent rapid growth and kinetic control of delivery of free Na and K to the crystal-fluid interface. This could be due to some combination of Na and K diffusion rates in the solution and complex ion breakdown involving Na and K.

Keywords: Jarosite, Mars, electron microprobe, terrestrial analogs

INTRODUCTION

Martiarn jarosite was identified using data collected by the Mars Exploration Rover (MER) Mössbauer instrument (Klingelhöfer et al. 2004). The Mössbauer instrument identified jarosite and hematite as important phases in outcrop and regolith of the equatorial site Meridiani Planum, but could not provide the detailed chemistry (major, minor, and trace), stable isotope data for S, H, and O, or ages from Ar–Ar or K–Ar techniques that terrestrial laboratories have provided for terrestrial samples. Martian jarosite could have formed from low-temperature processes (e.g., McLennan et al. 2005) or high-temperature (hydrothermal) processes (e.g., McCollom and Hynek 2005; Papike et al. 2006). Therefore, terrestrial analog studies for martian jarosite should include samples from a variety of environments. Navrotsky et al. (2005) and Papike et al. (2006) describe the important information we could acquire from martian jarosite if we can obtain a sample. However, sample return from Mars is a long way into the future. In the meantime, we will search for jarosite in martian meteorites. To be ready for such a discovery, we must better understand the chemistry of jarosite–alunite as a recorder of the aqueous solutions from which it formed.

A particularly good example of alunite–jarosite as a recorder of aqueous fluid evolution is provided by samples from the Goldfield Au-Ag mining district, Nevada (Keith et al. 1979; Papike et al. 2006). Our main focus in this paper is on a sample containing jarosite and alunite (Keith et al. 1979), labeled 185-78-1. This sample is from the Preble Mountain area and occurs in the same locale as the precious metal deposits, but it is not directly associated with the ore deposits. A map showing sample localities is provided in Keith et al. (1979). The other samples examined in this study are also from the Goldfield area and are labeled 90-6, 89-8, and 85-2. These samples contain only alunite and their localities are discussed in detail by Vikre et al. (2005).

Geochemical examination of samples 90-6, 89-8, and 85-2 shows alunite-pyrite S-isotope equilibrium temperatures of 215–305 °C for ledge wall rocks, and ⁴⁰Ar/³⁹Ar ages of mineralized alunite bands of 20.3 to 19.8 Ma (Vikre et al. 2005). The Keith et al. (1979) analysis of alunite and jarosite in sample 185-78-1 shows a jarosite K-Ar age of 20 Ma that is concordant with the age of mineralization. The normal sequence of crystallization in 185-78-1 is alunite followed by jarosite. Initially, alunite formed comb-like growths surrounding silicified rock breccia fragments that extend into fractures and vugs. Then both alunite and jarosite formed crystalline aggregates lining the vugs. In the final stage, jarosite alone crystallized and encrusted the remaining vein walls. Where the aggregates were absent, jarosite filled open spaces among alunite crystals and formed terminations on some. Keith et al. (1979) propose that the two minerals formed in one of two ways: (1) All of the Preble Mountain localities were first deficient in Fe and then were flooded with Fe-rich solutions, or (2) the late-stage hydrothermal fluids underwent changes in Eh and pH, leading to oxidation of Fe²⁺ in solution to Fe³⁺ and precipitation of jarosite. In this paper, we report new data for major and minor elements in Goldfield alunite and jarosite to distinguish between the two Keith et al. (1979) models, and