Redox variations in Mauna Kea lavas, the oxygen fugacity of the Hawaiian plume, and the role of volcanic gases in Earth’s oxygenation

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The behavior of C, H, and S in the solid Earth depends on their oxidation states, which are related to oxygen fugacity (fO2). Volcanic degassing is a source of these elements to Earth’s surface; therefore, variations in mantle fO2 may influence the fO2 at Earth’s surface. However, degassing can impact magmatic fO2 before or during eruption, potentially obscuring relationships between the fO2 of the solid Earth and of emitted gases and their impact on surface fO2. We show that low-pressure degassing resulted in reduction of the fO2 of Mauna Kea magmas by more than an order of magnitude. The least degassed magmas from Mauna Kea are more oxidized than midocean ridge basalt (MORB) magmas, suggesting that the upper mantle sources of Hawaiian magmas have higher fO2 than MORB sources. One explanation for this difference is recycling of material from the oxidized surface to the deep mantle, which is then returned to the surface as a component of buoyant plumes. It has been proposed that a decreasing pressure of volcanic eruptions led to the oxygenation of the atmosphere. Extension of our findings via modeling of degassing trends suggests that a decrease in eruption pressure would not produce this effect. If degassing of basalt was responsible for the rise in oxygen, it requires that Archean magmas had at least two orders of magnitude lower fO2 than modern magmas. Estimates of fO2 of Archean magmas are not this low, arguing for alternative explanations for the oxygenation of the atmosphere.

Significance

Volcanic degassing at Mauna Kea volcanoes decreases the oxygenation state of both Fe and S in the magmas, consistent with recent results from Kilauea volcano. The least degassed magmas from Mauna Kea are more oxidized than midocean ridge basalt magmas, possibly due to plate tectonic cycling of material from the oxidized surface to the deep mantle, which is then returned to the surface as a component of buoyant plumes. If the degassing trend observed for Mauna Kea applies to basaltic systems more broadly, decompression does not lead to significant changes in the reducing capacity of the evolved gases and thus cannot explain the rise of oxygen at the Archean/Proterozoic boundary.
glasses, it is reasonable to attribute observed correlations of volatile contents of glasses with their Fe$^{3+}$/ΣFe and S$^{6+}$/ΣS ratios nearly entirely to the effects of shallow-level degassing on the valence states of dissolved Fe and S in the liquid, and thereby to the effects of degassing on \( f_{O_2} \).

**Materials and Methods**

The HSDP recovered >3,000 m of core, most of which samples 150,000- to >500,000-yr-old subaerial and submarine basalts from Mauna Kea volcano (25, 26). The glasses range from undegassed to degassed with respect to \( H_2O \) and S, although even the so-called undegassed samples likely also lost significant \( CO_2 \) during ascent (24). The low-SiO$_2$ glasses have, on average, higher \( H_2O \) contents than high-SiO$_2$ glasses, but the total S contents of the two suites are similar (Fig. 1 A–D and ref. 24).

We focused on glassy samples from two intervals of the HSDP2 core drilled in 1999 (23). The first suite consists of high-SiO$_2$ pillow-rim glasses recovered from 2,702 to 2,841 m below sea level (mbsl), and the second suite consists of low-SiO$_2$ pillow-rim glasses recovered from 2,438 to 2,470 mbsl. The difference in SiO$_2$ contents between the two suites is thought to arise as the result of differences in the pressure of melt segregation in the mantle source of Mauna Kea magmas (low-SiO$_2$ lavas segregate at higher pressures (27)) and/or differences in the extent of melt–rock interaction before or during melt segregation (low-SiO$_2$ lavas reflect lower extents of melt–rock interaction (26)). The \( H_2O \) and S contents are positively correlated in both suites, and the samples have variable but generally low \( CO_2 \) contents (0.16 wt% to 0.81 wt% \( H_2O \); 350 ppm to 1,440 ppm S; 30 ppm to 189 ppm \( CO_2 \); see SI Appendix).

\( f_{O_2} \) (total Fe, expressed as FeO) concentrations of both suites span a narrow range (10.2 wt% to 12.4 wt%; \( f_{O_2} \) Appendix, Fig. 3D) and do not correlate with S contents, but instead plot below the empirical trend in Fe vs. S contents of basaltic magmas of comparable major element compositions at sulfide saturation (SI Appendix, Fig. 5D and ref. 24). Based on these observations, the volatile contents of these submarine glasses have been inferred to reflect variable extents of degassing of \( S+H_2O+CO_2 \)-bearing vapor from magmas that were shallowly stored below the seafloor (5 bars to 50 bars total pressure; \( f_{O_2} \) Appendix, Fig. 5D and ref. 24) and then erupted on the seafloor.

To determine the effect of degassing on magmatic \( f_{O_2} \), we measured Fe$^{3+}$/ΣFe and S$^{6+}$/ΣS ratios of these pillow glasses by micro-X-ray absorption near-edge structure (μ-XANES) spectroscopy (see SI Appendix for a description of analytical methods, spectral fitting procedures, and error assessments for both Fe and S; see Dataset 51 for results).

**Results and Discussion**

The high- and low-SiO$_2$ suites each have Fe$^{3+}$/ΣFe and S$^{6+}$/ΣS ratios that decrease with decreasing \( H_2O \) and S contents (Fig. 1 A–D), and the glasses within each suite that have the highest \( S+H_2O \) concentrations also have the highest proportions of oxidized Fe (Fe$^{3+}$) and S ($S^{6+}$). The low-SiO$_2$ glasses have a narrower range of Fe$^{3+}$/ΣFe and S$^{6+}$/ΣS ratios and have Fe$^{3+}$/ΣFe ratios 0.01 to 0.02 units higher than the high-SiO$_2$ glasses at similar S concentrations (Fig. 1D). Despite the subtle differences between the high- and low-SiO$_2$ glasses, the two suites together define a single overall trend in Fe$^{3+}$/ΣFe and S$^{6+}$/ΣS space (Fig. 1E). Our results demonstrate that degassing of a \( S+H_2O+CO_2 \) vapor is correlated with reduction of Fe$^{3+}$ to Fe$^{2+}$ and of $S^{6+}$ to $S^{2-}$ (Fig. 1). This result is consistent with recent observations of variable Fe$^{3+}$/ΣFe ratios in olivine-hosted melt inclusions from Erebuse, Kilauea (OIB; shown for comparison with our Mauna Kea data in Fig. 1A and B), and Agrigan (arc) volcanoes, although the major element compositions, the \( S+H_2O+CO_2 \) concentrations, and Fe$^{3+}$/ΣFe ratios in the case of Erebuse and Agrigan differ significantly from those studied here, and the Agrigan trend differs from what is observed for other arc glasses (see SI Appendix) (10, 16, 17, 28).

Our work extends the observation to include direct measurements of the simultaneous reduction of S$^{6+}$/ΣS ratios.

