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Sulfur isotope fractionation during the May 2003 eruption of Anatahan volcano, Mariana Islands: Implications for sulfur sources and plume processes

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Abstract

Sulfur isotope compositions of pumice and adsorbed volatiles on ash from the first historical eruption of Anatahan volcano (Mariana arc) are presented in order to constrain the sources of sulfur erupted during the period 10–21 May, 2003. The isotopic composition of S extracted from erupted pumice has a narrow range, from $\delta^{34}S_{V\text{-}CDT}$ +2.6‰ to +3.2‰, while the composition of sulfur adsorbed onto ash has a larger range (+2.8‰ to +5.3‰). Fractionation modeling for closed and open system scenarios suggests that degassing of SO_2 raised the $\delta^{34}S_{V\text{-}CDT}$ value of S dissolved in the melt from an initial composition of between +1.6‰ and +2.6‰ for closed-system degassing, or between −0.5‰ and +1.5‰ for open-system degassing, however closed-system degassing is the preferred model. The calculated values for the initial composition of the magma represent a MORB-like ($\delta^{34}S_{V\text{-}CDT} \sim 0$‰) mantle source with limited contamination by subducted seawater sulfate ($\delta^{34}S_{V\text{-}CDT}$ +21‰). Modeling also suggests that the $\delta^{34}S_{V\text{-}CDT}$ value of SO_2 gas in closed-system equilibrium with the degassed magma was between +0.9‰ and +2.5‰. The $\delta^{34}S_{V\text{-}CDT}$ value of sulfate adsorbed onto ash in the eruption plume (+2.8‰ to +5.1‰) is consistent with sulfate formation by oxidation of magmatic SO_2 in the eruption column. The sulfur isotope composition of sulfate adsorbed to ash changes from lower $\delta^{34}S$ values for ash erupted early in the eruption to higher $\delta^{34}S$ values for ash erupted later in the eruption. We interpret the temporal/stratigraphic change in sulfate isotopic composition to primarily reflect a change in the isotopic composition of magmatic SO_2 released from the progressively degassing magma and is attributed to the expulsion of an accumulated gas phase at the beginning of the eruption. More efficient oxidation of magmatic SO_2 gas to sulfate in the early water-rich eruption plume probably contributed to the change in S isotope compositions observed in the ash leachates.

1. INTRODUCTION

The purpose of this study is to investigate S sources, degassing processes, and the formation of sulfate salts adsorbed to ashes during the 2003 eruption of Anatahan. On 10 May 2003 Anatahan volcano (16°21′N145°40′E; see Fig. 1) erupted for the first time in recorded history, sending ash up to 13 km above sea level. Since the initial hydromagmatic subplinian eruption (de Moor, 2005; Pallister et al., 2005), the volcano has produced low viscosity lava domes, cinder cones, strombolian eruptions and weak explosive events (Smithsonian Institution, 2003–2009). On 6 April 2005, Anatahan entered the most explosive episode since the initial eruption, producing an ash column up to 15 km high. Two more low-level eruptive periods occurred in 2006 and 2008–2009 that were mostly recognized

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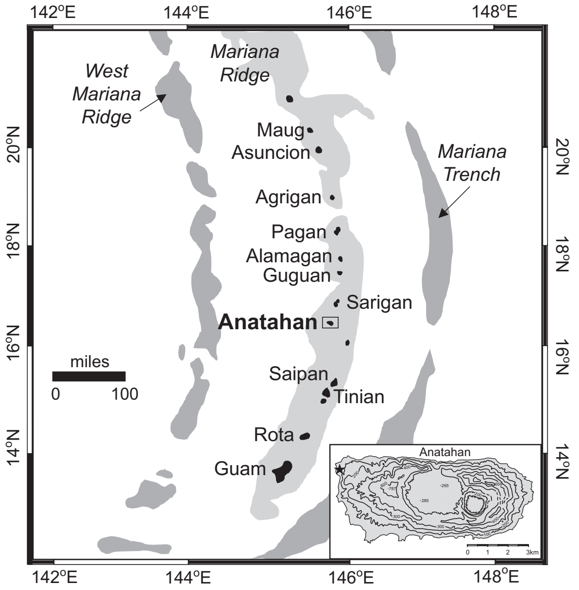

Fig. 1. Map of the Mariana Arc showing the location of Anatahan (from Wade et al., 2005). The inset shows the location of the West Beach sampling site as a star on the topographic map of the island (from Watanabe et al., 2005), which also shows the volcano's summit caldera and East Crater.

through seismic activity and remote sensing of $SO_2 \pm$ ash plumes (Smithsonian Institution, 2003–2009).

