Sulfur degassing at Erta Ale (Ethiopia) and Masaya (Nicaragua) volcanoes: Implications for degassing processes and oxygen fugacities of basaltic systems

J. M. de Moor
Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, 87131, USA (mdemoor@unm.edu)
Now at Observatorio Vulcanológico y Sismológico de Costa Rica, Universidad Nacional, Heredia, Costa Rica

T. P. Fischer and Z. D. Sharp
Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, USA

P. L. King
Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico, USA
Now at Research School of Earth Sciences, Australian National University, Acton, Canberra ACT, Australia

M. Wilke
Deutsches GeoForschungsZentrum, Helmholtzzentrum Potsdam, Potsdam, Germany

R. E. Botcharnikov
Institut für Mineralogie, Leibniz Universität, Hannover, Germany

E. Cottrell
National Museum of Natural History, Smithsonian Institution, Washington, D.C., USA

M. Zelenski
Institute of Experimental Mineralogy, Russian Academy of Sciences, Moscow, Russia

B. Marty
Centre de Recherches Petrographiques et Géochimiques, CNRS, Ecole Nationale Supérieure de Géologie, Vandoeuvre-les-Nancy, France

K. Klimm
Institut für Geowissenschaften, Goethe Universität Frankfurt, Frankfurt am Main, Germany

C. Rivard
European Synchrotron Radiation Facility, Grenoble, France

D. Ayalew
Department of Earth Sciences, School of Earth and Planetary Sciences, Addis Ababa University, Addis Ababa, Ethiopia

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We investigate the relationship between sulfur and oxygen fugacity at Erta Ale and Masaya volcanoes. Oxygen fugacity was assessed utilizing Fe$^{3+}/\sum$Fe and major element compositions measured in olivine-hosted melt inclusions and matrix glasses. Erta Ale melts have Fe$^{3+}/\sum$Fe of 0.15–0.16, reflecting $f$O$_2$ of $\Delta$QFM 0.0 ± 0.3, which is indistinguishable from $f$O$_2$ calculated from CO$_2$/CO ratios in high-temperature gases. Masaya is more oxidized at $\Delta$QFM +1.7 ± 0.4, typical of arc settings. Sulfur isotope compositions of gases and scoria at Erta Ale ($\delta^{34}$S$\text{gas}$ ≈ 0.5‰; $\delta^{34}$S$\text{scoria}$ ≈ 0.9‰) and Masaya ($\delta^{34}$S$\text{gas}$ ≈ 4.8‰; $\delta^{34}$S$\text{scoria}$ ≈ 7.4‰) reflect distinct sulfur sources, as well as isotopic fractionation during degassing (equilibrium and kinetic fractionation effects). Sulfur speciation in melts plays an important role in isotope fractionation during degassing and $S^6+/\sum S$ is <0.07 in Erta Ale melt inclusions compared to >0.67 in Masaya melt inclusions. No change is observed in Fe$^{3+}/\sum$Fe or $S^6+/\sum S$ with extent of S degassing at Erta Ale, indicating negligible effect on $f$O$_2$, and further suggesting that H$_2$S is the dominant gas species exsolved from the $S^2-/S^2$-rich melt (i.e., no redistribution of electrons). High SO$_2$/H$_2$S observed in Erta Ale gas emissions is due to gas re-equilibration at low pressure and fixed $f$O$_2$. Sulfur budget considerations indicate that the majority of S injected into the systems is emitted as gas, which is therefore representative of the magmatic S isotope composition. The composition of the Masaya gas plume (+4.8‰) cannot be explained by fractionation effects but rather reflects recycling of high $\delta^{34}$S oxidized sulfur through the subduction zone.

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1. Introduction

This study investigates sulfur (S) degassing processes and sources through the study of S isotope compositions and speciation of magmatic gases and basaltic scoria from Erta Ale (Ethiopia) and Masaya (Nicaragua). The goal is to constrain conditions of degassing such as oxygen fugacity, temperature, and pressure in each system to ascertain primary magmatic S isotope compositions, assess S isotope fractionation, and investigate the relationship between S degassing and oxygen fugacity.

The multiple valence states of S (2− to 6+) result in complex geochemical behavior in both low and high-temperature environments. Sulfur is one of the most abundant constituents of volcanic gases, occurring predominantly as SO$_2$ ($S^{4+}$) and H$_2$S ($S^2-$) and is an important volatile component of mafic magmas [Giggenbach, 1996]. Sulfur degassing has been proposed as a mechanism that modifies the oxygen fugacity of magmas [Anderson and Wright, 1972; Burgisser and Scaillet, 2007; Kelley and Cottrell, 2012] and subduction of oxidized sulfur (sulfate) may be partially responsible for oxidation of the subarc mantle [Evans, 2012; Kelley and Cottrell, 2009; Klimm et al., 2012]. Fluxes of SO$_2$ are routinely measured in volcano monitoring because atmospheric concentrations of this species are easily detectable due
to its absorption of ultraviolet light [Galle et al., 2002; Platt, 1994; Stoiber et al., 1983]. Sulfur dioxide is an important volcanic gas in terms of climate impact on earth due to the oxidation of SO2 to sulfate aerosols in the atmosphere [Sigurdsson, 1990]. Volcanic degassing of S has also been proposed as an important source of surface sulfur on Mars [Banin et al., 1997; Settle, 1979] and volcanic SO3 has been proposed as an effective greenhouse gas in the martian climate [Gaillard and Scaillet, 2009] that may have allowed liquid surface water to exist [Haley et al., 2007; Johnson et al., 2008]. On Earth, degassing of volcanic SO2 during the Paleoproterozoic may have initiated the modern biogeochemical sulfur cycle and atmospheric oxygenation [Gaillard et al., 2011]. The sulfur cycle is therefore important for chemical modification of Earth’s reservoirs, and is intricately linked with planetary-scale redox conditions.

[S] Sulfur isotope compositions ($^{34}S/^{32}S$ reported in delta notation relative to the Canyon Diablo Troilite standard) provide a tool for studying the sulfur cycle, sources of sulfur, degassing processes, and magmatic redox conditions though distinguishing source compositions from fractionation processes can be problematic. Mid-ocean ridge basalts (MORB) have a $\delta^{34}S$ value of $+0.3 \pm 0.5\%$ [Sakai et al., 1984] and variations in $\delta^{34}S$ of diamond-hosted sulfides suggest that the mantle may be heterogeneous due to subduction of material with variable S isotope composition [Chaussidon et al., 1987]. In general, high $\delta^{34}S$ values are associated with more oxidized forms of S (sulfate) whereas relatively low $\delta^{34}S$ values are associated with reduced S such as in sulfides. High $\delta^{34}S$ values of arc lavas have been attributed to recycling of subducted sulfate through subduction zones [Ält et al., 1993; Mandeville et al., 1998; Udéa and Sakai, 1984]. Seawater sulfate has a high S isotope composition of $+21\%$ primarily due to the sequestration of pyrite with low $\delta^{34}S$ (typically $\sim40\%$ lower than seawater sulfate) [e.g., Kurtz et al., 2003] formed by microbial reduction of seawater sulfate in oceanic crust and delivery of sulfate with $\delta^{34}S \sim +11\%$ to the oceans from weathering of continental crust [e.g., Holser et al., 1988]. Heavy S isotope signatures in magmas have also been used to argue for assimilation of oxidized crustal material [e.g., Gurenko et al., 2001].

[S] Sulfur isotope fractionation in magmatic systems is controlled by sulfur valence state in gas and melt, crystallization of S-bearing minerals, degassing, and temperature (see Marini et al. [2011] for a review of fractionation processes). Hydrothermal processes are associated with complex isotopic fractionation due to multiple S valence states in vapors (H2S, SO2), fluids (SO4$^{2-}$, S2$, S_{3}$, SO3$^{2-}$, polythionates, S3$^{-}$), and solid phases (sulfates such as anhydrite, elemental sulfur, pyrite, sulfides, and haune-nosean minerals), a wide range of temperatures, and slow isotopic equilibration at hydrothermal temperatures [e.g., Delmelle et al., 2000; Rye, 2005]. Gas interaction with hydrothermal fluids and deposition or remobilization of hydrothermal minerals or sublimates can modify the isotope composition of fumarolic gases [Delmelle et al., 2000; Giggenbach, 1987; Menyailov et al., 1986; Rowe, 1994]. Whereas fumarolic gases are subject to modification of S isotope signature from magmatic values by hydrothermal processes, plume gases from open vent volcanoes are more representative of magmatic gas compositions [Liotta et al., 2012]. Thus, in order to sample magmatic gases minimally affected by secondary processes this study focuses on the S isotope composition of persistent plumes directly emitted at high temperatures from open vent basaltic volcanoes. Sampling in close proximity to the degassing magma minimizes potential modification of gas S isotope compositions due to interactions with the atmosphere or hydrothermal systems.

[S] Equilibrium, mass-dependent S isotopic fractionation is significant even at magmatic temperatures and is primarily a function of sulfur speciation in melts and gases [Marini et al., 2011; Sakai et al., 1982]. The more oxidized S species tend to be isotopically enriched in $^{34}S$ due to stronger covalent bonding with the heavy isotope. Precipitation of sulfide or sulfate mineral phases from S saturated melts may significantly alter the S isotope composition of the residual melt in systems with S dissolved in multiple valence states [e.g., Marini et al., 2011]. Sulfur is dissolved in silicate melts as either S2 or SO4$^{2-}$ (S6+) in reduced and oxidized melts, respectively [e.g., Jugo et al., 2010; Wallace and Carmichael, 1994; Wilke et al., 2008], and is typically degassed as H2S (S2) or SO2 (S4+) (although minor gas species may occur such as C-O-S species and metal-S species). Figure 1 schematically shows the isotopic fractionation between melt and gas for different degassing scenarios. A melt dominated by S2 has lower $\delta^{34}S$ than SO2 gas if isotopic equilibrium is attained. However, a melt dominated by SO4$^{2-}$ has higher $\delta^{34}S$ than SO2 gas at equilibrium. Thus, equilibrium degassing of SO2 can lead to evolution.
of a melt toward higher or lower $\delta^{34}$S values depending on the dominant S species in the melt. A goal of this study is to evaluate isotopic equilibrium between magmatic gases and residual S in basaltic glasses from contrasting volcanic settings: a reduced rift zone and an oxidized subduction zone.

Erta Ale and Masaya were chosen as representative end-members of basaltic sulfur degassing where plume gases can be sampled in close proximity to the magma source and where no previous reports of magmatic S-bearing minerals existed. Erta Ale is a relatively reduced system with oxygen fugacity ($f_{O_2}$) close to the quartz-fayalite-magnetite (QFM) buffer [Bizouard et al., 1980; Giggenbach and Le Guern, 1976], whereas Masaya is relatively oxidized at $\Delta$QFM $>$ 1 [Mather et al., 2006a]. Both volcanoes degas persistently from open vents and lack extensive hydrothermal systems. Here, we report S isotope compositions of plume gases and scoria from Erta Ale and Masaya, $SO_2$ gas fluxes, and constraints on $f_{O_2}$, S speciation, and degassing temperature in order to assess S degassing, redox processes, isotope fractionation, and S sources in basaltic systems.

2. Geological Setting and $SO_2$ Fluxes

2.1. Erta Ale

Erta Ale volcano (13.60°N; 40.67°E) is located in the Afar region of the East African Rift in northern Ethiopia (Figure 2a). Rifting and magmatism in this area are driven by the African Superplume, which is a tilted low-velocity mantle structure that extends from the core-mantle boundary below southern Africa to the base of the lithosphere below northern east Africa [Ritsema et al., 1999]. Helium isotope ratios in the region reach values as high as 15 RA [Pik et al., 2006], where RA refers to the He isotope composition relative to that of air, and olivines from Erta Ale have $^{3}$He/$^{4}$He of 12.3 RA [Marty et al., 1996], indicating primordial $^{3}$He contribution from the lower mantle consistent with the influence of a deep plume. Radiogenic isotope and trace element compositions of basalts from the Erta Ale range are consistent with mixed depleted MORB and ocean island basalt (OIB) mantle sources [Barrat et al., 1998]. The crust in the region of Erta Ale was estimated by Hammond et al. [2011] to be 20 ± 2 km thick. Strontium and Nd isotopes indicate that no appreciable crustal contamination has influenced

![Figure 1. Schematic diagram showing end-member sulfur isotope fractionation degassing scenarios in simple melt-gas systems (i.e., no dense fluids or mineral phases). More oxidized S species bond more strongly with the heavy isotope, such that $\delta^{34}$S $SO_4^{2-}$ >> $SO_2$-$H_2S$-$S^{2-}$. (top left) At equilibrium, if a melt containing $S^{2-}$ degasses $SO_2$ gas, e.g., $\Delta$QFM ~ 0; $P$ ~ 1 bar) then the gas will have higher $\delta^{34}$S, resulting in residual melt with lower $\delta^{34}$S. (bottom left) The same melt degassing $H_2S$ (e.g., $P$ > 500 bars) will have little fractionation effect. Degassing of $SO_2$ or $H_2S$ from a melt with dissolved $SO_4^{2-}$ (high $f_{O_2}$; e.g., $\Delta$QFM ~ 2) will result in residual melt with higher $\delta^{34}$S, but degassing of $H_2S$ ($P$ >> 500 bars) has a larger fractionation effect.](image-url)
these magmas and that the crust is young and basaltic [Barberi and Varet, 1970; Barrat et al., 1998]. Erta Ale has a low Ba/La ratio of 5.8 [Zelenski et al., 2013] between that of MORB (~4) and OIB (~10) [Plank et al., 2002]. The composition of Erta Ale basalts erupted in November 2010 are classified as transitional basalts and phenocrysts phases are plagioclase (An$_{83-74}$) + clinopyroxene (En$_{46-48}$, Fs$_{9-13}$, Wo$_{41-43}$) + olivine (Fo$_{84-78}$) with no oxides, sulfides, or accessory phases [Field et al., 2012]. The 2010 lavas (Figure 2b) are similar in composition to older erupted rocks [Barberi and Varet, 1970; Barrat et al., 1998; Bizouard et al., 1980; Field et al., 2012]. Sulfides and oxides only occur in the more evolved magmas in the Erta Ale suite (trachytes to peralkaline rhyolites) and crystallize as late phases [Bizouard et al., 1980].