Magmatic \( f_{O_2} \) values relative to the quartz–fayalite–magnetite (QFM) oxygen buffer for each of our samples at 1 atmosphere and 1,200 °C were calculated based on their Fe$^{3+}$/ΣFe ratios and major element compositions (see SI Appendix) (Figs. 2 and 3A and B and refs. 8 and 29). Magmatic \( f_{O_2} \) decreases from ~QFM+1.0 in the least degassed samples (i.e., those with highest S and \( H_2O \) contents) to ~QFM–0.4 in the most degassed samples (Fig. 3). This ~1.4 orders of magnitude range in \( f_{O_2} \) from the least degassed to the most degassed samples is consistent with inferred and measured \( f_{O_2} \) values for other Hawaiian lavas, based on Fe–Ti oxide oxybarometry (30), gas-mixing experiments (31), gas equilibria (32–34), and XANES measurements of olivine-hosted melt inclusions and matrix glasses from Kilauea (Fig. 2 and refs. 17, 28). A key point is that whole-rock measurements (vertical gray bars, Fig. 2), which represent the final, degassed lava and can be altered rapidly and pervasively at Earth’s surface, record highly variable Fe$^{3+}$/ΣFe ratios that span more than four orders of magnitude in \( f_{O_2} \) (Fig. 2), making it difficult to infer from such measurements what the preeruptive \( f_{O_2} \) may have been for Hawaiian magmas. The Fe–Ti oxide record (light gray horizontal bar, Fig. 2), the constraints from gas-mixing experiments (black horizontal bar, Fig. 2), and the Fe$^{3+}$/ΣFe ratios measured in less degassed melt inclusions (blue vertical bars, Fig. 2) all indicate that the \( f_{O_2} \) of the crystallizing magmas is near QFM+0.2 to QFM+0.8, broadly consistent with the \( f_{O_2} \) of the least degassed magmas from this study.
Both the fractional and batch models predict a decrease in magmatic $fO_2$ during the degassing that would accompany depressurization during magma ascent. The fractional model results in a decrease in magmatic $fO_2$ from QFM+1.1 to QFM−0.2, or about 90% of the observed change in $fO_2$ observed in the Mauna Kea glasses (Fig. 3). Although the trends are similar for fractional and batch calculations, the models decrease in $fO_2$ only to QFM (batch) and QFM−0.2 (fractional) when they reach 1 bar (i.e., not quite as much as the fractional degassing model).

The decrease in $fO_2$ associated with degassing observed in the Mauna Kea glasses is dominated by changes in the speciation of S in the vapor phase. We demonstrate this first by using the same model to simulate degassing of S-free melts in which H$_2$O or CO$_2$ was the only dissolved volatile component (H$_2$O-only case, SI Appendix, Fig. S7A; CO$_2$-only case, SI Appendix, Fig. S8). We chose melts with much higher volatile contents than observed in the HSDP2 samples of this study to enhance the $fO_2$ response to degassing. In the H$_2$O-only and CO$_2$-only cases (see SI Appendix, Fig. S8 for CO$_2$-only case), the batch-degassing modeling predicts that the fully degassed basaltic melts (i.e., melts decompressed to 1 bar) are, respectively, 0.6 and 0.1 log units higher in $fO_2$ than the undegassed basaltic magmas that start with 4.5 wt% H$_2$O or 1,250 ppm CO$_2$ [note, however, that neither of these extremes results in a change in $fO_2$ large enough to explain the oxidized nature of arc and back-arc basalts relative to MORB (SI Appendix, Fig. S7A for H$_2$O-only case; SI Appendix, Fig. S8 for CO$_2$-only case)]. In the fractional degassing modeling of a H$_2$O-only vapor produces a basaltic melt at 1 bar total pressure that is 0.7 log units higher in $fO_2$ than the undegassed basaltic magma, slightly higher than the batch calculation.

In both the batch and fractional degassing scenarios when H$_2$O is the only volatile component, the increase in melt $fO_2$ results from the fact that dissolved H$_2$ is negligible in terrestrial magmas at low pressure (36), but the amount of H$_2$ in vapor coexisting with hydrous melt is not. Consequently, when dissolved H$_2$O is transferred from the melt into the vapor, H$_2$ is generated in the vapor by disproportion of H$_2$O (37), or gas mixing experiments (38). To evaluate the effect of varying CO$_2$ content on the $fO_2$ behavior of basaltic melts, we applied the D-Compress model to simulate degassing of S-free melts in which H$_2$O or CO$_2$ was the only dissolved volatile component (H$_2$O-only case, CO$_2$-only case).

We modeled the change in magmatic $fO_2$ with progressive degassing of a C–O–H–S vapor species using the software package D-Compress, which executes the gas–melt equilibrium model of ref. 35. This thermodynamically based model assumes that, at equilibrium, the chemical potentials of volatile species dissolved in a fluid (i.e., gas)-saturated silicate melt must be equal in the silicate melt and the fluid. Given some constraints on the system (i.e., initial H$_2$O and CO$_2$ contents, magmatic $fO_2$), D-Compress computes the concentration and speciation of C, H, O, and S in coexisting fluid and silicate melt as functions of pressure and temperature, based on experimental calibrations of the solubilities of H$_2$O, CO, CO$_2$, SO$_2$, H$_2$S, and S$_2$ species in silicate melts, and calculations of homogeneous equilibria in the gas phase for the same species. With D-Compress, we calculated redox conditions and coexisting vapor and silicate liquid compositions by progressively decreasing total pressure (at a constant temperature of 1,190 °C; the effect of variable temperature on $fO_2$ relative to QFM is negligible; see item i below) from the assumed starting pressure of 120 bars down to 1 bar, both for fractional (red curves, Fig. 3) and batch (blue curves, Fig. 3) degassing (see SI Appendix, Modeling the Impact of Degassing on Melt $fO_2$).

Both the fractional and batch models predict a decrease in magmatic $fO_2$ during the degassing that would accompany depressurization during magma ascent. The fractional model results in a decrease in magmatic $fO_2$ from QFM+1.1 to QFM−0.2, or about 90% of the observed change in $fO_2$ observed in the Mauna Kea glasses (Fig. 3). Although the trends are similar for fractional and batch calculations, the models decrease in $fO_2$ only to QFM (batch) and QFM−0.2 (fractional) when they reach 1 bar (i.e., not quite as much as the fractional degassing model).

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for batch degassing, on decompression to 1 bar, the melt is 1.3 log units lower in $f_{O2}$ than the undegassed melt (SI Appendix, Fig. S7B); the $f_{O2}$ decreases by more than 1.5 log units for fractional degassing. In systems in which S is the dominant volatile element, the change in $f_{O2}$ during degassing is more complex than for CO$_2$- and H$_2$O-dominant systems because S is present both as sulfide and sulfate in the melt, and in multiple oxidation states (i.e., S$_2$, H$_2$S, and SO$_2$) in the vapor as well. We nevertheless are able to infer that the decrease in $f_{O2}$ upon degassing for the modeled S-dominant basaltic melt (SI Appendix, Fig. S7B) is dominated by the conversion of sulfide dissolved in the melt to SO$_2$ in the vapor. That is, as suggested by many previous authors (e.g., refs. 6, 10, 16, 17, 28, 30, and 37), degassing reactions such as 3Fe$_2$O$_3$(melt) + FeS(melt) = 7FeO(melt) + SO$_2$(vapor) lead to a decrease in the Fe$^{3+}$/Fe$^{2+}$ ratios, to a decrease in $S^{6-}/S^{2-}$ ratios of the residual S dissolved in the melt (i.e., Fig. 1 A, C, and E), and thus to a decrease in the $f_{O2}$ of the system.

