

Magma are the Largest Repositories and Carriers of Earth's Redox Processes

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Magma is the most important chemical transport agent throughout our planet. This paper provides an overview of the interplay between magma redox, major element chemistry, and crystal and volatile content, and of the influence of redox on the factors that drive igneous system dynamics. Given the almost infinite combinations of temperature, pressure, and chemical compositions relevant to igneous petrology, we focus on the concepts and methods that redox geochemistry provides to understand magma formation, ascent, evolution and crystallization. Particular attention is paid to the strong and complex interplay between melt structure and chemistry, and to the influence that redox conditions have on melt properties, crystallization mechanisms and the solubility of volatile components.

KEYWORDS: melt structure, magma properties, iron, crystallization, volatiles

INTRODUCTION

Magma is an intricate, multicomponent, multiphase system, comprising a silicate melt, with or without suspended gas bubbles, and crystals. Each second, approximately 1,200 tons of magma arrives at the surface of the Earth at mid-ocean ridges. This magma builds the oceanic floor and makes up 90% of all volcanism on Earth. Besides shaping Earth's geology and geography, magma is the main carrier, from depth to surface, of all the most important chemical elements, particularly oxygen. Because the chemistry of Earth's rocks and minerals is, at a fundamental level, related to how oxygen atoms complex around metals, understanding how magma transfers and redistributes oxygen through the Earth remains one of the main goals in geochemistry, petrology and mineralogy.

The amount of oxygen available to react with elements in any thermodynamic system can be conveniently described by its fugacity, f_{O_2} (see Cicconi et al. 2020 this issue). Estimating and understanding the oxygen fugacity conditions of a multicomponent silicate liquid at any temperature is complicated by the non-linear dependence of f_{O_2} on bulk composition. Indeed, the physical and thermochemical properties of natural silicate melts depend strongly on the silicate network structure that is, in turn, controlled by melt composition. For this reason, many models of silicate melts tend to (over)simplify the structural role of certain elements, and sometimes even neglect differences between the different cations that build the network structure.

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In the following sections, we will try to rationalize the interplay between melt structure and bulk chemistry by using Fe as the archetype for redox exchanges in melts. Iron is, by far, the most common multivalent transition element on Earth (32%) and is the fourth most abundant element in the Earth's silicate mantle (the average elemental abundance is 6.3%). Because iron is orders of magnitude more abundant than other transition elements, it is intuitive that the proportion of ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron will control (buffer) the overall oxygen fugacity conditions of silicate melts. Ergo, the evaluation of iron redox equilibria and structural environments in melts and mineral assemblages is critical for determining a magma's thermodynamic and transport properties. However, it should be noted that other multivalent elements also play a crucial role in Earth systems in terms of exchanged electrons or oxygens. For instance, sulfur species deserve a special mention because the oxidation of sulfide to sulfate involves 8 electrons, and for any increment of the Fe^{3+}/Fe^{2+} redox ratio, there is an eight-fold increment for sulfur species (S^{6+}/S^{2-}) (see Cicconi et al. 2020 this issue; Moretti and Stefansson 2020 this issue). Despite this large electron transfer, the effectiveness of the sulfide to sulfate ratio as a buffer of the redox potential is limited by the abundance of sulfur in a melt, which is significantly lower than iron in most commonly encountered natural magmas.

COMPOSITION AND STRUCTURE: WHO CONTROLS WHAT?

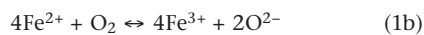
The effect of melt composition/structure upon properties is a hot topic in the geosciences and in the technological world. Understanding the structural role of cations allows us to predict melt redox conditions based on the physical, thermal, and rheological properties of melts, as well as the capacity of magmas to carry oxygen through the influence of melt composition on redox conditions.

To understand the link between magma structure and bulk composition, we need to revisit a few concepts regarding the structural role of elements in silicate melts. The main cation that builds the silicate network is silicon, which is bonded to four oxygens to form SiO_4 tetrahedral units. A three-dimensional network is formed when each tetrahedron connects to other SiO_4 units via apical oxygens (so-called bridging oxygens, BO). All other cations play one of two structural roles: (i) *network formers*, such as Si^{4+} , Ti^{4+} , P^{5+} , and Al^{3+} , which help to build the network; (ii) *network modifiers*, such as the metal cations Na^+ , K^+ ,

Mg²⁺, Ca²⁺, which disrupt the network by breaking inter-tetrahedral bonds to form non-bridging oxygens (NBO) and even non-network and free oxygens (Fincham and Richardson 1954; Mysen and Richet 2005; Le Losq et al. 2019 and references therein). Network modifiers have low cation field strengths (i.e., the ratio of the cation valence to the squared cation–oxygen distance), whereas network formers have high cation field strengths. Unfortunately, this simple picture is too good to be true: metal cations also serve to charge-balance tetrahedral units within an overall charge deficit, such as for AlO₄ where Al³⁺ replaces Si⁴⁺. Thus, in aluminosilicate melts, the overall role of metal cations depends on aluminium concentration in the network. From the redox perspective, Fe plays different roles depending on its oxidation state (Mysen and Richet 2005; Cicconi et al. 2015 and references therein): Fe²⁺ acts as a network modifier, whereas Fe³⁺ plays a more complex role that will be discussed later. Given the abundance of iron in melts, the various exchanges between Fe³⁺ and Fe²⁺ can have dramatic effects on melt structure and properties.

