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Anhydrite solubility in differentiated arc magmas

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Abstract

The solubility of anhydrite in differentiated arc magmas was experimentally studied at 200 MPa and 800–1000 °C over a range of oxygen fugacities, from 0.5 log units above the Ni–NiO buffer to the hematite–magnetite buffer. Anhydrite is stable only at oxidizing conditions ($fO_2 \geqslant \mathrm{Re{-}ReO_2}$), whereas sulfides only form under reducing conditions. The solubility of anhydrite in the melt ultimately regulates the amount of sulfur available to partition between melt and fluid phase during the eruption. At oxidizing conditions, the solubility product of anhydrite increases with temperature, nbo/t and melt water content. We provide a new calibration of the anhydrite solubility product ($K_{SP} = X_{CaO} * X_{SO3}$), which reproduces all available experimental data with greatly improved accuracy:

$$\ln K_{SP}^{\text{Anhydrite}} = 8.95 - 146.5\frac{\text{nbo}}{\text{t}} - 2.696\frac{10^4}{T(^\circ\text{K})} + 19.72\frac{\text{nbo}}{\text{t}}\,\frac{10^4}{T(^\circ\text{K})} + 0.409 \cdot \text{H}_2\text{O(wt.\%)}$$

In this equation, the molar fractions X_{CaO} and X_{SO3} in the melt as well as the number of non-bridging oxygen atoms per tetrahedron (nbo/t) are calculated on an anhydrous basis (H_2O refers to the melt water content, T is temperature in Kelvin). We apply our model to estimate the sulfur yield of some recent volcanic eruptions and we show that the sulfur yield of the 1991 Mt. Pinatubo dacite eruption was unusually large, because only a small fraction of the sulfur was locked up in anhydrite. In general, high sulfur yields are expected when anhydrite solubility in the melt is high, i.e. for somewhat depolymerized melts. For rhyolitic systems, most of the available sulfur will be locked up in anhydrite, so that even very large eruptions may only have a small effect on global surface temperatures. Our model therefore allows improved predictions of the environmental impact of explosive volcanic eruptions.

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1. INTRODUCTION

Volcanic eruptions have a major effect on Earth's atmosphere. Over long geologic timescales, climate is largely controlled by atmospheric CO_2 levels, which are maintained by the balance between CO_2 recycling in subduction zones and CO_2 release from volcanic activity (e.g. Pearson and Palmer, 2000). On short timescales, however, the CO_2 released by individual eruptions is negligible compared to the atmospheric CO_2 budget or to the present annual anthropogenic production of carbon dioxide (e.g. Williams et al., 1992). Nevertheless, individual eruptions can cause distinct changes in surface temperature. Global cooling has been observed in several years following major explosive eruptions in the historical record, the best-documented case probably being the 1991 Mt. Pinatubo eruption (McCormick et al., 1995; Robock, 2002). While it was initially believed that volcanic ashes are responsible for this cooling, it is now well established that the main cause is the injection of sulfur compounds into the stratosphere. Sulfur dioxide and other sulfur species are photochemically oxidized to SO_3, which rapidly attracts water to form H_2SO_4 ("sulfate") aerosols (McCormick

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et al., 1995; Robock, 2002). Unlike ashes, which settle down within a few weeks, these sulfate aerosols may remain in the stratosphere for more than a year, where they backscatter solar radiation and therefore cool the Earth's surface. There appears to be a good correlation between the sulfur yield of major explosive eruptions and global surface temperatures for the last centuries (Briffa et al., 1998). However, the precise magnitude of the cooling associated with some extremely large volcanic events, such as the 74 ka B.P. Toba eruption (Robock et al., 2009), is still subject to some uncertainty, as is the possible role of volcanic sulfur emissions in major mass extinction events (Self et al., 2008; Black et al., 2014). It is unquestionable, however, that sulfur is responsible for some of the most severe environmental effects of volcanic eruptions and understanding the sulfur budget of magmas and sulfur release from volcanoes is therefore a task of highest scientific and practical importance.