In a system containing H$_2$O, S, $\pm$ CO$_2$ at the $f_{O2}$ levels appropriate to Hawaiian magmas, the tendency of H$_2$O and CO$_2$ degassing to increase the $f_{O2}$ is overwhelmed by the tendency to decrease the $f_{O2}$ due to degassing of S-bearing species. For Hawaiian magmas, it is known that CO$_2$ is the dominant degassing volatile component until pressures of $\sim$100 bars (e.g., ref. 38), at which point H$_2$O and S come out nearly simultaneously. The degassing of dominantly CO$_2$ at pressures higher than that at which H$_2$O and S begin to transfer from melt to vapor in significant quantities increases $f_{O2}$ slightly, but further decreases in pressure result in simultaneous degassing of H$_2$O and S-bearing species at low pressure lead to significant decrease in $f_{O2}$ (SI Appendix, Fig. S8). We emphasize, however, that the effects of degassing on $f_{O2}$ will depend on the sequence of loss of the volatile species with decreasing pressure, which in turn depends on both the solubilities of volatile species and on the initial abundances of volatile components in the undegassed magma.

The least degassed Mauna Kea glass records an $f_{O2}$ that is approximately one order of magnitude higher than MORB glasses at similar MgO contents; i.e., corresponding to Fe$^{3+}$/2Fe$^{2+}$ of $\sim$0.22 for the HSDP2 samples, compared with Fe$^{3+}$/2Fe$^{2+}$ of $\sim$0.16 for MORB (SI Appendix, Fig. S10). This result is broadly similar to results from XANES measurements of matrix glasses and melt inclusions from Kilauea volcano (17, 28), although the highest $O_2$ values from the Mauna Kea glasses (QFM+1.0; this study) are higher than those from Kilauea (QFM+0.7; refs. 17 and 28). However, the Fe$^{3+}$/2Fe$^{2+}$ ratios and inferred $O_2$ values of degassed Mauna Kea glasses overlap with those of average undegassed MORB, and, if the reducing effects of low-pressure degassing were not taken into account, it might be concluded that parental magmas and mantle sources at Mauna Kea had $O_2$ values similar to those of MORB parental magmas and their mantle sources. However, the appropriate comparison is between the least-degassed samples from Mauna Kea and the MORB glasses. Although this comparison indicates that undegassed Mauna Kea magmas were, on eruption, more oxidized than MORB, caution must be exercised in generalizing this statement to their parental magmas and to their mantle source regions.

The mantle sources of Hawaiian magmas are at higher pressures and temperatures than MORB magmas (e.g., ref. 39 and references therein), and corrections must be made to the $O_2$ values based on measurements of fractionalized, lower-pressure and -temperature glasses to determine the $O_2$ values that prevailed in their mantle sources.

i) The relative change in $O_2$ of silicate liquids and the $O_2$ of the QFM oxygen buffer at constant pressure and increasing temperature is small [<0.005 log unit decrease from 1,200 °C to 1,400 °C at 1 GPa, and <0.02 log unit decrease in the same temperature range at 3 GPa (8, 29)], so the effect of the temperature differences between MORBs [1,400 °C to 1,525 °C (39)] and undegassed Hawaiian magmas [1,725 °C (39)] on inferences about their source $O_2$ relative to the QFM oxygen buffer can be neglected.

ii) In contrast, the relative change in $O_2$ of silicate liquids and the $O_2$ of the QFM oxygen buffer at constant temperature and increasing pressure is nonnegligible: The $O_2$ of a typical basaltic silicate liquid increases by 0.39 log units relative to QFM when pressure increases from 1 bar to 3 GPa at 1,300 °C and by 0.36 log units relative to QFM over the same pressure interval at 1,450 °C (8, 29). Thus, assuming a typical average pressure of 1.0 GPa for MORB melt generation (e.g., ref. 40) and 3 GPa for Hawaiian melt generation (e.g., ref. 41 and references therein), the approximately one order of magnitude higher $O_2$ (relative to the QFM buffer at 1 atmosphere) of the undegassed HSDP2 glasses relative to MORB glasses increases to $\sim$1.14 orders of magnitude (relative to the QFM buffer at the pressure of melt generation) difference in their sources after correcting for pressure alone.

iii) Considerable (and different amounts of) olivine fractionation occurred between the generation of primary melts in their mantle source regions and the eruption of the melts from which MORB and Hawaiian glasses were quenched. Assuming that crystallization occurs at a constant total oxygen content for the system, the effect of olivine crystallization is to increase Fe$^{3+}$/2Fe$^{2+}$ and increasing $O_2$ with progressive fractionation, potentially overprinting differences that may have existed between the unfractionated primary melts equilibrated with their residual mantle sources. Mauna Kea primary liquids are thought to have as much as 18 wt% to 20 wt% MgO, assuming they equilibrated with Fo$_{90}$ olivines in their sources (41), whereas MORB primary magmas are thought to have only 12 wt% to 14 wt% MgO, assuming they equilibrated with Fo$_{80}$ olivines in their sources (e.g., ref. 42; see SI Appendix). If this is correct, then primary Mauna Kea liquids fractionated a larger amount of olivine than MORB magmas (44% olivine removed for Mauna Kea, compared with 25% for MORB) to reach 7 wt% MgO. We calculated the Fe$^{3+}$/2Fe$^{2+}$ ratios and $O_2$ of primary mantle melts for MORB and Mauna Kea by taking an undegassed composition from each setting and adding the equilibrium composition olivine back to the melt in 0.1% increments, treating Fe$^{3+}$ and Fe$^{2+}$ as conservative elements (see SI Appendix). This results in a calculated $O_2$ of 0.12 to 0.14 log units (the uncertainty estimate accounts for the range of primary melt MgO contents described above) of the observed difference in $O_2$ between undegassed Mauna Kea and MORB melts. When combined with the temperature and pressure effect on silicate melts in items i and ii, this results in a calculated 0.1 log units difference in $O_2$ between Mauna Kea and MORB sources of 0.66 ± 0.1 log units, compared with the 0.16 log unit difference between the $O_2$ values of the erupted, highly fractionated melts preserved as glasses.

iv) It has been suggested that lower temperatures of melting can generate melts with higher abundances of Fe$^{3+}$ than melts produced during normal MORB melting and that it might be difficult to distinguish unambiguously melts of an intrinsically oxidized source from those of a lower-temperature source because both would have relatively high Fe$^{3+}$/2Fe$^{2+}$ ratios (43). Although we have not tried to quantify this effect, if the reverse temperature effect were true (i.e., that higher temperatures lead to melts with lower Fe$^{3+}$ abundances; e.g., ref. 15), the fact that the Hawaiian plume is generally thought to have an elevated mantle potential temperature of 1,725 °C compared with 1,400 °C to 1,525 °C for MORB sources (39) suggests that unmelten Hawaiian sources have even higher $O_2$ relative to MORB sources than suggested by direct comparison of differences in Fe$^{3+}$/2Fe$^{2+}$ ratios between the melts of these sources. To the degree that this temperature effect is important, it would suggest that the residual sources of the Hawaiian melts studied
here are more than ~0.66 log units more oxidized relative to QFM than MORB primary magmas; i.e., the ~0.66 log unit higher $f_{O_2}$ of Hawaiian primary magmas relative to MORB magmas would be a lower limit to the differences in the $f_{O_2}$ values of their source regions before melting.