Degassing at Erta Ale takes place from two pit craters and a fumarole field located within the elliptical summit caldera (Figure 2b). The lava lake at Erta Ale has probably been active for over a century, and during the 1960’s and 1970’s both craters-hosted lava lakes [Le Guern et al., 1979; Oppenheimer et al., 2004; Sawyer et al., 2008]. Eruptions at Erta Ale are characterized by overflowing of the lava lake(s) and minor fire fountaining [Le Guern et al., 1979]. The latest eruption occurred in November 2010, just over 1 month before our expedition. Lava flows filled the central pit crater, overflowed into the main crater, and constructed a small spatter and cinder cone around the lava lake crater, which was about 15 m in diameter in January 2011.

Sulfur dioxide flux measurements were conducted at Erta Ale in 2003 [Oppenheimer et al., 2004] and sulfur emissions from Erta Ale were also measured in 2005 and 2009 [Le Guern et al., 2007; Oppenheimer et al., 2009].
Table 1. Sulfur Dioxide Fluxes From Erta Ale

<table>
<thead>
<tr>
<th>Reference</th>
<th>Date</th>
<th>Source</th>
<th>Tons/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Jan 2011</td>
<td>Total</td>
<td>91.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lava lake</td>
<td>60.2</td>
</tr>
<tr>
<td>Sawyer et al. [2008]</td>
<td>Oct 2005</td>
<td>Lava lake</td>
<td>59.6</td>
</tr>
<tr>
<td>Oppenheimer et al. [2004]</td>
<td>Mar 2003</td>
<td>Total</td>
<td>112.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lava lake</td>
<td>60.5</td>
</tr>
</tbody>
</table>

2.2. Masaya

Masaya (11.98°N; 86.16°W) is located in Nicaragua on the Central American Arc (Figure 2c), where the Cocos plate is subducted under the Caribbean plate at a rate of 77 mm/yr [De Mets., 2001]. Masaya is a tholeiitic basalt complex [Martin and Sigmarsson, 2007; Walker, 1989] that consists of nested calderas that have had several episodes of subsidence associated with Plinian explosive eruptions [Williams, 1983]. Phenocryst phases in erupted lavas are plagioclase, olivine, and clinopyroxene with magnetite as a minor phase [Walker et al., 1993]. The volcanoes of Nicaragua are characterized by the highest Ba/La [Carr et al., 1990] and 10Be values [Brown et al., 1982] worldwide, indicating a strong slab component influence in magma genesis. Masaya has one of the highest Ba/La ratios (~98) of the Central American volcanoes [Carr et al., 1990]. The crust beneath the Nicaraguan arc was estimated to be 25 ± 4 km thick by MacKenzie et al. [2008]. Walker et al. [1993] argued that major element, trace element, and 87Sr/86Sr compositions of post caldera lavas indicate little to no influence of crustal contamination, whereas the compositions of older lavas suggest 15–30% assimilation of acidic igneous rocks.

Recent activity is centered at Santiago crater (Figure 2d), which is ~1 km in diameter and located at the summit of a young cone within the caldera. The volcano has been actively degassing for ~150 years with episodes of intense gas emission “crises” with only minor magmatic ash eruptions [Rymer et al., 1998]. Sulfur dioxide flux measurements have been conducted since the 1970’s [Stoiber et al., 1986] and there is a good temporal record for Masaya since the mid 1990’s [Martin et al., 2010; Nadeau and Williams-Jones, 2009] (Figure 2). The average SO2 flux since 1996 has been ~1000 tons/d, representing 1.3–2.8% of global volcanic SO2 emissions and ~23% of the total SO2 flux from Central American volcanoes [Hilton et al., 2002; Mather et al., 2006b]. Four traverses conducted on 11 January 2009 on the Llano Pacaya road for this study yielded a low SO2 flux estimate of 325 tons/d (1σ of four traverses is 119 tons/d and these measurements are subject to large errors of ~50%), indicating that at the time of sample collection Masaya was at a minimum in its degassing cycle (Figure 3). Causes of variability and sources of error in SO2 flux measurements at Masaya are thoroughly discussed in Nadeau and Williams-Jones [2009] and Martin et al. [2010].

3. Methods

3.1. Gas Collection for Sulfur Isotope Composition and Complete Gas Chemistry

We used a method for collection of plume S for isotopic analysis adapted from Menyailov et al. [1986]. Two bubblers were used in series and plume gas was pulled through the apparatus using a small electric pump at a flow rate of 1 L/m (Figure S1). The first bubbler contained 50 mL of 60 g/L zinc acetate (0.3 M Zn(C2H3O2)2) solution in 10% acetic acid, a method adapted from Kiba et al. [1955] for the collection of H2S. The second bubbler contained 50 mL of 100 g/L barium chloride (0.4 M BaCl2·2(H2O)) in 10% H2O2 solution acidified to
pH 3 with HCl. Laboratory tests using pure, as well as diluted H2S and SO2, and gas mixtures, indicate that these solutions are highly efficient at stripping H2S and SO2 from the gas phase. Sulfur dioxide bubbled through two bubblers in series containing the BaCl2 solution results in a precipitate in the first bubbler only, indicating that all SO2 is stripped by the first. When used in series, H2S is precipitated as ZnS in the first bubbler and SO2 that is not dissolved in the first bubbler is precipitated as BaSO4 in the second. The solution + ZnS from the first bubbler is centrifuged and the supernate is added to the solution from bubbler 2, which results in precipitation of dissolved SO2 as BaSO4. This solution is then centrifuged (with multiple rinses) and dried to collect pure BaSO4. The ZnS from the first bubbler is converted to Ag2S by addition of AgNO3, centrifuged (with rinses) and dried. The BaSO4 and Ag2S are weighed to 10^-3 mg precision to determine SO2/H2S ratio. Considering that ≤1 μg of ZnS precipitated from H2S could go undetected and the average mass of BaSO4 collected from SO2 per sample was 85 μg the detection limit in terms of H2S/(SO2 + H2S) ratio is estimated to be ~0.05.

The sample collection technique was tested to ensure that no isotopic fractionation occurred during sampling (Table S1, supporting information). Reference H2S or SO2 gas was bubbled through the sampling apparatus at a range of concentrations (pure or dilute H2S, and 100% to <0.3% by volume SO2) at flow rates up to 1 L/min. The resulting precipitates showed δ34S values within analytical precision (1σ is <0.3‰) of the reference gas for both gases. The method was compared to the traditional Giggenbach method [Giggenbach and Goguel, 1989] at Sulfur Springs, NM, where bubbling hot springs emit H2S and no SO2 [Goff et al., 1985], and both methods gave identical results for δ34S of H2S (Table S1).

Samples were collected from gas plumes at Erta Ale and Masaya as close as possible to the source. At Erta Ale, plume gas was collected ~30 m from the degassing lava lake surface and at Masaya gases were collected at the crater rim. A 1 μm pore size filter (47 mm diameter Polytetrafluoroethylene (PTFE)) was attached at the inlet of the sampling setup to collect plume sulfate aerosols. The apparatus was run until BaSO4 precipitate was visible in the second bubbler and a typical sample resulted in the collection of 10–40 mg of BaSO4 (0.05–0.2 mol S). No ZnS precipitate was observed in any of the plume samples from Erta Ale or Masaya. The filters from the inlet of the system were sonicated in 18 MΩ deionized water to dissolve sulfate aerosols, then precipitated as BaSO4 by adding BaCl2, centrifuged, dried, and weighed to determine SO4^2-/SO2 ratio.

Gas samples were also collected from a high-temperature fumarole (1085°C) in the north crater of Erta Ale for complete gas chemistry and fO2 assessment using techniques described by Giggenbach and Goguel [1989]. The fumarole was sampled using a quartz glass tube attached to silicon tubing and Giggenbach bottles containing ~50 mL of 4 N NaOH solution. Low solubility/inert gases partition into the headspace whereas...
Argon isotope compositions were determined in the NaOH solution. Headspace gases (N₂, O₂, H₂, He, Ar, and CO) were analyzed at the University of New Mexico on a Pfeiffer Quadrupole Mass Spectrometer (QMS; mass range from 0 to 120 amu) equipped with a Faraday detector and operated in dynamic mode. Calibration of the QMS was performed with standard gas mixtures (Scott Specialty Gases; Mix 14: 1% Ar, 1% He, 1% O₂, 1% CH₄, 1% CO, 95% N₂; Mix 104: 99.995% Ar, 0.005% N₂) and data processing using the Quadstar software that allows for correction of potential mass interferences. The QMS analyses have a precision of <0.1% (concentration). Carbon dioxide concentrations were determined by titration of NaOH solutions using 0.1 N HCl. Chloride and F concentrations were measured by ion chromatography on aliquots of caustic solution (i.e., 4 N NaOH solution + dissolved acid gases), diluted by a factor of ten, and filtered using Dionex OnGuard® II H cartridges to remove hydroxyl groups. Samples were analyzed on a Dionex ion chromatograph following the techniques of Mitchell et al. [2010]. Total S was determined gravimetrically after precipitation of BaSO₄ from the NaOH solutions, and SO₂/H₂S was measured by alkaline iodine titration [Giggenbach and Goguel, 1989].

Argon isotope compositions were determined on splits of headspace gas at Centre de Recherches Pétrographiques et Géochimiques (CRPG), Nancy, France. Gas samples were transferred into high-vacuum metal containers, which were connected to the CRPG noble gas line held at 3 × 10⁻⁹ mbar. After overnight pumping, an aliquot of the gas was expanded into the line. It was purified sequentially over three getters working between 750°C and room temperature. Helium and neon were separated from other noble gases using a cryogenic trap (active charcoal at liquid nitrogen temperature) and analyzed (detailed method to be presented elsewhere). Argon was desorbed from the trap and analyzed with a noble gas static mass spectrometer (VG 5400). Blanks were always negligible (<1%) compared to the sample amounts. Uncertainties mostly represent the external reproducibility of the standard gas (atmospheric argon) which was relatively high during the analysis (though <5%) period because the mass spectrometer was settled for He isotope analysis and therefore had a low sensitivity for argon.

Scoria Sample Preparation

Scoria from Erta Ale was collected from the cinder/spatter cone (N13°36.201'E40°39.800') formed during the November 2010 eruption. Scoria samples from Masaya were collected around the crater rim (N11°58.968'W86°10.195') and the freshest available scoria was picked in the field. In both cases, vesicular scoria consisted of clasts <2 cm. For isotopic analysis, unaltered scoria was picked from bulk samples and soaked in 18 MΩ deionized water for 24 h to remove any water-soluble sulfate on clast surfaces. Samples were then dried at 120°C and lightly crushed in a stainless steel mortar and pestle and sieved to <2 mm and >0.25 mm. This size fraction was then inspected under a binocular microscope and any visible crystals or altered fragments were removed, leaving 15–20 g of glass that was then rinsed in deionized water, dried, and pulverized in an Al₂O₃ ceramic shatterbox.

Sulfur was extracted from the pulverized samples by reaction with “Kiba reagent” or tin (II) strong phosphoric acid, which is dehydrated phosphoric acid containing ~5% Sn²⁺, following the methods of Sasaki et al. [1979]. The final product of the S extraction process is Ag₂S precipitate, which was separated from the solution by centrifuge with multiple rinses. The extraction method was tested for possible fractionation effects by converting sulfides, sulfates, and a basaltic glass with known δ³⁴S to Ag₂S. The samples used for these tests were an internal UNM lab pyrite sample (“Spanish pyrite”), barium sulfate precipitated from a 74°C gas sample (Giggenbach bottle method) from Momotombo volcano (Nicaragua) [Elkins et al., 2006], and a basaltic glass from the Juan de Fuca Ridge containing 1640 ppm S (P1326-2) (J. Stix and C. Mandeville, personal communication, 2009). No fractionation outside of analytical precision (~0.2‰) was observed: Spanish pyrite yielded +4.2‰ analyzed as FeS₂ and +4.0‰ analyzed as Ag₂S; Momotombo sample yielded +6.2‰ analyzed as BaSO₄ and +6.1‰ analyzed as Ag₂S. Silver sulfide derived from P1326-2 glass by Kiba extraction was analyzed twice, both analyses yielding δ³⁴S values of +1.4‰, which compare well with the value of +1.7 ± 0.6‰ measured at University of Toronto on three replicate Kiba extractions of the same sample (B. Wing and J. Stix, personal communication, 2010).

Olivine-hosted melt inclusions (Figure 4) and scoria samples were prepared for microanalysis to measure major elements, Fe³⁺/ΣFe, S concentration, and S⁰/ΣS. Olivines were separated from the lightly crushed scoria samples under binocular microscope and visually inspected for naturally
glassy melt inclusions free of cracks. Olivines are relatively common in the Erta Ale samples, but exceedingly rare in the samples from Masaya. The melt inclusions were free of contraction vapor bubbles (except for one inclusion from Erta Ale) and showed smooth edges with no daughter crystals or rims of post entrapment olivine crystallization. Olivines were mounted in Epothin™ epoxy, ground to expose the melt inclusions, and polished to 0.05 μm grit. Selected melt inclusions were mounted on quartz glass disks and doubly polished for Fe and S X-ray absorption near-edge spectroscopy. Shards of matrix glass and scoria clasts were prepared in the same way as melt inclusions.

3.3. Sulfur Isotope Analysis

Sulfur isotope measurements were conducted at the University of New Mexico by Continuous Flow Isotope Ratio Mass Spectrometry using a Costech Elemental Analyzer coupled to a Delta Plus XL Thermo Finnigan mass spectrometer via a Conflo II interface. Ag2S or BaSO4 (0.09–0.19 mg) is combusted in a quartz tube packed with ultrahigh purity copper wires and quartz chips at 1020°C in the presence of pure O2 gas [Fry et al., 2002]. By this method, the resulting SO2 gas equilibrates with quartz chips at high temperature to fix the oxygen isotope composition of SO2, which is then passed through a gas chromotograph (GC) column and measured in the mass spectrometer. International standards (all S isotope values are reported relative to the Vienna Canyon Diablo Troilite scale [Robinson, 1995] in δ34S_CDT notation; IAEA-S-1 = −0.3‰ (Ag2S), NBS123 = 17.44‰ (sphalerite), and NBS127 = 21.10‰ (barium sulfate) and a laboratory standard (CP1 = −4.60‰ (chalcopyrite)) were run at the beginning, at intervals between samples, and at the end of analytical sessions. Analytical precision calculated from the standards is better than ±0.3‰ (1σ). Analytical results were normalized to the standards listed above.

