Decompression experiments for sulfur-bearing hydrous rhyolite magma: Redox evolution during magma decompression

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ABSTRACT

We performed decompression experiments on sulfur-bearing hydrous rhyolite magma at a temperature of 800 °C to investigate redox evolution during magma decompression. The magma was continuously decompressed from 100 MPa to 10–50 MPa at rates of 10 and 100 MPa h⁻¹. The evolution of the ferric to total iron ratio (Fe³⁺/Fe total) during decompression was investigated using XANES, and redox evolution was determined based on a thermodynamic calculation and measured Fe³⁺/Fe total. Before decompression, the sample was buffered from NNO to NNO+1, and the pre-exsolved fluid phase and sulfide crystal coexisted. Sulfide crystals were found in all decompressed samples, and Fe³⁺/Fe total showed a slight decrease with decompression. It was confirmed that the sample in a gold capsule was not influenced by the change in redox conditions outside of the capsule for the timescale of the decompression experiments; thus, the decompressed sample reflected the redox evolution in magma during decompression.

Our experiments indicated that magma decompression causes a slight reduction when it includes water and sulfur. This evolution is qualitatively explained by sulfur degassing and fluid-melt redox equilibria. During the fluid-melt redox equilibria, magma is reduced if the existence of a pre-exsolved fluid phase is assumed, while the model calculation shows that magma is oxidized when it contains only water or no pre-exsolved fluid phases. This is because sulfur buffers the oxidation of magma through a reaction with oxygen in the fluid phase. Therefore, we inferred that the redox condition of magma is not oxidized during explosive volcanism with a pre-exsolved fluid phase and closed-system degassing. In contrast, if magma experiences open-system degassing, it may be oxidized, resulting in the breakdown of sulfide crystals as observed in some pyroclasts and lavas.

Keywords: Rhyolitic magma, decompression, redox evolution, sulfur, water

INTRODUCTION

Water and sulfur are the major volatile components in magma, along with carbon, chlorine, and fluorine (e.g., Wallace 2005; Wallace et al. 2015). During the ascent of magma to the surface (decompression) in volcanic eruptions, these volatiles show complicated degassing behavior. In particular, water and sulfur dissolve as at least two chemical species in silicate melt and react with each other in the fluid phase, and their degassing during the ascent controls redox evolution of magma (Burgisser and Scaillet 2007; Blundy et al. 2008; Moussallam et al. 2014; Humphreys et al. 2015). Investigating the processes of the redox evolution caused by water and sulfur degassing is essential to the understanding of the oxygen fugacity of magma and the mantle based on the petrological analysis of groundmass glass in pyroclasts and lavas (e.g., Carmichael 1991; Carmichael and Ghiorsso 1990; Kelley and Cottrell 2009; Moussallam et al. 2014, 2016) and also to modeling and prediction of the chemical species of volcanic gases emitted to the surface (Burgisser and Scaillet 2007; Gaillard et al. 2011).

During magma ascent, water (H₂O) dissolved as hydroxyl group and molecular water in silicate melt (e.g., Stolper 1982; Nowak and Behrens 1995) exsolves due to decompression and a decrease in H₂O solubility, resulting in the formation of bubbles. At least two species of sulfur, S²⁻ and S⁶⁺, dissolve into silicate melt depending on oxygen fugacity, temperature, and chemical composition (e.g., Baker and Moretti 2011). Sulfur diffuses into the bubbles during decompression, and the partition relation of sulfur between melt and bubbles depends on pressure, temperature, and oxygen fugacity (e.g., Scaillet et al. 1998; Keppler 1999, 2010). In the fluid phase (here, “fluid” refers to the aqueous fluid phase containing sulfur), sulfur appears as several chemical species (mainly H₂S and SO₂). Additionally, sulfide and sulfate crystals are stable as the solid phase, depending on oxygen fugacity, when sulfur fugacity in magma is high enough. For instance, pyrrhotite is a stable phase in silicic magma under a redox condition of < ∼NNO+1; anhydrite is found in more oxidized magmas (e.g., Scaillet et al. 1998; Clemente et al. 2004).