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Origin of secondary sulfate minerals on active andesitic stratovolcanoes

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Abstract

Sulfate minerals in altered rocks on the upper flanks and summits of active andesitic stratovolcanoes result from multiple processes. The origin of these sulfates at five active volcanoes, Citlaltépetl (Mexico), and Mount Adams, Hood, Rainier, and Shasta (Cascade Range, USA), was investigated using field observations, petrography, mineralogy, chemical modeling, and stable-isotope data. The four general groups of sulfate minerals identified are: (1) alunite group, (2) jarosite group, (3) readily soluble Fe- and Al-hydroxysulfates, and (4) simple alkaline-earth sulfates such as anhydrite, gypsum, and barite. Generalized assemblages of spatially associated secondary minerals were recognized: (1) alunite+silica±pyrite±kaolinite±gypsum±sulfur, (2) jarosite+alunite+silica; (3) jarosite+smectite+silica±pyrite, (4) Fe- and Al-hydroxysulfates+silica, and (5) simple sulfates+silica±Al-hydroxysulfates±alunite.

Isotopic data verify that all sulfate and sulfide minerals and their associated alteration assemblages result largely from the introduction of sulfur-bearing magmatic gases into meteoric water in the upper levels of the volcanoes. The sulfur and oxygen isotopic data for all minerals indicate the general mixing of aqueous sulfate derived from deep (largely disproportionation of SO_2 in magmatic vapor) and shallow (oxidation of pyrite or H_2S) sources. The hydrogen and oxygen isotopic data of alunite indicate the mixing of magmatic and meteoric fluids. Some alunite-group minerals, along with kaolinite, formed from sulfuric acid created by the disproportionation of SO_2 in a condensing magmatic vapor. Such alunite, observed only in those volcanoes whose interiors are exposed by erosion or edifice collapse, may have $\delta^{34}S$ values that reflect equilibrium (350±50 °C) between aqueous sulfate and H_2S. Alunite with $\delta^{34}S$ values indicating disequilibrium between parent aqueous sulfate and H_2S may form from aqueous sulfate created in higher level low-temperature environments in which SO_2 is scrubbed out by groundwater or where H_2S is oxidized. Jarosite-group minerals associated with smectite in only slightly altered volcanic rock are formed largely from aqueous sulfate derived from supergene oxidation of hydrothermal pyrite above the water table. Soluble Al- and Fe-hydroxysulfates form in low-pH surface environments, especially around fumaroles, and from the oxidation of hydrothermal pyrite. Anhydrite/gypsum, often associated with native sulfur and occasionally with small amounts of barite, also commonly form around fumaroles. Some occurrences of anhydrite/gypsum may be secondary, derived from the dissolution and reprecipitation of soluble sulfate. Edifice collapse may also reveal deep veins of anhydrite/gypsum±barite that formed from the mixing of saline fluids with magmatic sulfate and dilute meteoric water. Alteration along structures associated with both

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hydrothermal and supergene sulfates, as well as the position of paleo-water tables, may be important factors in edifice collapse and resulting debris flows at some volcanoes.

Keywords: Stratovolcanoes; Acid-sulfate alteration; Stable isotopes; Chemical modeling; Sulfates; Alunite; Jarosite; Hydroxysulfates

1. Introduction

Volcanoes annually expel more than 10.4 Mt of sulfur as gases and particulates into Earth's atmosphere (Andres and Kasgnoc, 1998). As sulfurous gases and fluids move through relatively quiescent often glacier-capped volcanoes, a significant amount of sulfur is captured as native sulfur, and as sulfate and sulfide minerals during alteration of the rocks. In this paper, we describe the field relationships, petrography, chemical stability, and stable isotopic compositions of various sulfate minerals from altered flanks and summits of five active stratovolcanoes. These data are used to constrain the origin of the secondary sulfate minerals in terms of the processes responsible for their parent aqueous sulfate and associated depositional environments.

Sulfate minerals have been noted around active fumaroles on stratovolcanoes since ancient times. More recently, Stoiber and Rose (1974) reported a number of sulfates from fumarole encrustations associated with Central American volcanoes and summarized the literature on earlier discoveries. Africano and Bernard (2000) described various sulfate minerals in the fumarolic environment of Usu volcano, Japan. Zimbelman et al. (2000) described natroalunite and minamiite around fumaroles on the summit of Mount Rainier, Washington. Gypsum and anhydrite have been described around fumaroles at numerous volcanoes (e.g., Goff and McMurtry, 2000). Alunite, jarosite, and simple sulfates have also been noted in the interiors of stratovolcanoes where exposed by edifice collapse (Zimbelman, 1996). Acid-sulfate and related argillic alteration have been shown to detrimentally affect the stability of a volcanic edifice (Lopez and Williams, 1993; Zimbelman, 1996; Watters et al., 2000; Watters et al., 2001). Therefore, understanding the processes controlling the distribution and formation of hydrothermal alteration on volcano edifices may be important in hazard mitigation. The sulfate minerals that form directly from magmas or from deep hydrothermal processes often related to porphyry copper deposits, for example, are not discussed in this paper.

2. Volcano descriptions

We studied active andesitic and dacitic stratovolcanoes in the eastern Trans-Mexican Volcanic Belt and in the Cascade Range of the western United States (Fig. 1, inset). The volcanoes can be grouped by: (1) their seismicity, with relatively low levels at Mount Adams and Mount Shasta and more moderate levels at Citlaltépetl, Mount Hood, and Mount Rainier (Clarke and Carver, 1992; Stanley et al., 1996; Moran et al., 2000), and (2) the presence or lack of domes, with Citlaltépetl, Mount Hood, and Mount Shasta containing abundant domes and Mount Adams and Mount Rainier generally lacking domes. All of these volcanoes contain ice caps on their upper slopes, exposed hydrothermally altered sulfate-bearing rock, active fumaroles, and have undergone edifice collapse. Representative occurrences of sulfate minerals were sampled from outcrops on the summits and upper flanks of all of these volcanoes and from a debris flow at Mount Rainier.

2.1. Citlaltépetl

Citlaltépetl (Pico de Orizaba, 5675 m), the easternmost major volcano in the ca. 1000-km Trans-Mexican Volcanic Belt, is North America's highest volcano and third highest peak. According to Carrasco-Núñez (1997) and Carrasco-Núñez and Gomez-Tuena (1997), Citlaltépetl volcano consists of three superimposed stratovolcano cones, each of which was accompanied by dome intrusions, with most rock of andesitic or dacitic composition (Fig. 1). The cone-building events occurred at 650 to 500 ka, 290 to 210 ka, and in Holocene time, including as recently as 700