3.4. Electron Probe Microanalysis

Electron probe microanalysis was conducted on a JEOL 8200 electron microprobe at the University of New Mexico. Glasses were analyzed (by wavelength dispersive X-ray analysis) for major elements and S, Cl, F using beam current of 10 nA, an accelerating voltage of 15 kV, and a beam diameter of 10 μm. Counting times were between 20 and 40 s for major elements, 60 s for S, and 40 s for Cl and F. Sulfur concentrations were measured using a spectrometer equipped with an LPET crystal with d-spacing of 4.375 Å and S k-α peak positions used in S concentration calibration were determined separately for Erta Ale and Masaya samples (5.37577 Å and 5.37221 Å, respectively). The detection limit for S was ~20 ppm and secondary basalt glass standards (892-1, P1326-2, and JDF46N from Dr. Charles Mandeville and Dr. John Stix) were run to ensure accuracy. Precision is estimated at 5% relative for major elements and 10% relative for minor elements. Olivine phenocrysts were analyzed using a beam current of 20 nA, accelerating voltage of 15 kV and a beam diameter of 2 μm.

3.5. Iron and Sulfur Speciation Analysis by XANES

Iron K-edge X-ray absorption near-edge structure (XANES) spectra were collected following the methods of Cottrell et al. [2009] on the X26A
beamline at the National Synchrotron Light Source at Brookhaven National Lab. Doubly polished wafers of glass and olivine-hosted melt inclusions were mounted on quartz glass slides. Spectra were collected in fluorescence using a Si (311) monochromator to control beam energy from 7020 to 7220 eV using a 9 × 5 μm X-ray spot. Sample location was confirmed using reflected light and Fe pre-edge peak mapping, though the large size of the melt inclusions (>100 μm for Erta Ale, Figure 4) ensured easy targeting of melt inclusions. Fluorescence yield was measured with 9 and 13 element Ge solid-state detectors. Basaltic standard glasses equilibrated at ΔQFM −2 to +4.5 (with Fe3+/ΣFe 0.088–0.611) [Cottrell et al., 2009] were run twice during the 3 day analytical session, and a reference glass equilibrated at ΔQFM 0 (LW_0; Fe3+/ΣFe 0.162) was run every few analyses to monitor and correct for drift. Three spectra were collected on each melt inclusion and spectra were carefully monitored for olivine interference, which is easily identified by the fine structure at the main edge and higher energies when crystals are in the beam path (see Figure S3 in supporting information). Between one and five spectra were collected on matrix glass samples depending on analyzable area. Spectra were deconvolved to quantify Fe3+/ΣFe following the method of Cottrell et al. [2009]. The pre-edge energy interval from 7110 to 7118 eV was extracted from the raw spectra. A linear function and a damped harmonic oscillator function were used to subtract the baseline of the main Fe absorption edge. Two Gaussian curves were fitted to the pre-edge peaks and the area-weighted average of the Gaussian peaks (centroid) was used as the calibration parameter to calculate Fe3+/ΣFe. The centroid values were corrected for drift using the ΔQFM 0 reference glass (run every 2–5 analyses). Reproducibility of sample centroid values was ±0.01 eV. Fe3+/ΣFe values were calculated from average centroid values following the calibration of Cottrell et al. [2009]. The precision of XANES using this suite of 13 standards is ±0.005 in Fe3+/ΣFe ratio of average centroid values (1σ values of average centroid values was 0.0036 for reference glass LW_0 for this analytical session), based on a full propagation of the uncertainty in each individual standard determined by Mössbauer spectroscopy (Fe3+/ΣFe on a single standard by Mössbauer precise to ±0.02), as described by Cottrell et al. [2009]. The absolute accuracy is pinned to the accuracy with which Fe3+/ΣFe ratios were determined on the standards by Mössbauer spectroscopy which, for these standards, agrees to within 1% with wet-chemical analyses [Cottrell and Kelley, 2011].

[24] XANES spectra at the S K-edge were collected at the European Synchrotron Radiation Facility (ESRF; Grenoble, France) at beamline ID21 using the scanning X-ray microscope (SXM). The setup uses a fixed-exit, Si (111) double-crystal monochromator to scan the energy of the incoming beam. The energy of the monochromator was calibrated using the position of the white line of the spectrum of gypsum (2482.84 eV). The incident beam intensity was measured using a photodiode and the spectra were collected in fluorescence mode using an energy dispersive Si-drift chamber solid-state detector with an active area of 80 mm². The beam was collimated using a pinhole to sizes ranging from 50 to 200 μm in diameter as required by the size of the melt inclusion. The energy was scanned quickly from 2450 to 2550 eV (400 steps) with a dwell time of 0.1 s per point. The quick-scans were stacked until an appropriate signal-to-noise ratio was achieved. The spectra were normalized by fitting the energy region before the edge with a polynomial function and subtracting it from the spectra to eliminate the background. The edge-jump was normalized to unity by fitting an arctangent and a Gaussian function to the spectra. For determining the sulfur oxidation state we used the method introduced by Jugo et al. [2010] and Wilke et al. [2011]. This method uses the signal intensity at specific energy positions of sulfide and sulfate. That is, the signal intensity for sulfide (I(S²⁺)) was integrated between 2475.7 and 2480 eV and the one for sulfate (I(S⁶⁺)), was integrated between 2481.5 and 2484 eV. The trend of I(S⁶⁺) over the sum of the two signals (∑I = I(S²⁺) + I(S⁶⁺)) as a function of sulfur oxidation state was determined from a sequence of calculated spectra using the spectra of fully oxidized and fully reduced glasses where the energy position was calibrated using a gypsum standard. For this study we used the calibration by Jugo et al. [2010] for basaltic composition. The error is estimated to be ±0.02 in units of S⁶⁺/∑S.

4. Results

4.1. Sulfur Isotope Compositions of Gases and Scoria

[25] Sulfur isotope compositions of plume gas and scoria from Erta Ale and Masaya are reported in Table 2 and Figure 5a. No ZnS was precipitated
from plume gas at Erta Ale or Masaya, indicating that H2S was an insignificant component of the gas (see section 3.1) and that S in these plumes is dominated by SO2. Sulfate aerosol $\delta^{34}$S values and SO4$^{2-}$/SO2 ratios are presented in Table 3. The SO4$^{2-}$/SO2 ratio measured in the Erta Ale plume was 0.006 $\pm$ 0.002 indicating that sulfate aerosols (average $\delta^{34}$S value of $+1.9 \pm 0.5\%$) are an insignificant proportion of the total S in the plume. Sulfur isotope compositions of plume gas (SO2) from Erta Ale has a value of $+0.5 \pm 0.6\%$ with a range of $-1.9\%$ to $+0.3\%$, whereas scoria from Erta Ale have an average value of $+0.9 \pm 0.3\%$ with a range of $+1.1\%$ to $+0.5\%$. These values span the range for MORB ($+0.3 \pm 0.5\%$) [Sakai et al., 1984], and the gas has a $\delta^{34}$S composition about 1.3% lower than that of scoria.

Plume gas (SO2) from Masaya has a $\delta^{34}$S composition of $+4.8 \pm 0.4\%$ whereas scoria yield $\delta^{34}$S = 7.4 $\pm$ 0.6% (Table 2). These values are significantly higher than MORB, and fall in the range of arc products from mafic volcanoes [Alt et al., 1993; de Hoog et al., 2001; Menyailov et al., 1986; Taran et al., 2002, 1995]. Similar to Erta Ale, the gas is isotopically lighter than the scoria, however, the difference between gas and scoria is

![Figure 5](image_url)

Table 2. Sulfur Isotope Compositions of Scoria and Plume Gas From Erta Ale and Masaya

<table>
<thead>
<tr>
<th></th>
<th>Erta Ale</th>
<th>Masaya</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{34}$S</td>
<td>$\delta^{34}$S</td>
<td></td>
</tr>
<tr>
<td>Scoria</td>
<td></td>
<td></td>
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<tr>
<td>EA-R1</td>
<td>1.08</td>
<td>7.80</td>
</tr>
<tr>
<td>EA-R2</td>
<td>1.11</td>
<td>7.28</td>
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<tr>
<td>EA-R9</td>
<td>0.71</td>
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<tr>
<td>EA-R10</td>
<td>0.51</td>
<td>6.60</td>
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<tr>
<td>Average</td>
<td>0.85</td>
<td>7.40</td>
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<tr>
<td>$1\sigma$</td>
<td>0.29</td>
<td>0.60</td>
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</table>

<table>
<thead>
<tr>
<th>Plume (SO2)</th>
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</thead>
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<tr>
<td>EA-BUB1-1</td>
<td>0.21</td>
<td>5.13</td>
</tr>
<tr>
<td>EA-BUB1-2</td>
<td>-0.58</td>
<td>4.25</td>
</tr>
<tr>
<td>EA-BUB1-3</td>
<td>-0.25</td>
<td>4.49</td>
</tr>
<tr>
<td>EA-BUB1-4</td>
<td>-0.05</td>
<td>5.06</td>
</tr>
<tr>
<td>EA-BUB1-5</td>
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<td>5.35</td>
</tr>
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<td>EA-BUB1-6</td>
<td>-1.28</td>
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</tr>
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<td>EA-BUB1-7</td>
<td>-1.85</td>
<td>4.83</td>
</tr>
<tr>
<td>EA-BUB1-8</td>
<td>-0.75</td>
<td>0.42</td>
</tr>
<tr>
<td>EA-BUB1-9</td>
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</tr>
<tr>
<td>EA-BUB2-1</td>
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</tr>
<tr>
<td>EA-BUB2-2</td>
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<td></td>
</tr>
<tr>
<td>EA-BUB2-3</td>
<td>-0.62</td>
<td></td>
</tr>
<tr>
<td>EA-BUB2-4</td>
<td>-0.35</td>
<td></td>
</tr>
<tr>
<td>EA-BUB2-5</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>EA-BUB2-6</td>
<td>-0.86</td>
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</tr>
<tr>
<td>EA-BUB2-8</td>
<td>-0.10</td>
<td></td>
</tr>
<tr>
<td>EA-BUB2-9</td>
<td>-0.50</td>
<td></td>
</tr>
<tr>
<td>EA-BUB3-1</td>
<td>-1.29</td>
<td></td>
</tr>
<tr>
<td>EA-BUB3-2</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>-0.47</td>
<td></td>
</tr>
<tr>
<td>$1\sigma$</td>
<td>0.57</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. (a) Sulfur isotope compositions of plume gas (SO2) and scoria from Erta Ale and Masaya as well as the field for MORB from Sakai et al. [1984]. Analytical uncertainty is $\pm 0.2\%$. (b) Sulfur speciation by S XANES versus oxygen fugacity calculated from Fe3+/ΣFe and major element compositions of melt inclusions and matrix glass for Erta Ale and Masaya. The ranges for mid-ocean ridge basalts and island arc basalts are from Jugo et al. [2010], as is the experimentally determined relationship between S6+/ΣS and oxygen fugacity (black curve). (c) Sulfur speciation in the melt (melt inclusions and matrix glass) versus S concentration for Erta Ale and Masaya.
larger, at ~2.6%. Estimates of $\text{SO}_4^{2-}/\text{SO}_2$ in the plume vary from 0.036 (this study) to 0.005 ([Allen et al., 2002; Martin et al., 2010]) and sulfate aerosol has an isotope composition of ~7% to +8% (this study and Mather et al. [2006a]).

### 4.2. Sulfur Content and Major Element Chemistry of Melt Inclusions and Matrix Glass

[27] Major and minor element compositions of melt inclusions and matrix glasses are reported in the supporting information in Tables S2–S5. The sulfur concentrations of olivine-hosted melt inclusions from Erta Ale vary between 140 and 1218 ppm (average = 394 ppm), whereas matrix glasses vary between 26 and 218 ppm (average = 112 ppm). Our melt inclusions from Masaya have low S content, from 92 to 224 ppm. Sadofsky et al. [2008] report S concentrations for olivine-hosted melt inclusions from Masaya of 296 to 480 ppm, whereas Horrocks [2001] found that the highest S content measured in plagioclase-hosted melt inclusions was 220 ppm. The average S concentration of matrix glass from Masaya is 34 ppm (range is 20–52 ppm).

[28] Major element compositions of melt inclusions, host olivines, matrix glass and olivine rims were analyzed to assess melt temperatures (by liquid and olivine-liquid thermometry) and to determine whether melt inclusions were modified by post-entrapment processes [e.g., Putirka, 2008]. Erta Ale melt inclusions and matrix glass are slightly more mafic (SiO$_2$ ~ 49.7 wt% ; MgO ~ 6.5 wt%; Mg# ~ 0.55) than those from Masaya (SiO$_2$ ~ 51.4 wt% ; MgO ~ 5.0 wt%; Mg# = 0.48). Olivine host crystals at Erta Ale have compositions of Fo$_{79–82}$ whereas Masaya olivines have compositions of Fo$_{74–75}$. Masaya glasses are richer in K$_2$O (1.4 wt%) and FeO$_T$ (13.0 wt%) and poorer in TiO$_2$ (1.3 wt%) and CaO (9.3 wt%) compared to Erta Ale glasses (0.6 wt% K$_2$O; 11.3 wt% FeO$_T$; 2.4 wt% TiO$_2$; 11.4 wt% CaO). Compositional differences between melt inclusions and matrix glasses are small for both volcanoes with relative differences for non-volatile elements of ~5%.

[29] Erta Ale glasses are significantly more F rich (~500 ppm) than Masaya (~200 ppm) and matrix glasses are slightly enriched in F relative to melt inclusions in both systems. Masaya glasses have higher chlorine content (~500 ppm) than Erta Ale glasses (~260 ppm Cl), and matrix glasses are slightly depleted in chlorine relative to melt inclusions.