After considering these petrogenetic factors, we conclude that the difference in $f_{O_2}$ between the sources of Mauna Kea magmas and MORBs, while less than that suggested by the “raw” Fe*/Fe ratios of undegassed Mauna Kea and MORB glasses, is still significant at $>0.6 \pm 0.1$ log units relative to QFM. The higher $f_{O_2}$ values of undegassed Hawaiian magmas relative to MORBs in turn reflect differences in the $f_{O_2}$ values of the Hawaiian plume relative to MORB sources. This suggests that differences in $f_{O_2}$ in the modern upper mantle are not restricted to the $\sim 1.3$ orders of magnitude difference between the subarc mantle wedge (generally attributed to recycling of oxidized sediments and crust by subduction) and the mantle beneath ridges (likely representative of most of the upper mantle) summarized in the Introduction. If, as is widely thought (18, 25, 44), the sources of OIBs, including Hawaii, contain near-surface material recycled by plate tectonics into the deep mantle that is then returned to the surface in the form of ocean island volcanism, the higher $f_{O_2}$ value relative to the QFM buffer inferred for the mantle sources of the Mauna Kea samples relative to the sources of MORBs could simply reflect that the recycled plume component(s) are more oxidized than the average mantle. This hypothesis is also consistent with observations that Mauna Kea submarine glasses from the studied intervals in the HSFD2 core have relatively radiogenic Sr (0.7035 to 0.7037) and nonradiogenic Nd isotopic compositions (0.51216 to 0.51219 (25)), two characteristics consistent with the presence of recycled components in the Hawaiian plume: either recycled sediment and/or oceanic crust (e.g., refs. 25, 45, and 46). If we approximate the primary melt of Mauna Kea magmas as a simple mixture between a primary melt of garnet-bearing lherzolite, with 5.6 wt% FeO* (3 GPa melt composition from ref. 47) and 1.0 wt% Fe2O3 [the Fe2O3 content corresponding to a melt at 3GPa, 1,450 °C, and QFM (8)], and average altered oceanic crust, with 5 wt% FeO* and 1.97 wt% Fe2O3 (13), it suggests that ~20% of the sources of Mauna Kea primary melts (with Fe*$/2$Fe $\sim$0.142; see SI Appendix) is derived from altered oceanic crust in the Hawaiian plume. This is similar to the high end of the range of other estimates for the amount of recycled material present in the Hawaiian plume [4 to 20% (45, 48, 49)] based on the major and trace element and isotopic compositions of Hawaiian lavas.

Using our results as a starting point, we now consider the influence of gas evolved during degassing of basaltic magmas on the oxidation state of the atmosphere. Volcanic gases are an important input to the inventory of H2, S, and C-bearing molecules in the atmosphere, oceans, and crust (e.g., ref. 50), and it has been hypothesized that a change in the oxidation state of volcanic gases played a role in the “Great Oxidation Event” at ~2.5 Ga (e.g., refs. 21 and 51–55). The general idea is that, before the rise of atmospheric O2, volcanic gas compositions were, overall, more reducing compared with their Proterozoic and Phanerozoic counterparts, leading to increased sinks for atmospheric O2 that would have limited the accumulation of O2 produced by oxygenic photosynthesis (i.e., volcanic gases had a value of $f_{O_2} > 1$ according to Holland’s criterion, eq. 1 below). Then, a change in magmatic $f_{O_2}$ (22) or volcanic degassing conditions (21, 53) led to a change in the composition of volcanic gases added to the atmosphere that resulted in their being more oxidizing, such that volcanic gases no longer contained enough reducing power to titrate the photosynthetic production of O2 which thereafter began to accumulate in the atmosphere [i.e., volcanic gases had a value of $f < 1$ (54)]. This capacity for volcanic gases to react with and remove atmospheric O2 has been referred to as the “reducing power,” and is characterized using Holland’s criterion based on the parameter, $f$ (54) ($m_i$ is the mole fraction of species $i$ in a volcanic gas), defined as

$$f = \frac{m_{H_2} + 0.6 m_{CO} - 0.4 m_{CO_2} + 3 m_{H_2S}}{3.5 (m_{SO_2} + m_{H_2S})} + \frac{1}{3.5} [1]$$

We calculated the $f$ value for the incremental gas composition in equilibrium with the decompressing magma that is provided from the modeled degassing trajectory of Mauna Kea lavas shown in Fig. 3. The value of $f$ at all pressure increments is $\sim 0.5$, does not vary significantly upon decompression from 120 bars to 1 bar, and is consistent with an atmosphere that allows for the accumulation of photosynthetically produced O2. Thus, to the degree that degassing of Hawaiian magmas can represent degassing of Archean magmas, they would not have been sufficiently reducing to preclude the accumulation of O2 in the ancient atmosphere if oxygenic photosynthesis was prevalent at that time. We note that the relative constancy from our modeling of $f$ during decompression is inconsistent with suggestions that a systematic decrease in the pressure of degassing from 100 bars to 1 bar (i.e., a result of the production of subaerial continental crust, thus enabling magmas to degas directly to the atmosphere) could have led to atmospheric oxygenation (i.e., by reducing $f$ from a value of $>1$ to $<1$). These suggestions were based on the increase in SO2/H2S ratio of volcanic gases with decreasing pressure, and the assumption that, at high pressure, emissions of SO2 are negligible. However, the SO2/H2S ratio of volcanic gases at these pressures can be $\sim0.5$ to 1.0, indicating that SO2 emissions at these pressures cannot be assumed to be negligible. Moreover, there are significant changes in C abundance and speciation in the gas phase over this pressure range that must be considered simultaneously with changes in sulfur speciation. Model degassing trajectories for modern MORB-like and arc-like magmas (SI Appendix, Fig. 11) demonstrate that the $f$ value of these gases can be low at high pressures when CO2 dominates the gas composition (at 1,000 bar, $f = -16$ for MORB and $f = -10$ for arc magmas) and increase dramatically as the total C content of the gas decreases and the proportion of CO2 to CO decreases (at 10 bar, $f = -5$ for MORB and $f = -3$ for arc magmas). Nevertheless, the degassing scenarios examined here have $f < 1$ for the entire degassing trajectory, and they do not suggest that any reasonable changes in volatile contents or pressures of degassing would lead to the production of volcanic gases with $f > 1$. Thus, given their $f_{O_2}$ values, degassing of any of the most abundant igneous rocks on Earth today would, regardless of the pressure of degassing or their volatile contents, support oxygen accumulation in the atmosphere. Only if we decrease the $f_{O_2}$ of the degassing magma in our calculations to QFM--2.3 do the released incremental volcanic gases have $f > 1$ (solid gray line, SI Appendix, Fig. S11C). Consequently, we take this to be the upper limit of $f_{O_2}$ for degassing magmas that would have been capable of diminishing atmospheric O2 concentrations. These results are broadly similar to calculations presented by ref. 55, except that they place the upper limit of $f_{O_2}$ for degassing magmas capable of diminishing atmospheric O2 concentrations somewhat higher, near QFM--1.8. In that work, average volcanic gas-phase chemistry was estimated from present-day measurements of volcanic gas emissions, which may contribute to the difference in upper limits between our study and that of ref. 55.

Our degassing calculations suggest that changes in the average degassing pressure of the most abundant modern basaltic magma types (i.e., the calculations on Mauna Kea lavas as representative of OIBs and on representative MORB and arc compositions summarized in SI Appendix, Fig. S11) could not have strongly influenced the oxygen-poor conditions at Earth’s surface before ~2.3 Ga. For volcanic processes to have been responsible for inhibiting the rise of oxygen in the Archean, magmas would have to have been, on average, more reduced than modern MORB magmas by more than two orders of magnitude (SI Appendix, Fig. S11).

