A review of the stable-isotope geochemistry of sulfate minerals in selected igneous environments and related hydrothermal systems

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Abstract

The stable-isotope geochemistry of sulfate minerals that form principally in *I*-type igneous rocks and in the various related hydrothermal systems that develop from their magmas and evolved fluids is reviewed with respect to the degree of approach to isotope equilibrium between minerals and their parental aqueous species. Examples illustrate classical stable-isotope systematics and principles of interpretation in terms of fundamental processes that occur in these systems to produce (1) sulfate in igneous apatite, (2) igneous anhydrite, (3) anhydrite in porphyry-type deposits, (4) magmatic-hydrothermal alunite and closely related barites in high-sulfidation mineral deposits, (5) coarse-banded alunite in magmatic-steam systems, (6) alunite and jarosite in steam-heated systems, (7) barite in low-sulfidation systems, (8) all of the above minerals, as well as soluble Al and Fe hydroxysulfates, in the shallow levels and surface of active stratovolcanoes. Although exceptions are easily recognized, frequently, the sulfur in these systems is derived from magmas that evolve fluids with high H_2S/SO_2. In such cases, the $\delta^{34}S$ values of the igneous and hydrothermal sulfides vary much less than those of sulfate minerals that precipitate from magmas and from their evolved fluids as they interact with igneous host rocks, meteoric water, oxygen in the atmosphere, and bacteria in surface waters.

Hydrogen isotopic equilibrium between alunite and water and jarosite and water is always initially attained, thus permitting reconstruction of fluid history and paleoclimates. However, complications may arise in interpretation of δD values of magmatic-hydrothermal alunite in high-sulfidation gold deposits because later fluids may effect a postdepositional retrograde hydrogen–isotope exchange in the OH site of the alunite. This retrograde exchange also affects the reliability of the SO_4–OH oxygen–isotope fractionations in alunite for use as a geothermometer in this environment. In contrast, retrograde exchange with later fluids is not significant in the lower temperature steam-heated environment, for which SO_4–OH oxygen–isotope fractionations in alunite and jarosite can be an excellent geothermometer. Sulfur isotopic disequilibrium between coexisting (but noncontemporaneous) igneous anhydrite and sulfide may occur because of loss of fluid, assimilation of country-rock sulfur during crystallization of these minerals from a magma, disequilibrium effects related to reactions between sulfur species during fluid exsolution from magma, or because of retrograde isotope exchange in the sulfides. Anhydrite and coexisting sulfide from porphyry deposits commonly closely approach sulfur–isotope equilibrium, as is indicated by the general agreement of sulfur–isotope and filling temperatures (315 to 730 °C) in quartz. The data from anhydrite and coexisting sulfides also record a

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significant range in H_2S/SO_4^{2-} and $\delta^{34}S_{\sum S}$ among deposits and even during the course of mineralization at a single deposit. Sulfur isotopic disequilibrium among aqueous sulfur species may occur in any hydrothermal environment except the relatively high-temperature (200–400 °C) low-pH (<3) magmatic-hydrothermal environment, in which SO_4^{2-} forms along with H_2S from the disproportionation of SO_2 during the condensation of a magmatic vapor plume. Magmatic-steam alunite forms from expanding SO_2-rich magmatic vapors that rise so rapidly that sulfur isotopic exchange between SO_4^{2-} and H_2S does not occur during disproportionation of SO_2. Such alunite has $\delta^{34}S$ values similar to that of the bulk sulfur in the magma. Residence times of SO_4^{2-} in steam-heated systems, although seldom long enough to permit more than partial sulfur–isotope exchange with streaming H_2S, often are long enough to permit oxygen–isotope equilibrium with water. In active stratovolcanoes, aqueous sulfate derived from the disproportionation of SO_2 and the oxidation of H_2S can also mix with that derived from the oxidation of pyrite near the surface. In the near-neutral low-sulfidation system at Creede, CO, isotopic exchange among hydrothermal aqueous species was so slow that sulfur and even oxygen isotopic signatures derived from bacteriogenic and thermochemical reduction of sulfate in moat sediments are observed in hydrothermal barite.

1. Introduction

Studies of the stable isotopes of sulfate minerals, especially when coupled with isotopic data on coexisting minerals, have been exceptionally powerful tools in the study of hydrothermal and volcanic systems for more than 40 years. A number of comprehensive reviews of the controls of the oxygen– and sulfur–isotope systematics of sulfur-bearing minerals in ore deposits have been written (e.g., Ohmoto and Rye, 1979; Ohmoto, 1986; Ohmoto and Goldhaber, 1997; Seal et al., 2000). The purpose of this paper is to review the principles governing the stable-isotope systematics of hydrothermal sulfate minerals in a variety of geological and geochemical environments involving typical convergent-margin *I*-type magmas (Chappell and White, 1974) and continental equivalents and their evolved fluids as they interact with igneous host rocks, meteoric water, and the atmosphere and biosphere. One of the characteristics of sulfate minerals in nearly all environments is their tendency to reflect sulfur isotopic disequilibrium between reduced and oxidized sulfur species and, in some cases, to reflect oxygen isotopic disequilibrium between SO_4^{2-} and water. This paper reviews some of the major processes that operate in selected magmatic and related hydrothermal systems and discusses what stable-isotope equilibrium or disequilibrium, as observed in the minerals of representative examples, reveals about the processes (and their rates) that operate in different environments within these systems.

Fig. 1. Models showing (a) inferred relationships between the porphyry and acid sulfate environments to magma, water-rich carapace, the brittle–ductile transition, and the location of sulfur-bearing minerals. The inferred process of parent aqueous sulfate formation is also indicated. The carapace of the magma is typically at 2–6 km depth. The magmatic-hydrothermal environment leading to alunite+pyrite+quartz+kaolinite assemblages results from the disproportionation of SO_2, producing SO_4^{2-} and H_2S in a magmatic vapor plume that typically is initially H_2S-dominant as it separates from brine at the brittle–ductile transition. The magmatic-steam environment leading to coarse-grained banded alunite results from expansion of rapidly rising SO_2-dominant low-density magmatic vapor that is probably derived directly from a magma. The steam-heated environment leading to alunite±jarosite+kaolinite results from the oxidation of H_2S by atmospheric oxygen at shallow levels. H_2S in a stratovolcano may be derived directly from magma as opposed to being boiled off of deeper hydrothermal fluids. Pyrite formed below the oxidized zone in this environment in stratovolcanoes may later undergo supergene oxidation, resulting in jarosite+gypsum+soluble sulfates+smectite. Magmatic-steam and magmatic-hydrothermal environments are separated for clarity. The water-saturated carapace is envisioned as defined by Burnham (1979). (b) Steam-heated environment overlying a boiling near-neutral hydrothermal system with 'adularia'–sericite-type mineralization driven by a deep heat source. Alunite±jarosite may be produced in the acid steam-heated environment overlying boiling hydrothermal fluids, and barite may be produced in a more neutral zone of mixing with meteoric water. The curved bold arrows indicate fluid flow. Modified from Henley and Ellis (1983), Rye et al. (1992), and Rye (1993). The system portrayed in panel (b) could also be drawn as a distal extension of the system in panel (a) (Hedenquist and Lowenstern, 1994).