### 4.3. Iron and Sulfur Speciation and Oxygen Fugacity Calculations

[30] Fe$^{3+}/\sum$Fe ratios are presented in Table 4. Melt inclusions from Erta Ale give values from 0.157 to 0.162, overlapping with the range observed in matrix glass of 0.147–0.160. Melt inclusions from Masaya have higher Fe$^{3+}/\sum$Fe ratios of 0.232–0.262 and matrix glasses are more oxidized with a range of 0.252–0.328. These values for the Masaya melt are in good agreement with the Mössbauer results from Mather et al. [2006a] which show Fe$^{3+}/\sum$Fe values 0.23–0.31 in whole rock scoria. Measured Fe$^{3+}/\sum$Fe values were used in assessing K$_D$ for Fe$^{2+}$/Mg between melt inclusions and olivine host crystals in order to assess post-entrapment modification (see section.

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**Table 3. Sulfur Isotope Compositions of Sulfate Aerosol, SO$_4$/$\text{SO}_2$ Molar Ratios and $\Delta^{34}$S SO$_4$/$\text{SO}_2$ in the Erta Ale and Masaya Plumes**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>SO$_4$/$\text{SO}_2$</th>
<th>$\delta^{34}$S $\nu$-CDT</th>
<th>$\Delta^{34}$S SO$_4$/$\text{SO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ERTA ALE</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High Flow Pump (18 L/min) in Series With Bubblers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EA-BUB1-FILT1</td>
<td>0.005</td>
<td>1.33</td>
<td>1.50</td>
</tr>
<tr>
<td>EA-BUB1-FILT2</td>
<td>0.008</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>EA-BUB1-FILT3</td>
<td>0.006</td>
<td>1.66</td>
<td>2.19</td>
</tr>
<tr>
<td>EA-BUB2-FILT1</td>
<td>0.007</td>
<td>1.51</td>
<td>1.52</td>
</tr>
<tr>
<td>EA-BUB2-FILT2</td>
<td>0.001</td>
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<td>n.d.</td>
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<tr>
<td>EA-BUB3-FILT1</td>
<td>0.007</td>
<td>1.75</td>
<td>2.29</td>
</tr>
<tr>
<td>EA-FILT4</td>
<td>0.006</td>
<td>3.09</td>
<td>3.39</td>
</tr>
<tr>
<td>Average</td>
<td>0.006</td>
<td>1.87</td>
<td>1.87</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.002</td>
<td>0.70</td>
<td>0.43</td>
</tr>
</tbody>
</table>

**MASSAY**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>SO$_4$/$\text{SO}_2$</th>
<th>$\delta^{34}$S $\nu$-CDT</th>
<th>$\Delta^{34}$S SO$_4$/$\text{SO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Flow Pump, Filter Packs, Tube Diffusive Samplers</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>MSY1</td>
<td>0.036</td>
<td>7.8</td>
<td>3.2</td>
</tr>
<tr>
<td>MSY2</td>
<td>0.023</td>
<td>7.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

* Mather et al. [2008] showed that S isotope composition of SO$_2$ collected on NaHCO$_3$ impregnated filters increases with filter loading (i.e., the amount of S and Cl collected on the filter). Thus, their minimum estimate for the S isotope composition of SO$_2$ (±5.1%) at Masaya is used.*
S2 in supporting information). No evidence is found for significant post entrapment effects.

[31] S\(^{6+}/\Sigma S\) ratios of melt inclusions and matrix glass are reported in Table 4. Melt inclusions from Erta Ale yield S\(^{6+}/\Sigma S\) ratios of 0.02–0.07 and matrix glasses display a similar range of 0.02–0.11. Glasses from Masaya are more oxidized, with melt inclusions showing S\(^{6+}/\Sigma S\) ratios of 0.67–0.71 and matrix glasses displaying values of 0.62–0.88.

[32] Oxygen fugacities of the Erta Ale and Masaya melts are assessed for the temperature and pressure range relevant to S degassing and are reported relative to the QFM buffer of Frost [1991]. Temperatures used in the calculation of fO\(_2\) (1156–1163°C for Erta Ale, 1097–1127°C for Masaya; errors are assigned as ±50°C following Putirka [2008]; Table 4) were based on the olivine-liquid geothermometer of Putirka [2008]. Temperatures derived from olivine-melt thermometry are in good agreement with the highest measured temperatures of the Erta Ale lava lake (1174°C) [Oppenheimer et al., 2004]. Oxygen fugacities were calculated from measured Fe\(^{3+}/\Sigma Fe\) ratios and major element compositions for the range of pressure relevant to sulfur degassing from basaltic melts following the algorithm of Kress and Carmichael [1991]. Lesne et al. [2011] experimentally investigated the degassing behavior of S in basaltic melts with compositions based on Masaya and Stromboli and found that S partitions significantly into the gas phase at less than ~1.5 kbar. Thus, oxygen fugacities were calculated for P = 1 bar and P = 1.5 kbar (Table 4) to bracket the P dependence of fO\(_2\), and for temperatures derived from olivine-liquid thermometry. Uncertainties on the fO\(_2\) values reflect the uncertainty in Fe\(^{3+}/\Sigma Fe\) ratios (section 3.5) and temperature estimates (here taken to be ±50°C).

[33] The relationship between melt S speciation (measured by XANES) and melt fO\(_2\) for Erta Ale and Masaya are shown in Figure 5b. Melt inclusions tend to show a better agreement with the curve of Jugo et al. [2010] than matrix glasses, perhaps because microanalyses of matrix glasses were not conducted on exactly the same spot whereas it is easier to target the same analytical area in melt inclusions. The relationship between S concentration and S speciation is shown in Figure 5c. No clear correlations between S concentration or S speciation is observed for either Erta Ale or Masaya.

Table 4. Results of S\(^{6+}/\Sigma S\) and Fe\(^{3+}/\Sigma Fe\) Measurements and fO\(_2\) Calculations

<table>
<thead>
<tr>
<th></th>
<th>S(^{6+}/\Sigma S)</th>
<th>Fe(^{3+}/\Sigma Fe)</th>
<th>T (°C)</th>
<th>fO(_2)</th>
<th>ΔQFM</th>
<th>pT</th>
<th>ΔQFM</th>
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<tbody>
<tr>
<td><strong>1 bar</strong></td>
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<tr>
<td><strong>Melt Inclusions</strong></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>EA-MI-4</td>
<td>598</td>
<td>0.067</td>
<td>0.157</td>
<td>1151</td>
<td>-8.92</td>
<td>0.96</td>
<td>-0.04</td>
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<td>EA-MI-13.2</td>
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<td>1155</td>
<td>-8.81</td>
<td>0.96</td>
<td>0.03</td>
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<td>EA-MI-7</td>
<td>196</td>
<td>0.018</td>
<td>0.162</td>
<td>1156</td>
<td>-8.72</td>
<td>0.95</td>
<td>0.11</td>
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<td>BS-H2-M12</td>
<td>1218</td>
<td>0.027</td>
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<td>1161</td>
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<td>n.a.</td>
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<td>n.a.</td>
<td>1152</td>
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<td><strong>Matrix Glass</strong></td>
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<td>EA-R1</td>
<td>218</td>
<td>0.021</td>
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<td>-9.11</td>
<td>0.99</td>
<td>-0.20</td>
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<tr>
<td>EAM17,mg</td>
<td>160</td>
<td>0.043</td>
<td>0.156</td>
<td>1155</td>
<td>-8.86</td>
<td>0.96</td>
<td>-0.02</td>
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<tr>
<td>EAM4,mg</td>
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<td>0.108</td>
<td>0.151</td>
<td>1151</td>
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<td>0.97</td>
<td>-0.10</td>
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<td>EAM11,mg</td>
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<td><strong>Masaya</strong></td>
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<td>MAS-MI-2,1</td>
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<td>MAS1-e11</td>
<td>48</td>
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<tr>
<td>MAS1-e12</td>
<td>20</td>
<td>0.883</td>
<td>0.328</td>
<td>1126</td>
<td>-6.96</td>
<td>1.11</td>
<td>2.24</td>
</tr>
<tr>
<td>MAS1-e13</td>
<td>39</td>
<td>0.616</td>
<td>0.252</td>
<td>1127</td>
<td>-7.77</td>
<td>1.15</td>
<td>1.43</td>
</tr>
</tbody>
</table>

aUncertainties in S\(^{6+}/\Sigma S\) and Fe\(^{3+}/\Sigma Fe\) ratios are ~±0.02. Oxygen fugacities were calculated based on the algorithm of Kress and Carmichael [1991] from Fe\(^{3+}/\Sigma Fe\) ratios and major element compositions and ΔQFM values are relative to the quartz-fayalite-magnetite buffer of Frost [1991] at given P and T. Temperatures are calculated from the olivine-liquid geothermometer of Putirka [2008]. See text for details.
4.4. Oxygen Fugacity of Gases From Erta Ale

[34] Complete gas compositions for Erta Ale, as well as $^{40}$Ar/$^{36}$Ar values, for gas samples collected in 2011 are reported in Table 5, together with a compilation of gas data available for Erta Ale. CO$_2$/CO ratios are used to calculate $f$O$_2$ in the gas phase by assessment of:

$$\text{CO} + 0.5\text{O}_2 \leftrightarrow \text{CO}_2$$  \hspace{1cm} (1)

following Giggenbach [1987] and using thermodynamic data from Robie and Hemingway [1995]. Whereas gas samples collected by Giggenbach and Le Guern [1976] and Le Guern et al. [1979] at Erta Ale in 1971, 1973, and 1974 show $f$O$_2$ values close to the QFM buffer, our samples show significantly higher CO$_2$/CO values, thus higher calculated $f$O$_2$ values. Importantly, our gas samples show Ar isotope compositions within analytical precision of the air value (295), and N$_2$/Ar and He/Ar ratios similar to air but O$_2$/Ar values lower than air (22.4). The fact that Ar isotope compositions are air like, whereas O$_2$/Ar is lower than air indicates that oxygen was consumed by combustion of reduced gas species upon mixing with air (within the sampled hornito) resulting in high CO$_2$/CO ratios.

[35] An overview of oxygen fugacities calculated from various sample types for Masaya and Erta Ale are shown in Figure 6.

5. Discussion

5.1. Oxygen Fugacity of Erta Ale and Masaya Magmas

[36] Oxygen fugacity is a parameter linked to the tectonic setting and differentiation history of melts. Melt inclusions and matrix glass from Erta Ale show indistinguishable $f$O$_2$ values in the range of $\Delta$QFM $\pm$0.20 to $\pm$0.15, with uncertainty of <0.4 log units (section 4.3 and Table 4). These values are in remarkable agreement with $f$O$_2$ calculated from CO$_2$/CO ratios (22.0 $\pm$ 1.6: $\Delta$QFM $\pm$0.2 $\pm$ 0.1) in high-temperature Erta Ale gas samples of Giggenbach and Le Guern [1976] as well as $f$O$_2$ for more evolved magmas from the Erta Ale suite from two-oxide thermobarometry [Bizouard et al., 1980]. In contrast, open path Fourier transform infrared (FTIR) measurements of gas emissions from Erta Ale yield higher CO$_2$/CO ratios of 57.1 $\pm$ 1.6 consistent with gas re-equilibration to measured gas temperatures [Sawyer et al., 2008] or high-temperature combustion of CO to CO$_2$. Le Guern et al. [1979] measured temperature increases with time on the surface of the lava lake, which they interpreted to reflect combustion of CO to CO$_2$ and H$_2$ to H$_2$O.

[37] Our own gas samples from a 1085°C fumarole show high and variable CO$_2$/CO ratios (56–89; Table 5) and significant mixing with air before discharging to the atmosphere, supportive of high-temperature combustion of CO to CO$_2$. The other reduced species that are susceptible to oxidation by atmospheric O$_2$ are H$_2$ and H$_2$S. Equation (1) indicates that 1 mol of CO$_2$ produced by combustion consumes 0.5 mol of O$_2$. Oxidation of H$_2$ by:

$$\text{H}_2 + 0.5\text{O}_2 \leftrightarrow \text{H}_2\text{O}$$  \hspace{1cm} (2)

consumes 0.5 mol of O$_2$ for each mole of H$_2$ combusted. Oxidation of H$_2$S by [e.g., Gerlach et al., 1996]:

$$\text{H}_2\text{S} + 1.5\text{O}_2 \leftrightarrow \text{SO}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (3)

indicates that 1.5 mol of O$_2$ is consumed for each mole of H$_2$S converted to SO$_2$. Considering equations (1)–(3), the gas compositions can be restored to obtain the O$_2$/Ar ratio of air and the pre-air contamination values of CO$_2$/CO, H$_2$O/H$_2$, and SO$_2$/H$_2$S. Recalculation of our average gas composition (Table 5) to CO$_2$/CO, H$_2$O/H$_2$, and SO$_2$/H$_2$S to $\Delta$QFM $\pm$0.1 at the maximum measured outlet temperature of 1085°C yields O$_2$/Ar of 22.5, that of air (22.4).

[38] These calculations indicate that combustion of CO, H$_2$, and H$_2$S by atmospheric O$_2$ is a significant process in modifying these gas compositions and that the pre-air contamination oxygen fugacity recorded by our gas samples is $\Delta$QFM $\sim$–0.1. It is relevant to note that complete gas chemistry derived from direct sampling of gas emissions is the only available method for assessing the effects of atmospheric oxidation of reduced gas species in volcanic systems. For the case of Erta Ale, the $f$O$_2$ calculated from glass Fe$^{3+}$/Fe$^{2+}$ values and the restored gas compositions are in good agreement. The samples from Giggenbach and Le Guern [1976], the oxybarometry of Bizouard et al. [1980], and the results of this study all suggest that the gas and melt at Erta Ale have the same $f$O$_2$; i.e., that the gas is buffered by Fe in the melt, as proposed by Giggenbach [1987].
Masaya melt inclusions yield more oxidized $f_{O_2}$ values of $\Delta QFM +1.3$ to $+1.6$. One clast from Masaya shows matrix glass $f_{O_2} (+1.48)$ in agreement with the melt inclusions, whereas two other clasts yield slightly higher $f_{O_2}$ values of $+2.09$ and $+2.29$. Our $Fe^{3+}/Fe^{2+}$ ratios and $f_{O_2}$ results are in agreement with those of Mather et al. [2006a]. The observation that Masaya glasses from the Central American Arc are significantly more oxidized than Erta Ale glasses from the East African Rift is consistent with prior studies showing that subduction zone magmas are more oxidized than magmas produced at spreading centers [e.g., Kelley and Cottrell, 2009].