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Vanadium contents in olivines in Archean komatiites suggest that magmatic \( \text{FO}_2 \) in Archean komatiites were between QFM–1 and QFM+2 (S6), which is outside of the range of \( \text{FO}_2 \) levels required to prevent oxygenation of the atmosphere, based on our calculations, as well as those presented by ref. 55. If these trace metal constraints accurately describe the redox state of average Archean magmas, then volcanic gases from Archean magmas would also have been unable to limit oxygenation of the atmosphere if photosynthetic microbes were present at that time. We conclude that, if volcanic processes are required to play a major role in inhibiting the rise of oxygen in the Archean, either photosynthetic microbes were not present or Archean basalts were significantly more reducing than modern magmas or than current evidence suggests for Archean basalts.

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44. White WM (2010) Oceanic island basalts and mantle plumes: The geochemical per-
METHODS

Fe XANES

We determined \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratios of pillow glass by micro-x-ray absorption near-edge structure (\( \mu \)-XANES) spectroscopy at beamline 13-IDE, Advanced Photon Source, Argonne National Laboratory. Spectra were collected in fluorescence mode from 7020 eV to 7280 eV using a Si [111] monochromator and a defocused beam diameter of 50x50 \( \mu \text{m} \). Counts were recorded on a multi-element silicon drift detector x-ray spectrometer, equipped with two Si drift diode detectors. Eight layers of aluminum foil were placed in the path of the incident photon beam in order to decrease the intensity of the incident photon beam prior to interaction with the surface sample, which could lead to auto-oxidation or auto-reduction of \( \text{Fe} \) species dissolved in the glass. The incident photon beam intensity resulted in on the order of \( 10^9 \)-\( 10^{10} \) counts on \( \text{Fe} \) on a LW standard glass (1).

Spectra were normalized and the pre-edge features were fit following techniques outlined by ref. 1, with some exceptions. Ref. 1 fit the pre-edge features using two background functions and two Gaussian curves to fit the \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) peaks, simultaneously solving for 11 curve parameters that are allowed to vary independently to produce a fit spectra by minimizing error between the fit and the data. In this study, we have attempted to minimize uncertainty or bias that may be introduced by allowing curve
parameters to vary, which might be reasonably expected to be constant. For instance, the width of the Gaussian curves should not be variable in glasses with similar compositions, but the intensities should vary as a function of the Fe$^{3+}$/Fe$^{2+}$ ratio of the glass. To fix these two curve parameters and reduce the number of free parameters in the fit solution to 9, we calculated the average full-width half-maximum of both the high energy and low energy Gaussian curves for all the samples analyzed in each beam session. We then re-fit each spectrum, keeping the full-width half-maximum of both Gaussian curves fixed and equal to the average value of all samples analyzed in that session (supplementary figure 1, 2).

We use the ratio of the areas of each Gaussian curve in our calibration to Fe$^{3+}$/ΣFe ratios, instead of the centroid positions that ref. 1 used. Ref. 1 utilized beamline X26a at the National Synchrotron Lightsource I, which has been decommissioned. Although X26a and 13-IDE both have μ-XANES capabilities, the hardware and configuration of 13-IDE are sufficiently different from X26a that data collection routines and spectra handling require a modified approach. For example, there is not significant drift in monochromator energy at 13-IDE, which results in greater energy reproducibility in the absorption spectra collected over several hours in a beam session, as well as greater session-to-session reproducibility. This, in combination with other factors, results in significantly improved energy resolution in the pre-edge region for Fe spectra, even when using the Si [111] monochromator (supplementary figure 1). The consequence of this is that the Gaussian-fit pre-edge features that correspond the 1s to 3d electronic transitions in Fe$^{3+}$ and Fe$^{2+}$ are well defined compared to those collected earlier and render the use of the centroid positions in Fe redox calibrations less necessary than in previous works (e.g.,
ref. 2). Here, we use the ratio of the area under the higher energy Gaussian curve to the area under the lower energy Gaussian curve, because this ratio is closely related to the physical phenomenon of \( \mu \)-XANES spectroscopy, and generate a calibration curve using the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratio determined by Mossbauer spectroscopy, reported by ref. 1. We also utilize the centroid calibration described in ref. 1, and note that the choice of centroid or area ratio calibrations does not impact the calculated \( \text{Fe}^{3+}/\Sigma \text{Fe} \) ratios of unknown samples meaningfully.

We performed an error analysis of the spectral fit parameters of spectra collected using the Si [111] monochromator using a bootstrap monte-carlo method. For a given spectrum, we assigned an arbitrary uncertainty on the deadtime corrected, normalized, detector measured counts on Fe per second for each data point in the pre-edge of 0.002. The units of this error are arbitrary, but we note that it is a liberal estimate based on observations over 20 beam sessions at two synchrotron facilities, including 10 sessions using the same detector array used in this study, 3 of which sessions were at the beamline used in this study. A normal distribution of data was generated for each data point in the pre-edge, with a standard deviation equal to the assigned analytical uncertainty and centroid equal to the actual measured value. A synthetic spectrum was then constructed by randomly sampling this distribution of data of each measured data point. This synthetic spectrum was fit using the same routine described above, and by ref. 1, and this was repeated 100 times for each collected spectrum. This exercise generates quantitative uncertainties for each spectral parameter, which can be propagated through the calibration to generate an uncertainty for \( \text{Fe}^{3+}/\Sigma \text{Fe} \) ratios, which is +/- 0.015 (absolute). This can be compared to the empirical precision of the area ratios on the standard glasses,
which is +/- 0.01 (n = 2 spots), corresponding to an uncertainty in Fe$^{3+}$/ΣFe ratios of 0.006 (absolute).

Finally, we considered differences between spectra produced at X26a and 13-IDE that may arise due to major differences between beamlines, such as the energy of their respective electron storage rings (~2.8 GeV at NSLS-I X26a, ~7 GeV at APS 13-IDE), the storage ring sampling methods (bending magnet at X26a, insertion device at 13-IDE), and the intensity of the incident photon beam (orders of magnitude more intense at 13-IDE). The analytical facilities are sufficiently complicated at the synchrotron level that it is not practical for this study to seek to understand the nature of each of these differences, so we present an empirical comparison of spectra collected at X26a before NSLS-I decommission with spectra collected at 13-IDE (supplementary figure 3). The spectra are collected on two submarine glass chips from the Gulf of Aden (3). Following the methods presented here, the first glass chip has calculated Fe$^{3+}$/ΣFe ratios of 0.171 (NSLS) and 0.188 (APS). The second glass chip has calculated Fe$^{3+}$/ΣFe ratios of 0.163 (NSLS) and 0.174 (APS). The first glass chip has Fe$^{3+}$/ΣFe ratios that are 0.017 (absolute) more oxidized when measured at APS than at NSLS, and the second glass chip has Fe$^{3+}$/ΣFe ratios that are 0.011 (absolute) more oxidized when measured at APS than at NSLS. The origin of this offset is not clear at this time, but in order to produce a dataset that can be compared with previously collected data at NSLS-I, we “correct” Fe$^{3+}$/ΣFe ratios calculated from spectra collected at APS by subtracting 0.02 units from each sample average.