De Moor et al. (2005) and Pallister et al. (2005) identified a mass-balance discrepancy between the mass of SO_2 emitted (measured by ground-based spectroscopy and satellite; Wright et al., 2005) and the mass of erupted magma (Trusdell et al., 2005) based on S concentrations in glass inclusions and matrix glass. This "sulfur excess" has been observed at other arc eruptions (Rose et al., 1982; Williams et al., 1990; Andres et al., 1991; Gerlach et al., 1996) and has variously been attributed to accumulation of a vapor phase at the top of magma chambers (Varekamp et al., 1984; Gerlach et al., 1996; Wallace, 2005; Shinohara, 2008), S contribution from un-erupted mafic magma (de Hoog et al., 2001a; Hervig et al., 2002; Wallace et al., 2003) and/or the remobilization of S stored in hydrothermal systems (Oppenheimer, 1996; de Moor et al., 2005; Wallace, 2005).

While the source of the measured SO_2 in eruption clouds must ultimately be from magma in crustal reservoirs, degassing processes between gas exsolution from the melt and SO_2 plume flux measurement are not well understood. Direct sampling of high temperature fumaroles represent compositions of gases derived from quiescent magma (Giggenbach, 1996; Fischer et al., 1997, 1998); however, these compositions are variably affected by hydrothermal processes and direct sampling is impossible during explosive eruptions. Filter sampling of gases and particles from plumes provides information on eruptive gas compositions and plume processes and has led to the identification of sulfate and chloride salts and sulfuric acid aerosols as common products in the plume (Cadle et al., 1979; Smith et al., 1982; Casadevall et al., 1984; Rose et al., 1988, 2006). It has been estimated that ~30% of the total emitted S can be scavenged from plumes by adsorption as sulfates onto ash, which is deposited (Rose, 1977; Varekamp et al., 1984; de Hoog et al., 2001a).

Ash leachate analysis, used to determine concentrations of adsorbed water-soluble components on ash, is an indirect method of determining gas compositions of plinian eruption columns (Taylor and Stoiber, 1973; Rose, 1977). Water soluble sulfate, chloride, and other salts, as well as H_2SO_4 aerosol droplets, are produced in the column and adsorbed onto ash particles (Rose, 1977; Smith et al., 1982; Hinkley and Smith, 1987). Ash deposits unaffected by rainwater leaching therefore preserve a stratigraphic record of chemical changes within eruption columns. Edmonds et al. (2003) showed that the S/Cl ratio measured remotely by ground-based open path Fourier Transform spectroscopy (OP-FTIR) corresponds closely with that measured in ash leachates, making for a valid proxy for eruption plume S and Cl chemistry.

The isotope composition of S dissolved in juvenile eruptive ejecta is a product of magmatic S sources and is subject to modification by degassing processes. Sulfur from Mariana arc volcanic rocks has a wide range in $\delta^{34}S$ values from $\delta^{34}S_{V\text{-}CDT}$ $-0.5‰$ to $+20.7‰$ (Woodhead et al., 1987; Alt et al., 1993). Alt et al. (1993) and Woodhead et al. (1987) argued that the higher $\delta^{34}S$ values of some Mariana Arc rocks indicate mixing between mantle-derived S (with an isotopic composition of ~0‰; Sakai et al., 1984) and recycled seawater sulfate ($\delta^{34}S_{V\text{-}CDT}$ $+21‰$) introduced into the mantle wedge by subduction. Alt et al. (1993) acknowledge that S fractionation during degassing from a MORB composition could reproduce the observed wide range of S isotope compositions, but argued against this as a likely mechanism of ^{34}S enrichment. Other authors (Sakai et al., 1982; Zheng, 1990; Mandeville et al., 1998, 2009) showed that open-system degassing can cause substantial $\delta^{34}S$ variability in volcanic rocks.

2. PREVIOUS WORK

The May 2003 Anatahan eruption products are classified as medium-K andesite with tholeiitic affinity (SiO_2 ~61.2 wt.%, MgO ~2.0 wt.%, K_2O ~1.5 wt.%, and Fe_2O_3 ~9.3 wt.%) (de Moor et al., 2005). Average oxygen fugacity of ΔNNO +1.2 (de Moor et al., 2005) was calculated based on the ratio of Fe_2O_3/FeO in whole rock samples (Kilinc et al., 1983). Magmatic temperatures estimated from two pyroxene geothermometry are 1050–1100 °C (de Moor et al., 2005; Pallister et al., 2005).

Abundant evidence indicates that Anatahan's 2003 eruptive episode was initially phreato-magmatic in character. Pallister et al. (2005) report quench-textured lapilli and fine-grained (generally <100 μm in diameter) hydrothermal minerals (such as clays, and S bearing minerals) in the ash. The abundance of accretionary lapilli in the basal units indicates a water-rich eruption column (Fig. 2; de Moor et al. (2005)). Loss on ignition (LOI) values decrease systematically through the eruptive deposits, from 2.3 wt.% (earliest deposits) to 1.4 wt.% (latest deposits), and was