### 5.2. Assessment of Possible Melt Saturation With Sulfide or Sulfate Mineral Phases and Degassing Prior to Melt Inclusion Entrapment

No sulfide or sulfate minerals have been observed in our scoria samples from Erta Ale or Masaya, neither as an accessory phase nor as inclusions within phenocrysts. To our knowledge, there are no published reports describing S-bearing mineral phases in either system. Sulfides only occur in the more evolved magmas in the Erta Ale suite (trachytes to peralkaline rhyolites) and crystallize as late phases [Bizouard et al., 1980], and Field et al. [2012] found no oxides or sulfides in the 2010 lavas, consistent with this study and that of Bizouard et al. [1980]. Similarly, we have not found any S-bearing mineral phases in samples from Masaya, and oxides are the only accessory phase to occur in erupted products [Martin and Sigmarsson, 2007; Walker et al., 1993]. However, sulfide resorption may occur in basaltic systems [Nadeau et al., 2010; Sisson, 2003] and sulfide precipitation is a mechanism that could affect the S isotope compositions of magmas [e.g., Marini et al., 2011]. Therefore, in this section we address $S$ solubility with respect to mineral phases.

The melt sulfur content at sulfide or sulfate saturation (SCSS) is a function of melt composition, $f_{O_2}$, $f_{S_2}$, $T$, $P$, and $H_2O$ content (see reviews

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![Figure 6. Comparison of oxygen fugacity estimates for different sample types for Erta Ale and Masaya. Melt inclusions and matrix glass from this study. MORB and Arc ranges from Jugo et al. [2010]. Erta Ale oxides (“Erta Ale oxides” field) from ilmenite and Ti-magnetite pairs from evolved rocks of the Erta Ale range series from Bizouard et al. [1980]. Oxygen fugacity estimates from CO$_2$/CO in gas phase: (1) Giggenbach and Le Guern [1976] samples collected in 1974, (2) Le Guern et al. [1979] samples collected in 1971, (3) Sawyer et al. [2008] plume measurements by FTIR, (4) Gas samples collected in 2011 for this study with $f_{O_2}$ calculated from measured CO$_2$/CO, and (5) average for gas samples collected in 2011 corrected for atmospheric oxidation. Masaya whole rock field from Mössbauer measurements of Masaya whole rock [Mather et al., 2008], melt inclusions and matrix glass from this study. There are no $f_{O_2}$ estimates available for gas emissions from Masaya.](image)
Table 5. Gas Compositions From Erta Ale, With Oxygen Fugacity Calculated Relative to the Quartz-Fayalite-Magnetite Buffer of Frost [1991]*

<table>
<thead>
<tr>
<th>Sample ID/Reference</th>
<th>Year</th>
<th>Method</th>
<th>T (°C)</th>
<th>H2O</th>
<th>CO2</th>
<th>SO2</th>
<th>H2S</th>
<th>HCl</th>
<th>HF</th>
<th>He</th>
<th>H2</th>
<th>Ar</th>
<th>O2</th>
<th>N2</th>
<th>CO</th>
<th>CO2/CO</th>
<th>ΔQFM</th>
<th>O2/Ar</th>
<th>40Ar/36Ar</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA-G-1</td>
<td>2011</td>
<td>Direct</td>
<td>1085</td>
<td>602.7</td>
<td>203.4</td>
<td>114.46</td>
<td>110.3</td>
<td>4.20</td>
<td>16.3</td>
<td>19.7</td>
<td>0.002701</td>
<td>7.368</td>
<td>0.3907</td>
<td>1.34</td>
<td>31.58</td>
<td>71.64</td>
<td>+0.73</td>
<td>3.4</td>
<td>292.2</td>
<td>10.7</td>
</tr>
<tr>
<td>EA-G-2</td>
<td>2011</td>
<td>Direct</td>
<td>1085</td>
<td>578.8</td>
<td>223.8</td>
<td>115.61</td>
<td>110.7</td>
<td>4.94</td>
<td>15.6</td>
<td>20.4</td>
<td>0.001654</td>
<td>7.499</td>
<td>0.4368</td>
<td>1.049</td>
<td>33.92</td>
<td>77.51</td>
<td>+0.80</td>
<td>2.4</td>
<td>293.8</td>
<td>10.4</td>
</tr>
<tr>
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<td>Direct</td>
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<td>614.5</td>
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<td>113.38</td>
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<td>12.4</td>
<td>18.1</td>
<td>0.000343</td>
<td>4.886</td>
<td>0.4164</td>
<td>1.033</td>
<td>35.54</td>
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<td>295.5</td>
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<td>180.8</td>
<td>101.85</td>
<td>93.25</td>
<td>8.60</td>
<td>12.6</td>
<td>21.3</td>
<td>0.002462</td>
<td>6.521</td>
<td>0.3965</td>
<td>0.997</td>
<td>29.28</td>
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<td>289.9</td>
<td>10.7</td>
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<td>14.3</td>
<td>20.2</td>
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<td>0.4777</td>
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<td>37.04</td>
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<td>105.05</td>
<td>100.6</td>
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<td></td>
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<td>624.9</td>
<td>181.4</td>
<td>105.05</td>
<td>98.85</td>
<td>6.21</td>
<td>14.2</td>
<td>19.9</td>
<td>0.001699</td>
<td>12.375</td>
<td>0.4236</td>
<td>9.515</td>
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<td>66.45</td>
<td>0.11</td>
<td>22.5</td>
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<tr>
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<td>FTIR</td>
<td>730–1130</td>
<td>935.8</td>
<td>36.6</td>
<td>n.a.</td>
<td>24.7</td>
<td>n.a.</td>
<td>1.9</td>
<td>0.4</td>
<td>n.a.</td>
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<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
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<td>61.00</td>
<td>−0.61 to +0.57</td>
<td>n.a.</td>
<td>n.a.</td>
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<td>Giggenbach and Le Guern [1976]</td>
<td></td>
<td>1974</td>
<td>Direct</td>
<td>1125–1135</td>
<td>794.0</td>
<td>104.0</td>
<td>73.6</td>
<td>65.0</td>
<td>8.6</td>
<td>4.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>14.9</td>
<td>0.01</td>
<td>0.5</td>
<td>1.8</td>
<td>4.6</td>
<td>22.61</td>
<td>0.17</td>
<td>48.2</td>
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<td></td>
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<td>Direct</td>
<td>1100–1210</td>
<td>n.a.</td>
<td>547.3</td>
<td>n.a.</td>
<td>212.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>41.0</td>
<td>7.90</td>
<td>104.8</td>
<td>207.4</td>
<td>24.0</td>
<td>22.81</td>
<td>0.17</td>
<td>13.3</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
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<td>n.a.</td>
<td>365.2</td>
<td>220.9</td>
<td>219.5</td>
<td>0.5</td>
<td>n.a.</td>
<td>n.a.</td>
<td>28.5</td>
<td>3.70</td>
<td>60.6</td>
<td>305.8</td>
<td>13.8</td>
<td>26.46</td>
<td>−0.05</td>
<td>16.4</td>
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<tr>
<td>Gerlach [1980]</td>
<td>1974</td>
<td>Recalc</td>
<td>1125–1135</td>
<td>771.3</td>
<td>117.0</td>
<td>88.9</td>
<td>73.0</td>
<td>9.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>15.9</td>
<td>n.a.</td>
<td>n.a.</td>
<td>5.2</td>
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<td>n.a.</td>
<td></td>
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<tr>
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<td>Recalc</td>
<td>1075</td>
<td>695.6</td>
<td>178.0</td>
<td>99.4</td>
<td>87.9</td>
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<td>n.a.</td>
<td>n.a.</td>
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<td>n.a.</td>
<td>n.a.</td>
<td>7.8</td>
<td>22.82</td>
<td>−0.28</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
</tr>
</tbody>
</table>

*The O2/Ar value for air is 22.4 and the 40Ar/36Ar value of air is 298.

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by Baker and Moretti [2011] and Backnaes and Deubener [2011]). The Liu et al. [2007] solubility model is generally accepted as being successful in predicting SCSS [Baker and Moretti, 2011] except for the case of melts with high H2O-contents, in which case SCSS is significantly underestimated [Beermann et al., 2012; Moune et al., 2009]. Olivine-hosted melt inclusions from Erta Ale have at most 0.15 wt % water [Field et al., 2012] indicating that it is appropriate to apply the Liu et al. [2007] SCSS model. Results show that the Erta Ale melt would be saturated with sulfide at 1610–2640 ppm S for the compositions of Erta Ale melt inclusions and matrix glass, at temperature of 1150°C, and pressure between 1 and 1500 bars. The highest S concentration measured in melt inclusions from Erta Ale is 1220 ppm, lower than sulfide saturation concentrations.

Similarly, the compositions of Masaya melt inclusions and matrix glass indicate SCSS of 1055–1860 ppm from the Liu et al. [2007] model for a temperature of 1100°C and pressures between 1 and 1500 bars. Sadofsky et al. [2008] report a water content of 1.7 wt % for Masaya melt inclusions, and the highest S concentration measured in melt inclusions from Masaya is 480 ppm, well below sulfide saturation. The predominance of S6+ in these relatively oxidized melts (section 5.1) makes it more appropriate to consider the sulfur content at sulfate (i.e., anhydrite) saturation. Jugo et al. [2010] demonstrate the SCAS (sulfur content at anhydrite saturation) is ~1.2 wt % at QFM >1.5, similar to that calculated for the Masaya melt (section 5.1). The Li and Ripley [2009] model for sulfur content at anhydrite saturation yields saturation concentrations of 3300–7070 ppm, which is far higher than S concentrations observed in the melt. The Baker and Moretti [2011] model takes the effect of water into account and gives SCAS of 1620–29,100 ppm for Masaya melts.

Lee et al. [2012] argued that Cu content of whole rocks can be used as a tracer of sulfate saturation, with Cu depletion indicating precipitation of sulfides. Masaya lavas have some of the highest Cu contents of any lavas along the Central American arc with an average of ~250 ppm Cu [Carr and Rose, 1987], far higher than the depleted values of <50 ppm expected for magmas that have experienced sulfide saturation [Lee et al., 2012]. Erta Ale lavas have ~120 ppm Cu [Zelenski et al., 2013], which is also elevated and above the range in MORB (40–90 ppm) or bulk continental crust (~30 ppm) [Lee et al., 2012]. We thus conclude that neither the Erta Ale melts nor the Masaya melts show any evidence for saturation in S-bearing mineral phases.

In the interpretation presented below, we use the highest measured S concentrations from olivine-hosted melts inclusions from Erta Ale (~1200 ppm S; this study) and Masaya (~500 ppm S) [Sadofsky et al., 2008] in assessing sulfur mass balance and isotope fractionation. Olivine crystallization occurs at relatively low pressure at both Erta Ale and Masaya [Field et al., 2012; Walker et al., 1993]. Water concentrations were measured in Masaya olivine-hosted melt inclusions by Sadofsky et al. [2008] who reported a value of 1.7 wt % H2O, and the major element totals for our melt inclusions from Masaya suggest H2O contents of 0.5–1.7 wt % (by difference from 100%). These are low water contents for an arc magma with high Ba/La and consistent with low-pressure crystallization of olivine. Similarly, Field et al. [2012] measured low concentrations of CO2 (≤200 ppm) and H2O (≤1300 ppm) in olivine-hosted melt inclusions, and calculated low pressures (<0.5 kbar) for olivine crystallization. Field et al. [2012] report lower S concentration of 205 ppm S in one of their Erta Ale inclusions, similar to the most degassed inclusions from this study (Figure 5c). We cannot discount that some S degassing may have occurred prior to melt inclusion entrapment, but rely on the highest measured S concentrations as the best available constraint on the undegassed S concentration in the Erta Ale and Masaya melts. In particular, the S concentrations in Masaya melt inclusions are low compared to arc basalts with melt inclusions trapped at higher pressure, which typically range ~1000 ppm S [Wallace and Edmonds, 2011]. This is also the value used by Stix [2007] in modeling magma degassing rate at Masaya, therefore we also consider the case where the undegassed melt at Masaya contains 1000 ppm S.

5.3. Conceptual Model of S Degassing and Primary S Isotope Compositions

Erta Ale and Masaya are both type examples of open system volcanoes that degas persistently with minor eruption of magma. A conceptual model for S degassing at Erta Ale and Masaya is given in Figure 7 with fluxes and isotope compositions for each system. If the highest S concentration measured in melt inclusions is representative of the undegassed S content of the melt, then
Magma degassing rates can be calculated from SO$_2$ fluxes [e.g., Andres et al., 1991; de Moor et al., 2005; Kazahaya et al., 1994; Pallister et al., 2005; Palma et al., 2011; Stix, 2007; Stoiber et al., 1986]:

$$Q_m = 100 \frac{M_{S}}{M_{SO_2}} \frac{Q_{SO_2}}{\Delta S}$$

where $Q_m$ is the magma degassing rate in kg/s, $Q_{SO_2}$ is the measured flux of SO$_2$ gas in kg/s, $\Delta S$
is the sulfur lost from the melt in wt %, and $M_S$ and $M_{SO_2}$ are the molecular masses of S and SO$_2$, respectively. At Erta Ale, the magma degassing rate is estimated at ~520 kg/s or $1.6 \times 10^{10}$ kg/yr (using an SO$_2$ flux of 1.16 kg/s, a melt S content of 1218 ppm S, and a degassed melt content of 100 ppm). The 2010 eruption produced ~6 x $10^6$ m$^3$ of lava [Field et al., 2012] and the 1968–1974 eruptions produced ~9.7 x $10^6$ m$^3$ [Oppenheimer and Francis, 1997], yielding erupted masses of 8.1 $\times 10^8$ and 1.5 $\times 10^{10}$ kg, respectively (using a vesicularity of 50% [Field et al., 2012] and a melt density of 2700 kg/m$^3$). These values yield eruption rates of 2.3 $\times 10^8$ kg/yr (1975–2011) to 4.9 $\times 10^8$ kg/yr (1968–2011), which are almost 2 orders of magnitude lower than the magma degassing rate. Matrix glass contains ~100 ppm S (section 4.2), resulting in a S flux of 0.7 $\times 10^6$ mol/yr to 1.8 $\times 10^6$ mol/yr from the volcano as lava. In comparison, the S flux by degassing of the volcano is almost 3 orders of magnitude higher at ~5.7 $\times 10^8$ mol/yr and strongly dominates the sulfur output budget. The flux of sulfate aerosol is estimated at 3.4 $\times 10^6$ mol/yr based on the SO$_2$ flux and SO$_4$/SO$_2$ ratio measured in the plume (Table 3).