S XANES
We determined $S^{6+}/\Sigma S$ ratios of pillow glass by micro-x-ray absorption near-edge structure ($\mu$-XANES) spectroscopy, also at beamline 13-IDE, Advanced Photon Source, Argonne National Laboratory. Spectra were collected in fluorescence mode from 2447 eV to 2547 eV, with a dwell time of two seconds on each point, using a Si [111] monochromator and a defocused beam diameter of 50x50 $\mu$m. Counts were recorded on a multi-element silicon drift detector x-ray spectrometer, equipped with two Si drift diode detectors. All analyses were done in a helium atmosphere, to avoid interaction between the incident photon beam and atmosphere. As with iron, to avoid significant beam damage during analysis, the beamline hardware was tuned so that the incident photon beam intensity was on the order of $10^9$-$10^{10}$ counts on S on the submarine MORB glass TR101-15D-8g, which has 1790 ppm S (supplementary figure 4a). Each sample was analyzed with a stationary beam in triplicate, moving the beam position for each of the three analysis spots.

In the absence of an independent method for accurately determining $S^{6+}/\Sigma S$ ratios, we follow the approach of ref. 4 to calculate $S^{6+}/\Sigma S$ ratios from our absorption spectra. We take a MORB glass with all sulfur present as $S^{2-}$ and an experimental glass with all sulfur present as $S^{6+}$ as our two endmember absorption spectra (supplementary figure 4a). Each unknown is fit using linear combinations of the MORB and experimental glasses. Since each of those glasses represents an endmember speciation of S, we assume that the intensity of absorption spectra features for both $S^{2-}$ and $S^{6+}$ respond linearly to the concentration of $S^{2-}$ and $S^{6+}$ dissolved in the sample glass, and report $S^{6+}/\Sigma S$ ratios equal to the mixing proportions of the endmember spectra necessary to fit each unknown spectra (supplementary figure 4b). The glasses in this study have low sulfur contents.
compared to recent experimental glasses (4-6), which results in a decreased signal to noise ratio in collected spectra. We estimate that the uncertainty on these sulfur XANES measurements is +/- 0.01 (absolute), based on the reproducibility of spectra from individual natural samples.

To test the extent of possible beam damage, we collected several spectra in one location on a series of back-arc basin glasses that have spectral features indicative of the presence of both S²⁻ and S⁶⁺, exposing the same pool of glass to the incident photon beam for 110 consecutive minutes (supplementary figure 5). There are noticeable changes in the sulfur absorption spectra over this time period. The S⁶⁺ absorption feature decreases in intensity. At the same time, the broad S²⁻ absorption feature increases in intensity, but at slightly higher energy than the center position of this feature. This could be due to the generation of S⁴⁻ as the result of beam damage (5, 6). The overall differences in intensity of the absorption features between spot 1 and spot 10 (i.e., after 110 minutes of beam exposure) are small, and unlikely to impact the calculated S⁶⁺/ΣS ratios determined here. Nonetheless, we collect a single spectrum in eleven minutes, and then move the position of the incident photon beam before collecting another spectrum on the same sample, limiting the exposure time of any glass pool.

VOLATILES IN HSDP2 SUBMARINE GLASS

Supplementary figure 6 shows the key relationships between S and FeO*, and S and H₂O described in the main text. The S contents of all but two glasses are below the sulfur content of MORB magmas that are sulfide-saturated, from ref. 7, modified after ref. 8. The sulfur contents range from ~200 ppm to ~1400 ppm within a narrow range of
FeO*, suggesting that sulfur degassing is taking place in a sulfide-undersaturated melt. This is supported by petrographic descriptions from ref. 8 that note these glasses do not appear to have sulfide blebs present. Both suites have H$_2$O and S contents that are positively correlated. The low SiO$_2$ glasses appear to have higher initial H$_2$O contents, but similar initial S contents, relative to the low SiO$_2$ glasses (i.e. low SiO$_2$ glasses have higher H$_2$O/S ratios than high SiO$_2$ glasses; supplementary figure 6b), but both suites are consistent with concomitant sulfur and water degassing.

**COMPARISON TO OTHER DEGASSING-REDOX STUDIES**

Supplementary figure 7 shows the relationship between Fe$^{3+}$/ΣFe ratios and calculated magmatic fO$_{2s}$, and S and H$_2$O contents in submarine pillow glasses from this work, and in two other recent studies of olivine hosted melt inclusions (9, 10). The Agrigan melt inclusions are more oxidized than the HSDP2 submarine glasses in this study (Supplementary Fig. 12 a-f). The Agrigan melt inclusions are also more water rich than the HSDP2 submarine glasses (Supplementary Fig. 12e). The relationship between Fe$^{3+}$/ΣFe ratios and S and H$_2$O contents is less systematic than is observed for HSDP2 submarine glasses (Supplementary Fig. 12 a, b). This could be because the HSDP2 submarine glasses are more restricted in their major element compositions, or because melt inclusion processes introduce variability in Fe$^{3+}$/ΣFe ratios +/- H$_2$O contents, +/- S contents of the Agrigan dataset, or some combination of the two. The Agrigan melt inclusions also record more oxidized magmatic fO$_{2s}$ than the HSDP2 submarine glasses (Supplementary Fig. 12 d-f). The Erebus melt inclusions span a wide range in Fe$^{3+}$/ΣFe ratios and S contents, and a wider range in H$_2$O contents than the HSDP2 submarine
glasses, but are not as water rich as the Agrigan melt inclusions (Supplementary Fig. 12 a, b, d, e). The relationship between Fe$^{3+}$/ΣFe ratios and S and H$_2$O contents in Erebus melt inclusions are less systematic than the submarine glasses from this study, similarly to the Agrigan melt inclusions (Supplementary Fig. 12 a, b). The general sense of decreasing Fe$^{3+}$/ΣFe ratios with increasing extents of degassing is broadly similar between the three datasets, despite differences in sample types (i.e., submarine glass vs. olivine-hosted melt inclusions), magma compositions, and magma storage conditions (Supplementary Fig. 12 a, b). The extent of reduction per ppm S loss (or per wt% H$_2$O lost) is greatest for Erebus melt inclusions and HSDP2 submarine glasses (i.e., the slope of the relationship between S and H$_2$O and Fe$^{3+}$/ΣFe ratios is steepest for these samples; Supplementary Fig. 12 a).

**MODELING THE IMPACT OF DEGASSING ON MELT fO$_2$**

We modeled the change in magmatic fO$_2$ with progressive degassing of a C-O-H-S vapor species using the gas-melt equilibrium model of ref. 11. This thermodynamic model computes C, H, O, and S concentrations and speciation in coexisting fluid (i.e., gas) and silicate melt as functions of pressure, temperature, and fO$_2$, based on experimental calibrations of melt solubility and homogeneous equilibrium in the gas phase for H$_2$, H$_2$O, CO, CO$_2$, SO$_2$, H$_2$S, and S$_2$ species. The melt is assumed in this model not to crystallize any solids or to precipitate a separate sulfide phase. We modified the solubility models of ref. 11 so that they fit the experimental results of ref. 12 for H$_2$O and CO$_2$ solubility. In Figure 3a and b, the calculation begins at a total pressure of 120 bar, a temperature of 1190°C, and an fO$_2$ for the initial (i.e., undegassed) melt (QFM+1.1) that
is slightly higher than the highest $f$O$_2$ constraint from this study; the volatile contents of the initial melt were set at 1.05 wt% H$_2$O, 1370 ppm S, and 0 ppm CO$_2$, near the highest volatile contents measured in the samples from this study (except for the assumed zero concentration of CO$_2$; if the initial melt is allowed to have CO$_2$ at the 100-200 ppm level, the model curves predict less total reduction in $f$O$_2$). We assume the melt has the major element composition of sample SR0914-10.50, a high-SiO$_2$ glass with high S content (1370 ppm S). The modeling assumes that the initial melt is vapor saturated at the starting pressure and temperature of the calculation. We calculated redox conditions and coexisting vapor and silicate liquid compositions by progressively decreasing total pressure (at a constant temperature of 1190°C) from the assumed starting pressure of 120 bars down to 1 bar both for fractional (red curve, Fig. 3a, b) and batch (blue curve, Fig. 3a, b) degassing.