Since most silicate minerals hardly sequester any sulfur in their structure, the behavior of sulfur during an eruption is mainly controlled by two factors: (1) the partitioning of sulfur between the silicate melt and a fluid phase, before and during an eruption; and (2) the stability of accessory phases (Baker and Moretti, 2011; Parat et al., 2011a,b), mostly pyrrhotite FeS and anhydrite $CaSO_4$ that may lock up a large fraction of the total sulfur present in the magma. The main idea behind this reasoning is that re-equilibration between fluid and melt phases is a fast process that may even happen during eruptions (e.g. Fiege et al., 2014a), while solid phases such as pyrrhotite and anhydrite are relatively unreactive and unlikely to decompose during the rather short timescales of an explosive eruption (Hanic et al., 1985). Sulfur in the form of pyrrhotite and anhydrite is therefore unlikely to produce any immediate environmental effects. This is consistent with the fresh appearance of anhydrite phenocrysts in Mt. Pinatubo pumices (Bernard et al., 1991; see also Wallace and Gerlach, 1994 for further discussion). Breakdown of anhydrite during an eruption has been suggested as a possible mechanism for creating sulfur excesses in eruptions (Devine et al., 1984). A sulfur excess implies that the amount of sulfur released by a volcano is larger – often by orders of magnitude – than the amount of sulfur that may have been released by the degassing of the erupted magma (Westrich and Gerlach, 1992; Gerlach and McGee, 1994; Keppler, 1999; Wallace, 2001). However, it is now widely accepted that this phenomenon is related to the presence of a free gas phase in the magma chamber that extracted sulfur out of the entire magma reservoir prior to the eruption. This reservoir may also include batches of deep basic melts intruded below the erupted silicic magma (Edmonds et al., 2010). Rather than creating sulfur excesses, the stability of anhydrite may actually limit this effect by making sulfur unavailable for degassing during an eruption.

Since sulfur may occur in different oxidation states over the range of oxygen fugacities occurring in crust and mantle, the redox state of a magma is probably the most important variable controlling the behavior of sulfur during an eruption. In silicate melts, sulfur appears to be dissolved either as S^{2-} or S^{6+}, depending on the magmatic oxidation state (Carroll and Rutherford, 1988; Klimm et al., 2012). In high-temperature hydrothermal fluids and volcanic gases, SO_2 is often the most prominent sulfur species, with H_2S occurring only at rather reducing conditions (e.g. Fischer, 2008; Oppenheimer et al., 2011). Recent studies (Binder and Keppler, 2011; Ni and Keppler, 2012), however, suggest that S^{6+} likely in the form of some sulfate species may also occur in magmatic fluids at moderately oxidizing conditions near the Re–ReO_2 buffer, consistent with the observation of direct emission of sulfate aerosols by some volcanoes (Mather et al., 2006). Fluid/melt partition coefficients of sulfur are generally high, in the range of 40–500, and they appear to increase by about one order of magnitude when the oxygen fugacity decreases to the Ni–NiO buffer or below (Webster and Botcharnikov, 2011 and references therein). However, this does not necessarily mean that sulfur degassing becomes more efficient in reducing magmas, because low oxygen fugacities may also stabilize pyrrhotite FeS, which may sequester most of the sulfur in the magma. Under more oxidizing conditions ($fO_2 > \mathrm{Ni{-}NiO}$), crystallization of anhydrite may have a similar effect, but the solubility of anhydrite in melts appears to be generally larger than that of pyrrhotite. Moreover, anhydrite solubility is much less systematically studied (e.g. Carroll and Rutherford, 1987; Luhr, 1990, 2008; Li and Ripley, 2009; Beermann et al., 2011; Baker and Moretti, 2011; Parat et al., 2011a,b; Nowak, 2015).

In the present study, we provide new experimental data on anhydrite solubility in silicate melts as a function of temperature and oxygen fugacity in three natural magma compositions corresponding to the eruptions of El Chichón (Mexico, 1982, trachy-andesite), Mount Pinatubo (Philippines, 1991, dacite) and Mount Unzen (Japan, 1991–1995, rhyodacite). In addition, new data for a simple CaO-doped haplogranitic melt were also obtained. We use these data to calibrate a new model of anhydrite solubility in silicate melts. This model allows estimating what fraction of sulfur may be locked up in anhydrite during an eruption. We expect that this model will contribute to a better forecasting of the environmental effects of large explosive eruptions.

2. EXPERIMENTAL AND ANALYTICAL METHODS

2.1. Starting materials

Five starting glasses were prepared from stoichiometric mixtures of analytical grade SiO_2, TiO_2, $Al(OH)_3$, Fe_2O_3, $Mg(OH)_2$, $CaCO_3$, Na_2CO_3, and K_2CO_3. The mixtures were dehydrated and decarbonated by heating from room temperature to 1100 °C in 12 h and holding at the same temperature for a further 12 h. About 10 g of each mixture were then melted for 2 h at 1600 °C in a Fe-pre-saturated platinum crucible and quenched in distilled water. The resulting glasses were free of crystals and were crushed into a fine powder. The composition of the glasses closely matches the composition of the magmas selected for this study (Table 1). These are the trachy-andesite of the 1982 eruption of El Chichón (Carroll and Rutherford, 1987),