The magma degassing rate at Masaya is far higher than at Erta Ale. Using a melt S content of 480 ppm from Sadofsky et al. [2008], a degassed melt content of 30 ppm S (section 4.2) and an average SO$_2$ flux of 1000 tons/d (11.6 kg/s) [Martin et al., 2010; Nadeau and Williams-Jones, 2009] the magma degassing rate is estimated at ~12,975 kg/s or 4.1 $\times 10^{11}$ kg/yr. Given the variability of SO$_2$ gas emission from Masaya (3.8–27.6 kg/s; Figure 3), the magma degassing rate may vary between ~4000 and ~29,000 kg/s. If the undegassed melt concentration was 1000 ppm [Stix, 2007] then calculated magma degassing rates would be half of that reported above. An insignificant mass of this degassed magma is erupted, with 14 minor explosions since 1950 with minimal ash deposition [Venzke et al., 2002]. In order to provide some constraint on the magma eruption rate, we consider the 1772 and 1670 lava flows, which have masses of 2.5 $\times 10^8$ and 2.0 $\times 10^{10}$ kg [Venzke et al., 2002; Williams, 1983], yielding a magma eruption rate of 6.7 $\times 10^7$ kg/yr (for the time period 1670–2011), which is 4 orders of magnitude lower than the magma degassing rate. This large discrepancy dwarfs the uncertainties in the magma degassing rate due to uncertainties in the initial S content. Considering a melt content of 30 ppm after degassing yields a flux of <2 $\times 10^4$ mol/yr S in lava. In comparison, the S gas flux is $5.7 \times 10^8$ mol/yr, and that of sulfate aerosols is ~2.1 $\times 10^8$ mol/yr.

Persistent degassing with minor erupted magma at open vent basaltic volcanoes has been attributed to convective degassing of magma in the conduit [Kazahaya et al., 1994; Palma et al., 2011; Shinohara, 2008]. In open vent basaltic systems such as Erta Ale and Masaya, low-density volatile-rich magma ascends from magma chamber depths into the conduit and vapor bubbles form once volatile saturation is reached due to decrease in pressure. The formation of bubbles further decreases the density of the magma and gas separation occurs in the upper conduit. The degassed magma is denser and bubble poor and descends [Kazahaya et al., 1994; Palma et al., 2011; Shinohara, 2008]. Convective degassing thus allows magma to lose almost all volatiles to the surface through decompression degassing, without eruption of magma.

Figure 7 shows the S mass balance for steady state convective degassing at Erta Ale and Masaya. Undegassed melt enters the base of the conduit system carrying dissolved S (1200 ppm at Erta Ale, 480 ppm at Masaya) from the source. If we consider a volume of undegassed melt rising up the conduit, CO$_2$-rich bubbles will first nucleate and further drive buoyant rise [e.g., Shishkina et al., 2010]. These bubbles grow by diffusion of volatiles from the melt into the bubble as volatiles partition into the gas phase [e.g., Sparks, 2003]. Thus, for the case of sulfur, almost all of the S in the volume of melt (>90% based on the difference in S concentration between melt inclusions and matrix glass; note that if a higher undegassed S concentration is used then the calculated extent of S degassing increases) is partitioned into bubbles by diffusion from the melt, and is released to the gas plume by magma-gas separation. At the top of the conduit, the melt has lost >90% of its dissolved S to the gas phase, and the S gas fluxes are constrained by direct measurement (5.7 $\times 10^8$ mol/yr at Erta Ale, 5.7 $\times 10^9$ mol/yr at Masaya). Degassed magma (with ~100 ppm S at Erta Ale, ~30 ppm S at Masaya) is denser than volatile-rich melt and sinks by convection. The flux of degassed magma returning to depth is almost the same as the magma degassing rate because insignificant magma is erupted. The mass of S returned to depth by convection is thus calculated at 5 $\times 10^7$ mol/yr for Erta Ale and 4 $\times 10^8$ mol/yr for Masaya. These values would decrease if higher undegassed melt S concentrations were adopted.
The total S flux into the base of the system is the sum of S released as gas, S released as aerosol, S returned to depth by convection of degassed magma, and S erupted in rocks. As the S isotope compositions of gas, aerosol, and degassed melt are known, the S isotope composition of the S source (i.e., undegassed melt) can be calculated (Figure 7), but is essentially identical to that of the gas because the vast majority of the S leaves the system as gas. Note that if higher undegassed melt S concentrations are used the only value in the S mass balance that changes is the S returned to depth by degassed magma (because this is calculated from the magma degassing rate), which decreases and thus yields a larger proportion of the total S in the system released as gas.

Lacking evidence for significant crustal assimilation in recent eruptive products from either volcano [Barberi and Varet, 1970; Barrat et al., 1998; Walker et al., 1993], the emitted sulfur must ultimately be from subcrustal sources (i.e., mantle or subduction fluids; also see section 5.8). Low-pressure crystallization (<0.5 kbar) is the dominant process of melt differentiation at both volcanoes, with estimated degrees of crystallization at <20% olivine + plagioclase + clinopyroxene [Field et al., 2012; Walker et al., 1993]. The relative roles of shallow magma convection and time scales of replenishment of shallow tholeiitic magma chambers by parental mantle-derived melts in maintaining persistent gas emissions from open vent volcanoes is not fully resolved [Wallace and Edmonds, 2011], though influx of hot volatile-rich melts seems necessary for maintaining convection and gas flux. Field et al. [2012] suggested that the 2010 eruption at Erta Ale was driven by replenishment of the magma system by fresh magma. Walker et al. [1993] considered periodic influx of mafic magma a necessary condition for maintaining the long-lived and chemically homogenous magma reservoir at Masaya. We therefore assume that the S isotope composition of the gas phase emitted from Erta Ale and Masaya is representative of the composition of S injected into the system from the mantle (carried in melt), although there may be some delay in degassing if S is first stored in a deeper magma chamber before it is released by convective degassing.

At both volcanoes, the isotope composition of scoria, representing the residual S in the melt, has higher $\delta^{34}S$ than the gas indicating a degassing fractionation effect. The fractionation effect is larger at Masaya, with observed $\Delta^{34}S_{\text{gas-melt}} \sim -2.6\%$ whereas at Erta Ale the observed difference is smaller at $\Delta^{34}S_{\text{gas-melt}} \sim -1.3\%$.

### 5.4. Equilibrium Degassing Fractionation Factors

The S isotope compositions of gas and melt can be assessed based on isotopic equilibrium between S species present in the gas and melt. Below, we use degassing fractionation modeling to assess fractionation effects during S degassing at Erta Ale (section 5.5) and Masaya (section 5.6). How S isotopes partition between gas and melt phases during equilibrium degassing is a function of the S species present in the melt (primarily a function of $f_{O_2}$; Figure 5b) and the S species present in the gas (a function of $f_{O_2}$, P, T, and $f_{H_2}O$). The more oxidized forms of S tend to retain the heavy isotope due to relatively stronger covalent bonding compared to bonds with the light isotope such that $\delta^{34}S_{\text{SO}_4^{2-}-\text{SO}_2} > \text{SO}_2 > \text{S}^{2-}$ $\approx \text{H}_2\text{S}$. Isotopic fractionation is temperature dependent and fractionation factors ($\alpha_{x-y}$ where x and y are different S species) are taken from the experimental results of Miyoshi et al. [1984]:

$$1000 \ln \alpha_{\text{SO}_4^{2-}-\text{H}_2\text{S}} = 6.5(10^6/T^2)$$
$$1000 \ln \alpha_{\text{SO}_2^{2-}-\text{S}^{2-}} = 7.4 \left(10^6/T^2\right) - 0.19$$

and the thermodynamic calculations of Richet et al. [1977]:

$$1000 \ln \alpha_{\text{SO}_2^{2-}-\text{H}_2\text{S}} = 4.7 \left(10^6/T^2\right)^2 - 0.5$$

Combinations of these equations allow:

$$1000 \ln \alpha_{\text{SO}_2^{2-}-\text{SO}_4^{2-}} = 1000 \ln \alpha_{\text{SO}_2^{2-}-\text{H}_2\text{S}} - 1000 \ln \alpha_{\text{SO}_4^{2-}-\text{H}_2\text{S}}$$
$$1000 \ln \alpha_{\text{SO}_2^{2-}-\text{S}^{2-}} = 1000 \ln \alpha_{\text{SO}_2^{2-}-\text{SO}_4^{2-}} - 1000 \ln \alpha_{\text{S}^{2-}-\text{SO}_4^{2-}}$$
1000 ln $\alpha_{H_2S-S^-}$ = $1000 \ln \alpha_{SO_4^{2-}-S^2^-}$ - $1000 \ln \alpha_{SO_2^{2-}-H_2S}$

Equation (10)

Equilibrium sulfur isotope fractionation between the bulk gas and melt phases (considering the major S species in gas and melt) is given by the equation of Mandeville et al. 2009:

$$1000 \ln \alpha_{gas-melt} = X A 1000 \ln \alpha_{SO_4^{2-}-SO_3^{2-}} + X B 1000 \ln \alpha_{SO_3^{2-}-SO_2^{2-}} + Y B 1000 \ln \alpha_{SO_2^{2-}-S^2^-} + Y A 1000 \ln \alpha_{H_2S-S^-} \quad (11)$$

Where X is the mole fraction $SO_4^{2-}$ dissolved in the melt, Y is the mole fraction of $H_2S$ in the gas phase, and B is the mole fraction of $SO_2$ in the gas phase. A fourth term $(YA 1000 \ln \alpha_{H_2S-S^-})$ is included in equation (11) for the fractionation between $H_2S$ and $S^2^-$ (for completeness; not in the original equation of Mandeville et al. 2009), though this term is close to zero at high temperature and was therefore ignored by Mandeville et al. 2009. It is important to note that equation (11) can be rearranged to obtain the original gas-melt fractionation equation of Sakai et al. 1982:

$$1000 \ln \alpha_{gas-melt} = 1000 \ln \alpha_{H_2S-S^-} - (1 - B) \quad (12)$$

However, we prefer the more generic form of the gas-melt fractionation equation (equation (11)) because equation (12) was formulated for a system dominated by $S^2^-$ in the melt and $SO_2$ in the gas and thus implies that the fractionation between these species (i.e., $1000 \ln \alpha_{SO_4^{2-}-S^2^-}$) dominates the isotope fractionation between the gas and the melt. This is not the case for highly oxidized melts where the overwhelming majority of S in the melt can exist as $S^{6^+}$ (Figure 5b) or systems in which $H_2S$ may be the dominant S gas species.

We assessed equilibrium fractionation factors between melt and gas for Erta Ale and Masaya considering constraints on S speciation in the melt and the degassing temperature. The S speciation in the gas may vary with pressure (see Figure 8), and thus we model the $SO_2/H_2S$ ratio as a function of melt $//O_2$ and pressure:

$$\log f_{SO_2} = \log f_{H_2S} (1 - B) \quad (13)$$

from Gerlach et al. 1996, where $K$ is the equilibrium constant for equation (3), which is calculated from:

$$-\Delta G_T = R T \ln K \quad (14)$$

where $R$ is the gas constant and $\Delta G_T$ is the Gibbs free energy of reaction at T:

$$\Delta G_T = -511.89 + 7.318x10^{-2}T + 3.3367x10^6T^{-2} \quad (15)$$

from Robie and Hemingway 1995. The fugacity coefficient for water ($\gamma_{H_2O}$) in the gas phase is...
calculated from Holland and Powell [1991], and mole fractions for H₂O (i.e. moles H₂O/total moles gas) in the gas were estimated from direct measurements of gas emissions from Erta Ale (H₂O mole fraction 0.6–0.95) [Giggenbach and Le Guern, 1976; Sawyer et al., 2008; this study] and Masaya (H₂O mole fraction of 0.85–0.95) [Burton et al., 2000; Martin et al., 2010].

[61] Experimental studies show that S partitions strongly from the melt into a gas phase at pressures less than ~1.5 kbar [Lesne et al., 2011; Webster and Botcharnikov, 2011]. These results are consistent with melt inclusion studies, where pressure is estimated from CO₂ and H₂O solubility at Etna [Spilliaert et al., 2006] and Stromboli [Métrich et al., 2010]. We thus adopt 1.5 kbar as the maximum pressure at which there is a significant proportion of the total S in the melt + gas system in the gas phase. Figure 8 shows the modeled molar ratio of SO₂/(SO₂+H₂S) in the gas phase as a function of pressure, oxygen fugacity, and temperature. At 1 bar, gases at both Erta Ale (ΔQFM = 0.0) and Masaya (ΔQFM = 1.7) are modeled to be strongly dominated by SO₂, which is consistent with the observation that no H₂S was detected in the plumes of either volcano by our sampling method. High-temperature fumarolic gases collected at Erta Ale in 1971 and 1974 have average SO₂/(SO₂+H₂S) ratios of 1.00 and 0.92, respectively [Giggenbach and Le Guern, 1976; Le Guern et al., 1979], with the highest SO₂/ (SO₂+H₂S) ratios corresponding to samples with significant atmospheric O₂. Therefore combustion of H₂S by reaction with atmospheric oxygen [e.g., Gerlach, 1980] could further promote SO₂ in plume gases, which is also consistent with oxidation of other reduced gases such as CO and H₂ upon exposure to the atmosphere [Le Guern et al., 1979]. However for the conditions at Erta Ale (ΔQFM = 0, and T ≈ 1150°C) the model shows that the gas phase is dominated by H₂S at pressure greater than 40 bars (Figure 8). For the degassing conditions at Masaya (ΔQFM = 1.7, and T ≈ 1100°C), SO₂ is dominant in the gas even at pressures up to 1500 bars.