Supplementary figure 8 shows the relationship between gas phase and melt redox defined by the degassing models used in the main text. We show degassing trajectories for a melt containing H$_2$O as the only volatile element (gray long dashed line, Supplementary Fig. 8), a melt containing S as the only volatile element (solid gray line, Supplementary Fig. 8), a melt containing CO$_2$ as the only volatile element (dash-dot gray line, Supplementary Fig. 8), a melt containing both H$_2$O and S (short dashed gray line, Supplementary Fig. 8), and a melt containing H$_2$O, S, and CO$_2$ (solid black line, Supplementary Fig. 8).

It is possible (and indeed likely for CO$_2$; e.g., ref. 13) that the least degassed of our samples were themselves the degassing products of more volatile-rich liquids. In principle, the original magmatic $f$O$_2$ before degassing from such melts could be estimated
by incrementally adding the composition of the saturating vapor to the least degassed melt composition, calculating the $fO_2$ of this volatile-enriched melt and finding the pressure at which it is vapor saturated, and then repeating this up to arbitrarily high volatile contents and pressures. However, the most volatile-rich glasses in this study are approximately saturated with a liquid sulfide phase based both on thin section study and their position on an Fe-S plot for basaltic melts (Supplementary Fig. 6a; refs. 7, 8).

Degassing (or the addition of gas to) a melt containing sulfide blebs cannot be as simply modeled as degassing from a sulfide under-saturated melt. For example, when on decompression, S transfers from the silicate liquid to a vapor phase, the silicate liquid would respond by dissolving a fraction of the sulfide phase in order to maintain the appropriate sulfur content at sulfide saturation. This not only would tend to buffer the S content of the melt even while degassing proceeds, but it would likely increase the FeO* content of the melt (which in turn would influence the sulfide solubility) and would therefore have feedback on $fO_2$. These processes have not, to our knowledge, been quantitatively modeled, and they are beyond the scope of this study. Consequently, we have not explored any degassing history and $fO_2$ for liquids more volatile-rich than the HSDP2 samples with the highest S and H$_2$O contents.

**IMPACT OF PRESSURE AND TEMPERATURE ON SILICATE MELT $fO_2$ RELATIVE TO QFM**

The mantle source for Hawaiian magmas undergoes melting at higher pressure and temperatures than the mantle source for mid-ocean ridge magmas. We calculated the effect that this will have on absolute $fO_2$ calculated from Fe$^{3+}$/∑Fe
ratios, as well as $f_O^2$ relative to the QFM oxygen buffer, using the algorithm of ref. 14 and the definition of the QFM oxygen buffer according to ref. 15. Supplementary figure 9 shows the results of these calculations, and demonstrates that increasing pressure from 1 to 3 GPa causes an increase in the absolute $f_O^2$ of both silicate melt and the QFM oxygen buffer, but that the absolute $f_O^2$ of the silicate melt increases slightly more than that of QFM, leading to a change in $f_O^2$ relative to QFM of ~0.14 log units for the silicate melt at 3 GPa. The opposite is true for a silicate melt at higher temperature. The difference in absolute $f_O^2$ between a silicate melt and QFM decreases with increasing temperature by <0.02 log unit from 1200°C to 1400°C. We conclude that the higher pressures and temperatures of equilibration for primary melts in Hawaii can account for ~0.13 log units of the observed offset between the $f_O^2$ of undegassed Hawaiian melts and undegassed MORB.

THE EFFECT OF OLIVINE REMOVAL ON Fe REDOX

Hawaiian primary magmas are thought to be in equilibrium with Fo90-Fo91 olivine, and as a result, likely crystallize significantly higher mass fraction of olivine prior to eruption than MORB magmas at the same MgO content. We calculated the $Fe^{3+}/\sum Fe$ ratios and $f_O^2$ of primary mantle melts for MOR and Hawaiian settings by taking an undegassed composition from each setting and adding the equilibrium composition olivine back to the melt in 0.1% increments, treating $Fe^{2+}$ and $Fe^{3+}$ as conservative elements (Supplementary Fig. 10). We use a $K_{D}^{Fe^2+/Mg}$ between olivine and melt of 0.34. We recalculate the equilibrium olivine composition at each increment, and continue the calculation until the melt composition is in equilibrium with Fo89, Fo90,
and Fo91 olivine. A MORB primary melt in equilibrium with Fo90 olivine has 16 wt% MgO, 0.12 Fe$^{3+}/\sum$Fe, and has $fO_2 \sim$QFM-0.3. A Hawaiian primary melt with the same Fe$^{3+}/\sum$Fe ratio and $fO_2$ is in equilibrium with Fo93.5 olivine and has 26 wt% MgO, both of which are considered too high to be reasonable for Hawaiian mantle and melts. If Hawaiian primary melts are in equilibrium with Fo91 olivine, they have 19 wt% MgO, 0.14 Fe$^{3+}/\sum$Fe, and $fO_2 \sim$QFM+0.2. We conclude that the difference in primary melt compositions between Hawaii and MOR settings can account for ~0.5 log units of the observed offset between undegassed Hawaiian and MORB melts.

**FIGURE CAPTIONS**

Figure 1. A stacked plot of pre-edge features on the same standard glass, analyzed at beamline X26a at NSLS (light gray line) and beamline 13-IDE at APS (black line). The spectrum at NSLS was collected using a Si [311] monochromator. The spectrum at APS was collected using a Si [111] monochromator.

Figure 2. A plot of a pre-edge feature from standard glass LW-0 and the fit parameters, obtained using the methods described here.

Figure 3. A comparison of Fe$^{3+}/\sum$Fe ratios calculated from spectra collected on the same glasses from APS and NSLS, using area ratio calibrations described here. Error bars represent the uncertainty on spectral fits using the monte carlo boot strap simulation described here.
Figure 4. Sulfur absorption spectra of (a) endmember composition glasses, and (b) unknown HSDP2 glass SR0915-0.4. The red dashed line in panel b represents the fit to the unknown data, obtained using linear combinations of the spectra in panel a.

Figure 5. Two sulfur absorption spectra demonstrating the effects of beam damage on the intensity of the $S^{6+}$ absorption feature.

Figure 6. Plots of S versus (a) FeO* concentrations, and (b) H$_2$O concentrations in HSDP2 submarine glasses. The dark black line in panel a is the sulfur concentrations in MORB that are sulfide saturated, from Mathez et al. (1974) and modified from Seaman et al. (2004).