Bulk Chemistry, Silicate Melt Structure, Oxygen Transport

The statement that magmas can be considered as oxygen transporters may appear, at first sight, to be rather surprising. The key to this claim lies in the many multivalent elements present in magmas, e.g., Fe, Ti, V, Cr, Eu, and Ce. These elements have different structural roles in silicate melts, and they present distinct oxidation states and coordination numbers, some of which are uncommon even in minerals (e.g., five-fold coordinated ⁵Ni²⁺) (Galoisy and Calas 1993). There exists a plethora of redox reactions involving these elements. The equilibrium constant of each redox couple depends on temperature, pressure, bulk chemical composition (*T–P–X*), and the interplay of these variables in closed systems, all of which also determines the oxygen fugacity of the system. Conversely, in open systems, what controls *f*_{O₂} arises through the exchange of mobile components between the magmatic system and the surrounding environment. For instance, the proportions of ferrous and ferric iron can be described by equilibria expressed either as oxide components (Equation 1a) or as ionic species (Equation 1b)



A lot of experimental work has been carried out to rationalise the impact of temperature, pressure, composition and *f*_{O₂} on the equilibrium oxidation state of Fe in magmas, and several simple, empirical models have been proposed, (e.g.,

Kress and Carmichael 1991; Borisov et al. 2018). But complications arise from the complex relationships between *real* ionic species (e.g., ionic complexes of iron, which in turn depend on how they are measured) and their components (the corresponding oxides). This distinction between ionic species and oxide components is critical in understanding redox behaviour. Of particular importance is how the activity of oxide components varies with the distribution of the three kinds of oxygens described above (BO, NBO and free), which in turn depends on the melt structure at the *P–T–X* conditions of interest. Fortunately, geoscientists have a set of concepts that help them to rationalize the links between melt structure, chemical composition and redox species. At the scale of short-range ordering (e.g., coordination polyhedra), redox processes reflect how the charge is distributed (or transferred) between the central cation and the surrounding oxygens (the ligand field). In other words, redox exchanges are related to the mean electronic polarization state of the oxygen ligand, which, in turn, is determined by the proportions of the three kinds of oxygen in the melt (BO, NBO and free). Consequently, atomistic properties (electronegativity, electronic polarizability, optical basicity) of complexing cations can be related to the equilibrium disproportionation of the BO, NBO and free oxygens that make up the melt's structural framework. This also strongly relates to the activity of the free/non-network oxygens (*a*O²⁻). The latter represents the basicity of the melt and measures the polarization state of the ligand. It should be seen as analogous to pH, and, as such, is the key to solving the compositional dependence of redox equilibria in melt species (e.g., Duffy 1993; Ottonello et al. 2001; Moretti 2005; Dimitrov and Komatsu 2010 and references therein). Thus, in a similar fashion to aqueous solutions, the effect of silicate melt composition results in the intimate connection between redox exchanges and the melt's acid–base character, as reflected in its structure.

Most multivalent element equilibria follow the general rule of redox controlled by melt basicity, with the oxidation–reduction equilibrium shifting toward more oxidized species with increasing basicity of the melt (i.e., by increasing the amount of modifier oxides). Network modifier cations form ionic bonds with surrounding oxygen ions, whereas network formers form covalent bonds. Thus, glass covalence is inversely correlated to basicity. Because greater network-modifying ion activity results in an increase in melt depolymerization, this ion activity parameter can broadly be related to the ratio of non-bridging oxygens (NBO) per tetrahedral cations (T) in glasses and melts: NBO/T.