5.5. Degassing Fractionation of Sulfur Isotopes at Erta Ale and S Diffusion in Reduced Melt

[62] Figure 9a shows an empirical S isotope fractionation model for open system degassing at Erta Ale. Gas from the Erta Ale plume has a sulfur isotope composition ~1.3‰ lower than that of the degassed scoria. The fraction of S in the gas phase (0.93; lower x axis) is calculated from the S budget for the magmatic system (Figure 7). The isotope composition of the gas plume is −0.5 ± 0.6‰. Scoria (representative of degassed melt) has S concentrations in the matrix glass of 26–218 ppm, and δ³⁴S values of +0.5‰ to +1.1‰. An initial S concentration of 1200 ppm is used for undegassed melt based on the highest S concentration measured in olivine-hosted melt inclusions. The equations for open system degassing are from Holloway and Blank [1994]:

\[
\delta^{34}\text{S}_{\text{melt}} = (\delta^{34}\text{S}_{\text{source}} + 1000) \left( F_m \left( \alpha_{\text{gas-melt}}^{-1} \right) \right) - 1000
\]

\[
\delta^{34}\text{S}_{\text{gas}} = (\delta^{34}\text{S}_{\text{source}} + 1000) \left( F_g \left( \alpha_{\text{gas-melt}}^{-1} \right) \right) - 1000
\]

[63] The gas is modeled as an accumulated phase derived from steady state convective degassing (section 5.3), calculated by integrating equation (17).

[64] Values for \( \alpha_{\text{gas-melt}} \) were varied iteratively to reproduce the compositions of scoria and plume gas. At Erta Ale, \( \Delta^{34}\text{S}_{\text{gas-melt}} \) is negative (~1.3‰) and therefore values for \( \alpha_{\text{gas-melt}} \) must be <1 in order to reproduce the isotope compositions measured in the scoria/degassed melt. The model results in an empirical fractionation factor between gas and melt (\( \alpha_{\text{gas-melt}} \)) of 0.9991–0.9997.

[65] The measured negative \( \Delta^{34}\text{S}_{\text{gas-melt}} \) and empirical values for \( \alpha_{\text{gas-melt}} < 1 \) cannot be reconciled with equilibrium degassing of a melt that is dominated by S²⁻ (Figures 5b and 9b). At equilibrium, the gas phase would be isotopically heavy relative to the melt, the opposite of what is observed at Erta Ale. Figure 9b shows hypothetical equilibrium degassing fractionation curves for constant \( f_{\text{O}_2} \) conditions at Erta Ale (i.e., ΔQFM = 0). Three cases are considered for the S speciation in the gas phase (Figure 8): All gas as SO₂ (i.e., low-pressure degassing), all gas as H₂S (i.e., high-pressure degassing), and degassing of equal proportions of SO₂ and H₂S. Under equilibrium degassing conditions the melt would be isotopically lighter than the gas, the opposite of what is observed.

[66] The observation that the scoria is isotopically heavy relative to the plume gas can be explained by kinetic fractionation during S degassing. Sulfur...
Diffusion is slow in basaltic melts \(10^{-12} \text{ m}^2 \text{s}^{-1}\) at 1300°C in anhydrous basalt [Behrens and Stelling, 2011; Freda et al., 2005], about an order of magnitude lower than \(\text{H}_2\text{O}\) diffusion, and about a factor of two lower than \(\text{CO}_2\), and is amongst the slowest species to diffuse through melts. Diffusion plays a fundamental role during volatile partitioning into the gas phase [Behrens and Stelling, 2011; Sparks, 2003; Sparks et al., 1994]. The light isotope of S has higher translational velocity than the heavy isotope at all temperatures. The difference in translational velocity between \(^{32}\text{S}\) and \(^{34}\text{S}\) for the ideal gas case is calculated from

\[
\frac{v_2}{v_1} = \sqrt{\frac{m_1}{m_2}}
\]

which determines the maximum translational (kinetic) isotopic fractionation factor:

\[
\frac{v_2}{v_1} \approx \sqrt{\frac{m_1}{m_2}}
\]

where \(K.E. = \frac{1}{2}mv^2\) is the kinetic energy, \(m\) is mass, and \(v\) is velocity, such that:

\[
\alpha_{\text{kinetic}} = \sqrt{\frac{m_1}{m_2}}
\]

Table 6 shows theoretical kinetic fractionation factors between S species considered relevant to S diffusion in melts. For the end-member case of pure translational fractionation between \(^{32}\text{S}^2\) and \(^{34}\text{S}^2\), a large effect (\(\alpha_{\text{kinetic}} = 0.970\)) would be expected and this kinetic fractionation is

<table>
<thead>
<tr>
<th>S Species</th>
<th>(\alpha_{\text{kinetic}})</th>
<th>(1000 \ln \alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{32}\text{S}^2 /^{32}\text{S}^2)</td>
<td>0.970</td>
<td>-30</td>
</tr>
<tr>
<td>(^{32}\text{S}^2 /^{34}\text{S}^2)</td>
<td>0.971</td>
<td>-2.9</td>
</tr>
<tr>
<td>(^{32}\text{S}^2 /^{32}\text{S}^4)</td>
<td>0.990</td>
<td>-10</td>
</tr>
<tr>
<td>(^{34}\text{S}^2 /^{34}\text{S}^4)</td>
<td>0.993</td>
<td>-7</td>
</tr>
<tr>
<td>(^{32}\text{S}^4 /^{32}\text{S}^4)</td>
<td>0.979</td>
<td>-226</td>
</tr>
<tr>
<td>(^{34}\text{S}^4 /^{34}\text{S}^4)</td>
<td>0.571</td>
<td>-560</td>
</tr>
</tbody>
</table>

\[\text{Figure 9.} \quad (a) \text{Open system model for degassing fractionation at Erta Ale with } \alpha_{\text{gas-melt}} \text{ empirically fit to reproduce isotope compositions of plume gas and scoria, with a source composition of } -0.4\% \text{. The gas is modeled as an accumulated phase. The fraction of S in the gas phase (i.e., value of } F \text{ for plume gas) is calculated from mass balance (see section 5.3 and Figure 7). The melt is modeled with an initial S content of 1200 ppm, and the field for scoria is shown as a gray box. Values for } \alpha_{\text{gas-melt}} \text{ have to be } <1 \text{ in order to reproduce the compositions of scoria and are estimated to be between 0.9991 and 0.9997. (b) Erta Ale degassing fractionation model with curves for equilibrium degassing fractionation between a melt with } \text{S}^{33} / \text{S}^{34} = 0.01 \text{ (DFQFM 0.0). Cases are shown for degassing of pure } \text{SO}_2, \text{ pure } \text{H}_2\text{S} \text{ and gas containing equal proportions of } \text{SO}_2 \text{ and } \text{H}_2\text{S}. \text{ The isotope compositions of scoria and plume gas cannot be reproduced by equilibrium degassing fractionation.}\]

![Figure 9](image-url)
independent of temperature. At Erta Ale, $S^{2-}$ is dominant in the melt ($S^{6+/\Sigma S} < 0.07$) and diffusion of $S^{2-}$ through the melt may thus dictate whether chemical and isotopic equilibrium is obtained between gas and melt. $S^{2-}$ complexes with $Fe^{2+}$ in reduced melts [e.g., Carroll and Webster, 1994; Haughton et al., 1974; Klimm et al., 2012; O’Neill and Mavrogenes, 2002; Wallace and Carmichael, 1992; Wilke et al., 2011], thus the effective size and mass of the diffusing species may be much larger than that of $S^{2-}$ [Behrens and Stelling, 2011]. A very large kinetic fractionation is plausible between $S^{2-}$ and $SO_4^{2-}$ diffusion in melts with $\alpha_{\text{kinetic}} = 0.571$ (Table 6).

[70] The empirically calculated values for $\alpha_{\text{gas-melt}}$ of 0.9991–0.9997 for Erta Ale are closer to unity than those derived for the theoretical cases of $S^{2-}$, FeS, or $S^{2-}/SO_4^{2-}$ kinetic fractionation, as has to be the case for diffusion through a complex medium such as melt [Schauble, 2004]. Sulfur diffusion is a complex processes involving the breaking and reforming of bonds with cations in the melt and debate still surrounds the effect of melt S speciation (i.e., $S^{2-}$ versus $SO_4^{2-}$) in controlling S diffusion [Behrens and Stelling, 2011].

[71] Our results show signs of significant kinetic fractionation related to slow S diffusion in melts at Erta Ale. This isotopic fractionation effect is observable due to the reduced nature of the Erta Ale melt. Because $S^{2-}$ is the dominant dissolved S species, equilibrium and kinetic effects work in opposite directions. The equilibrium effect favors $^{34}S$ in the gas (Figures 1 and 9b), whereas the kinetic effect favors $^{32}S$ in the gas. At Erta Ale, the kinetic effect dominates over the equilibrium effect.

[72] The relative effects of equilibrium versus kinetic fractionation can be considered based on [e.g., Schauble, 2004]:

$$\alpha_{\text{gas-melt}} = \alpha_{\text{equilibrium}} \times \alpha_{\text{kinetic}}$$

(21)

[73] The empirical (modeled) $\alpha_{\text{gas-melt}}$ of 0.9991–0.9997 (Figure 9a) and range in calculated $\alpha_{\text{equilibrium}}$ values of 1.002–1.0002 (Figure 9b) result in calculated $\alpha_{\text{kinetic}}$ values of $0.9971$–$0.9995$ (Table 6). However, Figure 8 shows that $H_2S$ is the dominant gas species for the a large portion of the pressure range where S degassing occurs (i.e., 100–1000 bars) [Lesne et al., 2011]. This tends to minimize the equilibrium degassing fractionation effect (Figure 9b), and thus the kinetic effect as well (equation (21)). Considering reasonable degassing conditions (degassing of S at $<1.5$ kbar, with the fraction of S remaining in the melt as a linear function of P), most of the S lost from the melt was degassed at $P > 50$ bars, with “effective” $H_2S$ degassing accounting for $>70\%$ of the degassing experienced by the melt. Rapid re-equilibration between $SO_2$ and $H_2S$ with decreasing pressure is achieved in the gas phase at magmatic temperatures [Giggenbach, 1987; Taran et al., 1995], resulting in high $SO_2/H_2S$ ratio in the gases released at the surface. At $SO_2/(SO_2+H_2S)$ in the gas equal to 0.1 and $S^{6+/\Sigma S}$ in the melt of 0.01, $\alpha_{\text{equilibrium}}$ is calculated at $1.0004$ (equation (11)). Utilizing equation (21) and the best fit for $\alpha_{\text{empirical}}$ of 0.9995 (Figure 9), our best estimate for $\alpha_{\text{kinetic}}$ is 0.9991, which we attribute to the relative diffusivities of $^{32}S^{2-}$ and $^{34}S^{2-}$ (or ionic complexes thereof).

[74] Sulfur diffusion coefficients are available for basaltic melts from Freda et al. [2005]. The diffusion “rate” (change in diffusion distance over time) can be approximated from [Zhang, 2010]:

$$\frac{dx}{dt} = 0.5\sqrt{Dt}$$

(22)

where $dx/dt$ is the change in diffusion distance over time, D is the diffusion coefficient in m$^2$/s, and t is time in seconds. For t from $10^{-5}$–$10^3$ s, $dx/dt$ is in the range of $10^{-4}$–$10^{-9}$ m/s. In comparison, the measured velocity of large bubbles bursting at the surface of the Erta Ale lava lake by Bouche et al. [2010] was 4–7 m/s, who also estimated that the conduit feeding the lava lake is $\sim 3$ m in radius. Considering the magma degassing rate of 520 kg/s $(0.2$ m$^3$/s at a density of 2700 kg/m$^3$, section 5.3) and simple piston flow up a conduit of 3 m radius requires melt velocities of $\sim 10^{-2}$ m/s. Thus, bubbles have higher velocity than melt and low S diffusion prevents equilibration between gas and melt during magma ascent at Erta Ale. This dynamic degassing promotes a kinetic isotopic fractionation effect, which dominates over equilibrium fractionation. The kinetic effect can be observed because kinetic and equilibrium fractionation work in opposite directions due to the reduced nature of the melt.

5.6. Degassing Fractionation at Masaya

[75] The oxygen fugacity at Masaya is typical of arc magmas and sulfate is the dominant S species in the melt (section 4.3). Equilibrium degassing of $SO_2$ from a melt with $S^{6+/\Sigma S} > 0.66$ results in a
fractionation factor \(<1\) (i.e., gas lighter than melt). Thus, the observed negative \(\Delta_{\text{gas-melt}}\) at Masaya is generally consistent with degassing from an oxidized magma. Figure 10 (left) shows modeling results with empirical values of \(\alpha_{\text{gas-melt}}\) of 0.9985–0.9995, which reproduce the isotope compositions of plume gas and scoria from a source with \(\delta^{34}\text{S} = 5.1\%\) (Figure 7). These fractionation factors are consistent with equilibrium degassing fractionation of oxidized melt in which \(S^{6+}\) is the dominant S species in the melt. Figure 10 (right) shows that the isotope compositions of scoria and plume gas can be reproduced with equilibrium degassing fractionation conditions consistent with the oxygen fugacity of the Masaya melt (\(\Delta_{\text{QFM}} > +1.3\) and \(S^{6+}/\sum\text{S} > 0.7\); see Table 4 and section 5.1) and a gas phase dominated by \(\text{SO}_2\) (\(\text{SO}_2/\sum\text{S} > 0.9\); see Figure 8 and section 5.4).

[75] However, for magmas with \(S^{6+}\) as the dominant S-melt species equilibrium fractionation and kinetic fractionation both favor melt with higher \(\delta^{34}\text{S}\) than the gas. Gray curves labeled “d” in Figure 10 (right) show the case in which a kinetic fractionation effect is superimposed on equilibrium degassing fractionation. The isotope compositions of plume gas and scoria can be reproduced with a kinetic effect, however this would suggest that the melt at Masaya is at the low end of the \(f_{\text{O}_2}\) range calculated for melt inclusions and matrix glass. This may be the case if the matrix glasses have experienced posteruption oxidation due to interaction with the atmosphere or that melt inclusions from Masaya may have been affected by \(\text{Fe}^{2+}\) diffusion through the olivine host crystals (section S2). Though the case for kinetic fractionation Erta Ale is strong, it is far more ambiguous at Masaya due to the fact that both kinetic and equilibrium effects favor gas with \(\delta^{34}\text{S}\) lower than that in the melt.