Figure 7. (a) Fractional (black curve) and batch (gray curve) degassing calculations as in (Fig. 3a, b main text), where H$_2$O is assumed to be the only volatile component dissolved in the melt in order to isolate the effects of degassing of H$_2$O from melts from those of S and CO$_2$. White circles are submarine glass and melt inclusions from Mariana arc volcanoes (7), gray circles are submarine glass from the Mariana Trough back-arc spreading center (7), and black circles are submarine MORB glasses (44). (b) Fractional (black curve) and batch (gray curve) degassing calculations as in (a), where S is assumed to be the only volatile component in the melt in order to isolate the effects of degassing of S from melts from those of H$_2$O and CO$_2$. 
Figure 8. Plot of magmatic $f_{O_2}$ versus pressure for several batch degassing trajectories, using the D-COMPRESS algorithm presented by Burgisser et al. (2015).

Figure 9. Plots of (a) pressure and (b) temperature versus $f_{O_2}$ for silicate melts (squares and inverted triangles) and the QFM oxygen buffer (solid and dashed black lines). The $f_{O_2}$ is calculated according to Kress and Carmichael (1991) and QFM is defined according to Frost (1991).

Figure 10. Plot of $Fe^{3+}/\Sigma Fe$ ratios versus MgO concentration for submarine glasses from MORB (Cottrell and Kelley; 2011) and HSDP-2 (this study). Calculations show olivine addition trajectories for undegassed MORB and HSDP-2 samples, with endpoints at melts in equilibrium with Fo89, Fo90, and Fo91 olivine.

Figure 11. Plots with the results of fractional degassing models calculated using the D-COMPRESS software from Burgisser et al. (2015), showing pressure (bars) versus (a) $f_{O_2}$ of the melt, and (b, c) the Holland $f$ factor of the gas phase. The solid black curves represent modern degassing scenarios from OIB (stars, same degassing model from Fig. 3a, b, for HSDP2 glasses), MORB (circles; initial melt has $f_{O_2} = QFM+0.3$, 0.1 wt% H$_2$O, 200 ppm CO$_2$, 1700 ppm S), and arc (triangles, initial melt has $f_{O_2} = QFM+1.5$, 4.5 wt% H$_2$O, 800 ppm CO$_2$, 1982 ppm S) settings. All models assume no sulfide phase is allowed to precipitate. We use the same solubility models as for the HSDP2 models described in the text. The curve for MORB degassing extends to 1 bar pressure, however the average pressure of MORB eruptions is 300 bars (marked with a horizontal gray line
on all panels to demonstrate the melt and gas phase chemistries of MORB magmas on eruption to the seafloor). The arc degassing curve approximates the trend in volatile contents and $fO_2$ of melt inclusions from Agrigan volcano in the Mariana arc (Kelley and Cottrell, 2012). The gray curve is a fractional degassing scenarios for a reduced (initial melt has $fO_2 = \text{QFM}-2.3$, 0.75 wt% H$_2$O, 250 ppm CO$_2$, 2500 ppm S) basaltic magma. The $f$ factor is calculated from the output gas chemistries from the D-COMPRESS software of Burgisser et al. (2015), as in equation 1 from the text.

Figure 12. Plots of Fe$^{3+}/\Sigma$Fe ratios versus (a) sulfur concentrations, (b) H$_2$O concentrations, (c) total Fe expressed as FeO, and calculated magmatic fO$_2$ relative to QFM versus (d) sulfur concentrations, (e) H$_2$O concentrations, (f) total Fe expressed as FeO in HSDP2 submarine glasses and olivine hosted melt inclusions from Moussallam et al. (2014, black squares) and Cottrell and Kelley (2012, white squares). Calculated fO$_2$ for Agrigan and Erebus magmas are taken directly from the original publications. The fO$_2$s for HSDP2 submarine glasses are calculated at 1200 C and 1 atm according to the algorithm of Kress and Carmichael (1991) relative to the position of the quartz-fayalite-magnetite oxygen buffer according to Frost (1991).

REFERENCES CITED


Supplementary Figure 1

Arbitrary absorption units

Energy (eV)

Standard glass LW-0

APS Si [111] mono

NSLS Si [311] mono
Supplementary Figure 2

- data, LW-0, this study
- total fit
- background fit curves
- Gaussian fit curves

Arbitrary absorption units

Wavelength (nm): 7106, 7108, 7110, 7112, 7114, 7116, 7118
Supplementary Figure 3

![Graph showing the relationship between $\frac{\text{Fe}^{3+}}{\sum \text{Fe}}$ (APS 13-IDE) and $\frac{\text{Fe}^{3+}}{\sum \text{Fe}}$ (NSLS X26a).](image)

The graph illustrates a linear trend with a 1:1 ratio indicated by a dashed line. The data points for APS 13-IDE are marked with squares and error bars, suggesting variability in the measured values.
Supplementary Figure 4

a. Graph showing absorption vs. energy (eV) for TR101-15D-8g and PC-35 glass, with annotations for S^2-, S^2-1, and S^6+.

b. Graph showing absorption vs. energy (eV) for SR0915-0.4 data, 1310 ppm S, with annotations for 91.5% TR101-15D-8g and 8.5% PC-35.
Mariana trough glass, 553 ppm S
spot 1, 11 minutes exposure to beam
spot 10, 110 minutes exposure to beam
Supplementary Figure 6

a. SCSS

S (ppm) vs. FeO* (wt%)

b. H2O/S = 4

H2O/S = 7

S (ppm) vs. H2O (wt%)

MgO (wt%) vs. S (ppm)

H2O (wt%) vs. MgO (wt%)
Supplementary Figure 7

H$_2$O only, 4.5 wt% c.

S only, 6000 ppm d.
Supplementary Figure 8

H$_2$O only, 5.0 wt %
S only, 6000 ppm
CO$_2$ only, 1000 ppm
H$_2$O-S
5.0 wt % H$_2$O, 2000 ppm S
H$_2$O-S-CO$_2$
1.5 wt % H$_2$O, 2500 ppm S
1700 ppm CO$_2$
Supplementary Figure 9

a. 

QFM, 1300 ºC (constant) 
MORB, 1300 ºC (constant) 
undegassed HSDP, 1300 ºC (constant)

b. 

QFM, 1 GPa (constant) 
MORB, 1 GPa (constant) 
undegassed HSDP, 1 GPa (constant)
Supplementary Figure 10

Fe$^{3+}$/∑Fe vs. MgO (wt%) plot with various markers indicating different QFM variations (ΔQFM +0.4, ΔQFM +0.3, ΔQFM +0.2, ΔQFM -0.3, ΔQFM -0.3, ΔQFM -0.4) and MgO content.

$K_{0} Fe^{2+}/Mg$ oliv-melt = 0.34
Supplementary Figure 11

**a.** ΔQFM, melt

**b.** Holland $f$, gas

**c.** Holland $f$, gas

**Legend:**
- **HSDP2 degassing**
- **MORB degassing**
- **Arc degassing**
- **Hypothetical degassing scenario**

**QFM-2.3**

- $CO_2^{\text{melt,init}} = 250$ ppm
- $S^{\text{melt,init}} = 2500$ ppm
- $H_2O^{\text{melt,init}} = 0.75$ wt%
Supplementary Figure 12

- **low SiO\textsubscript{2} HS\textsubscript{2}DP2 glasses**
- **high SiO\textsubscript{2} HS\textsubscript{2}DP2 glasses**
- **Agrigan melt inclusions (Kelley and Cottrell, 2012)**
- **Erebus melt inclusions (Moussallam et al., 2014)**