[76] It is necessary to consider the conditions that could favor isotopic equilibrium at Masaya versus kinetic degassing at Erta Ale. Experimental estimates of the effect of water on S diffusion in basaltic melt show that S diffusion is higher by a
factor of three to seven in H$_2$O-rich melts [Freda et al., 2005]. Considering that Masaya melt inclusions have about a factor of 10 higher H$_2$O content than Erta Ale melt inclusions [Field et al., 2012; Lesne et al., 2011], S diffusion is expected to be more rapid in Masaya melts, perhaps promoting equilibration with the gas phase. Shorter diffusion pathways would also impede kinetic fractionation effects, so higher bubble to melt ratio at Masaya could provide a plausible explanation for the lack of observable kinetic effects.

[7] A further consideration is differences in the dynamics of degassing at Masaya versus Erta Ale. Masaya is thought to have a conduit-fed shallow magma reservoir at ~1 km depth based on geo-physical studies [Métais et al., 1997; Stix, 2007; Williams-Jones et al., 2003]. Sulfur input from the conduit into the shallow magma reservoir is balanced by steady state degassing at the vent [Stix, 2007]. The plumbing system at Masaya may therefore result in a longer gas residence time at low pressure allowing equilibration between the gas and melt.

5.7. Implications for S Degassing and Redox Conditions of Melts

[78] Sulfur plays an important role in the oxidation state of magmas [Anderson and Wright, 1972; Behrens and Stelling, 2011; Burgisser and Scaillet, 2007; Kelley and Cottrell, 2009, 2012; Klimm et al., 2012; Lee et al., 2012]. Sulfur degassing may oxidize or reduce melts [Burgisser and Scaillet, 2007; Kelley and Cottrell, 2012; Metrich et al., 2009] depending on the S speciation in gas and melt phases. Oxygen fugacity is a major controlling variable determining the redox states of S in the melt and the gas, but the $f_{O2}$ of a magma may also be modified by open system degassing [e.g., Burgisser and Scaillet, 2007]. Erta Ale is an important natural laboratory for testing these hypotheses because it is one of the few localities where high-temperature gases and pristine scoria can be sampled. Our data show that melt inclusions and matrix glasses have indistinguishable $f_{O2}$ of AQFM 0.0 ± 0.3 (Table 4 and Figure 6). This result is in close agreement with $f_{O2}$ calculated from CO$_2$/CO ratios (22.0 ± 1.6; ΔQFM −0.2 ± 0.1) in high-temperature Erta Ale gas samples of Giggenbach and Le Guern [1976], our gas samples after correction for reaction with air (CO$_2$/CO = 27.3; ΔQFM −0.1; Table 5) as well as $f_{O2}$ calculated from two-oxide thermobarometry for more evolved magmas from the Erta Ale suite [Bizouard et al., 1980] (Figure 6). The Erta Ale magma system shows no change in $f_{O2}$ with degassing or crystallization (also see section 5.1).

[79] Though SO$_2$ is strongly dominant in the Erta Ale plume, degassing at higher pressure that favors H$_2$S must be dominant otherwise reduction of the melt, dominated by S$^{2-}$, would be expected from:

$$6\text{Fe}^{3+}_{\text{melt}} + S^{2-}_{\text{melt}} \leftrightarrow S^{4+}_{\text{gas}} + 6\text{Fe}^{2+}_{\text{melt}}$$ (23)

[80] Thus, degassing of 1 mol of SO$_2$ would result in reduction of 6 mol of Fe$^{3+}$ and loss of 500 ppm S from the melt would reduce the Fe$^{3+}$/ΣFe in the melt to ~0.02 (ΔQFM ~ −3.5), which is not observed. Rather, H$_2$S degassing and gas re-equilibration to SO$_2$ takes place at low pressure via the “gas buffer” reaction [Giggenbach, 1987; Taran et al., 1995]:

$$\text{H}_2\text{S} + 2\text{H}_2\text{O} \leftrightarrow \text{SO}_2 + 3\text{H}_2$$ (24)

[81] Thus, S speciation in the gas phase is strongly pressure dependent (because the right hand side of equation (24) has more moles than the left hand side), and H$_2$S degassing from a melt with S$^{2-}$ results in no redistribution of electrons. Degassing of H$_2$S from a melt with S$^{2-}$ also results in minimization of the equilibrium isotope fractionation effect (Figure 9b), which allows us to recognize the effect of diffusive S degassing from the melt through stable isotope geochemistry at Erta Ale. Oxidation of H$_2$S to SO$_2$ during high-temperature mixing with air is another process that produces high SO$_2$/H$_2$S in the emitted gas at Erta Ale. It is however important to note that as long as no (or negligible) S is lost from the gas phase (i.e. negligible loss to aerosol deposition) the isotope composition of the bulk gas is not affected.

[82] The high-$f_{O2}$ conditions of the Masaya magma promotes SO$_2$ as the dominant gas species, even at pressure >500 bar (Figure 8). Considering the case with SO$_2$ as the only S gas species at Masaya, constant Fe$^{3+}$/ΣFe can be maintained in the melt if S degassing occurred by:

$$0.75S^{6+}_{\text{melt}} + 0.25S^{2-}_{\text{melt}} \leftrightarrow S^{4+}_{\text{gas}}$$ (25)

[83] Degassing of SO$_2$ from a melt with $S^{6+}/\sum S > 0.75$ results in oxidation of Fe$^{2+}$ (if no other buffers are present). For example:
0.875S^{6+}_{\text{melt}} + 0.125S^{2-}_{\text{melt}} + \text{Fe}^{2+}_{\text{melt}} 
\rightarrow \text{S}^{4+}_{\text{gas}} + \text{Fe}^{3+}_{\text{melt}} \quad (26)

[84] This could provide a reasonable explanation for the fact that the Masaya matrix glass is slightly more oxidized (in terms of Fe^{3+}/ΣFe) than melt inclusions, though it is equally plausible that the matrix glass experienced oxidation due to interaction with atmospheric oxygen. However, the salient point is that any melt with S^{6+}/ΣS > 0.75 will oxidize Fe^{2+} [Metrich et al., 2009] due to S degassing if S^{6+} and S^{2-} contribute to the gas phase in the same proportion in which they exist in the melt. However, if diffusion of S^{2-} controls S degassing (i.e., diffuses through melt faster than SO$_4^{2-}$), then melt with S^{6+}/ΣS > 0.75 can become more reduced by S degassing.

5.8. Implications for S Isotope Fractionation and S Sources in Magmatic Systems

[85] Previous studies of S isotope compositions of arc rocks have argued that degassing is unlikely to significantly alter their isotope compositions [Alt et al., 1993; de Hoog et al., 2001]. In recent years, improvements in understanding the relationship between fO$_2$ and S speciation in melts through advances in XANES analysis [Jugo et al., 2010; Metrich et al., 2009] show that oxidized melts typical of arc basalts (ΔQFM > +1) are dominated by dissolved sulfate (S$^{6+}$) to a greater extent than earlier research indicated [Nilsson and Peach, 1993; Wallace and Carmichael, 1992, 1994]. Jugo et al. [2010] and Wilke et al. [2011] show that the transition from sulfide to sulfate in melts occurs over a narrower range in fO$_2$ (S$^{6+}$/ΣS from 0.1 to 0.9 in ~ 1 log unit) than previously thought (S$^{6+}$/ΣS from 0.1 to 0.9 in ~ 2 log units) [Jugo et al., 2005]. The experimental results of Jugo et al. [2010] show that basaltic melts have higher S$^{6+}$/ΣS at lower fO$_2$ compared to previous results, which has significant implications for S isotope fractionation during basaltic degassing.

[86] Our equilibrium degassing modeling shows that melts at redox conditions of ΔQFM > +1.2 (i.e. with S$^{6+}$/ΣS$^{\text{melt}}$ > 0.67) will evolve to higher δ$^{34}$S values at any reasonable pressure (1–1500 bars) and SO$_2$(SO$_2$ + H$_2$S) ratio (0–1). We have demonstrated that in the case of diffusive S degassing, kinetic isotopic fractionation effects must also be considered. Thus, degassing fractionation is likely to affect most basaltic melts/rocks that have lost a significant portion of their original S to the vapor phase, and degassing under most reasonable fO$_2$ and pressure conditions results in preferential retention of the heavy isotope in oxidized melt. We note that the observed Δ$^{34}$S$_{\text{gas-melt}}$ at Masaya is −2.6‰, and that the total range in S isotope compositions of primary products spans ~4‰. In this regard, it is important to note that arc basalts and andesites span a sulfur isotope range of 0‰ to ~ +10‰ [Marini et al., 2011]. Our sulfur budget assessment of output fluxes from Masaya (Figure 7), an arc volcano with very high Ba/La and slab fluid signature [Carr et al., 1990; Carr and Rose, 1987] and no evidence for saturation in any S-bearing mineral phases (section 5.2), indicates a source isotope composition of ~ +5.1‰ (Figure 7).

[87] Recent eruptive products from both Masaya and Erta Ale show no geochemical evidence for crustal contamination [Barberi and Varet, 1970; Barrat et al., 1998; Walker et al., 1993]. Crustal sources of sulfur are an unlikely explanation for the clearly distinct primary S isotope compositions observed at Erta Ale and Masaya (i.e., −0.4‰ and +5.1‰, respectively) given the similarity in crustal thickness (i.e., 20 ± 2 km at Erta Ale [Hammond et al., 2011] versus 25 ± 4 km at Masaya [MacKenzie et al., 2008]). Furthermore, sulfate-rich evaporitic deposits (up to 1000 m in thickness) are common in the Afar region near Erta Ale [Bosworth et al., 2005] providing an abundant potential source of isotopically heavy S (close to that of seawater sulfate (i.e., +21‰). Seawater sulfate is also fixed in the altered oceanic crust [e.g., Alt, 1995] at oceanic spreading centers (such as the Afar triple junction) by hydrothermal circulation providing an additional potential source of isotopically heavy crustal sulfur. The Dallol hydrothermal system located to the north west of Erta Ale serves as an example of modern vigorous hydrothermal activity in the region [Darrah et al., 2013]. Yet, high δ$^{34}$S values are not observed at Erta Ale. Rather, elevated S isotope compositions are observed at Masaya where the crust is composed of accreted arc rocks [MacKenzie et al., 2008] and acidic volcanic rocks [Walker et al., 1993], which do not provide an obvious rich source of isotopically heavy S. Therefore, we discount crustal S as the cause of the distinct S isotope compositions observed at Erta Ale and Masaya. Rather, the positive S isotope compositions observed at Masaya is attributed to its tectonic setting on a subduction zone.
The average isotope compositions of Masaya plume gas is +4.8‰ and within error of the calculated source isotope composition of +5.1‰ because the majority of the S input is released as S gas (Figure 7). Thus, for the case of open vent volcanoes we consider magmatic gases to be more representative of the primary S isotope composition than scoria or lavas. High-temperature gas samples from Momotombo (Ba/La > 100) [Carr and Rose, 1987], located S of Masaya, have δ34S values of +4.2 to +6.8‰ [Menyailov et al., 1986] (comparing well with our Momotombo gas value of +6.2‰; see section 3.2) and high-temperature SO2 from Poas volcano in Costa Rica has δ34S values of ~+7‰ [Rowe, 1994]. The SO2 flux from Masaya represents ~23% of the total SO2 flux from the Central American arc [Hilton et al., 2002; Mather et al., 2006b] and we thus consider a value of +5‰ to be a reasonable representative of S emitted from the Central American arc segment.

Marini et al. [2011] suggested through a model-driven reanalysis of published isotope compositions that magmatic differentiation processes (i.e., degassing and crystallization) from a typical mantle source with δ34S ~ 0 can account for the S isotope variation exhibited by volcanic rocks, gases, and mineral phases. Here, we show that plume gases from an open vent arc volcano, where S gases strongly dominate the total output from the magma system and no sulfide saturation or crustal contamination is evidenced, exhibit source isotope compositions that fall well above the value of 0 ± 2‰ adopted by Marini et al. [2011] for the mantle. The results of this study therefore support previous research attributing high δ34S values observed in arc products to recycling of oxidized sulfur (subducted sulfate) through subduction zones [Alt et al., 1993; de Hoog et al., 2001; de Moor et al., 2010; Mandeville et al., 2010, 1998, 2009; Ueda and Sakai, 1984]. Data sources: Masaya and Erta Ale—this study; Kilauea: gas δ34S values from Sakai et al. [1982], fO2 for gases and rocks from Gerlach [1993]; Momotombo: gas δ34S values from Menyailov et al. [1986], fO2 for gases and rocks estimated from Benhamou et al. [1988]; Miyakejima: gas δ34S from Ohba et al. [2008] and magmatic fO2 from reference therein [Yasuda et al., 2001]; Popocatepetl: gas δ34S from Goff et al. [1998] corrected for sampling fractionation effects according to Ohba et al. [2008] and magmatic fO2 estimated from Witter et al. [2005].
[91] We find minimal difference in Fe oxidation state (as measured by Fe XANES) between melt inclusions and matrix glass at Erta Ale indicating minimal change in $f_{O_2}$. Sulfur in the melt at Erta Ale is dominated by $S^{2-}$ (as measured by S XANES), and the dominance of $H_2S$ degassing (rather than $SO_2$ degassing) is inferred based on thermodynamic modeling showing that $H_2S$ is the dominant gas exsolved from the Erta Ale melt at pressure $> 50$ bars. Rapid gas-phase re-equilibration of $H_2S$ to $SO_2$ occurs as a function of depressurization (with $f_{O_2}$ maintained at $\Delta QFM = 0$), which accounts for the observation that $SO_2$ (rather than $H_2S$) is emitted from the vent.

[92] The isotope compositions of the Masaya plume and scoria are consistent with equilibrium degassing of an oxidized arc magma. However, a small kinetic isotope fraction effect during degassing cannot be ruled out. Equilibration between gas and melt may be related to higher water content in the melt or longer gas residence time in the magma. The isotope composition of the Masaya magma source ($\sim +5\%$) is higher than that of ambient mantle ($0.3 \pm 0.5\%$) [Sakai et al., 1984], consistent with a significant contribution of subducted sulfate to the mantle wedge at the Central American arc. Sulfate-rich fluids released from subducted slabs can oxidize the subarc mantle as reflected by S isotope compositions and oxygen fugacities of arc products.

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