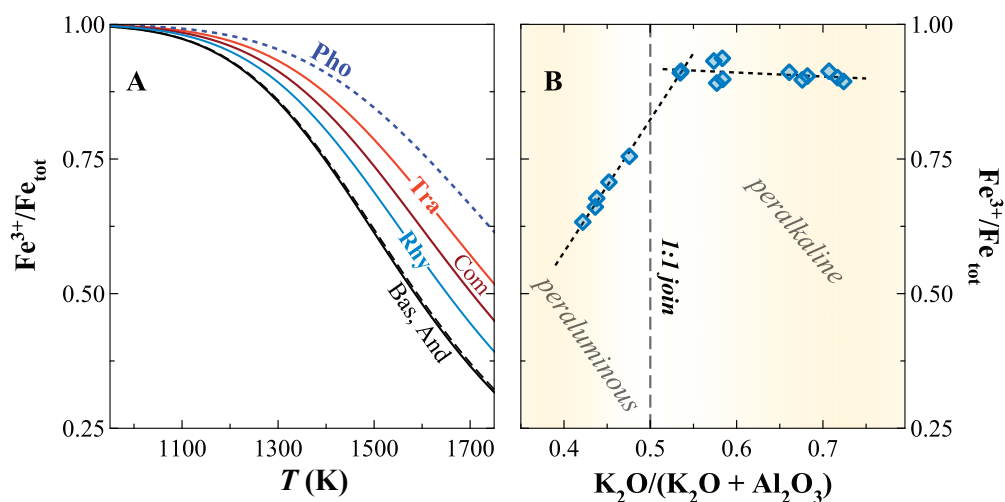


FIGURE 1 (A) Evolution of the Fe³⁺/Fe_{tot} ratio with temperature for different melt compositions in air. Abbreviations: Rhy = rhyolite; Tra = trachyte; Com = comendite; And = andesite; Bas = basalt. Compositions with higher alkali contents (Pho, Tra, Com) are more oxidized than alkali-poor ones (Bas, And, Rhy), which follows the basicity of the melt. DATA ESTIMATED FROM THE ALGORITHM OF KRESS AND CARMICHAEL (1991). (B) The Fe³⁺/Fe_{tot} redox fraction versus the K₂O/(K₂O + Al₂O₃) molar ratio. At constant temperature, depending on the alkali/Al ratio, the Fe redox ratio shows contrasting behaviour. DATA FROM DICKENSON AND HESS (1982).

Armed with this set of conceptual tools, we turn again to iron. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in a rock provides information about the amount of oxygen available in the system and its changes upon magma migration, for example to a different P or T . Iron exhibits variable oxidation states and coordination geometries, and experimental studies have shown that several Fe species are stable in silicate melts, including $^{[4]}\text{Fe}^{3+}$, $^{[5]}\text{Fe}^{3+}$, $^{[5]}\text{Fe}^{2+}$, and also 6-fold coordinated ferrous and ferric ions $^{[6]}\text{Fe}^{2+}$, $^{[6]}\text{Fe}^{3+}$ (e.g., Dingwell and Virgo 1987; Wilke et al. 2004; Cicconi et al. 2015 and references therein). Thus, while Fe^{2+} is predominantly considered as a network modifier, Fe^{3+} displays amphoteric behaviour within the silicate network. Indeed, depending on temperature, bulk chemistry, the identity of the predominant network modifier cations, and Al concentration and coordination, Fe^{3+} can act both as a network former and as a network modifier. Generally speaking, oxidized species, such as Fe^{3+} , are stabilized by larger proportions of modifier cations, which increases melt basicity. This trend can be better visualized when calculating the Fe redox ratio using the Kress and Carmichael (1991) algorithm (Fig. 1A). When a magma composition changes from phonolite to rhyolite to andesite/basalt, the alkali content decreases strongly. Alkalis have basicity values much higher than network-forming cations, so they contribute strongly to increasing the overall basicity of the melt, and thereby influence the equilibrium constant of Equation (1) that determines the Fe redox ratio. In addition to alkali content, the Fe redox ratio also depends on the alkali/ Al_2O_3 molar ratio. In natural and synthetic peralkaline systems (alkalis $>$ Al), increasing the molar alkali content induces a stabilization of Fe^{2+} , whereas in metaluminous systems (alkalis = Al) or peraluminous systems (alkalis $<$ Al), increasing the molar alkali content drives a strong stabilization of Fe^{3+} (Dickenson and Hess 1982) (Fig. 1B). At constant alkali/Al (or silica) ratios, the cation field strength (CFS) will influence the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, with higher $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios for K than for Li (CFS K $<$ CFS Na $<$ CFS Li). This can be explained by considering oxygen activities around cations (larger cations will induce larger negative charge on the oxygen ion; i.e., higher electronic polarizability), and the ability of K^+ ions to be more efficient in stabilizing Fe^{3+} in tetrahedral sites (Cicconi et al. 2015 and references therein).

Assessment of the average Fe valence and coordination environment is very important in understanding the influence of Fe on magma properties. The technique of X-ray absorption spectroscopy (XAS) is an element-selective tool used to study Fe speciation in melts and glasses. The spectra acquired on divalent and trivalent iron-bearing minerals show clear differences in absorbed energy positions, as well as in spectra shape, with the spectrum related to oxidized species shifted toward higher energies (e.g., Wilke et al. 2004 and references therein). The detailed study of some features (e.g., Fe K-edge pre-edge peak) can provide further insights into Fe speciation (and local symmetry): for example, many experimental data show that Fe^{2+} ions have a higher average coordination number. This can be appreciated in studies of the Fe K-edge pre-edge peak in minerals and glasses, when the pre-edge centroid energy is plotted against its integrated intensity. Upon iron reduction, the pre-edge centroid energy shifts toward lower values, and the overall intensity of the pre-edge decreases (Fig. 2). Because the area under the pre-edge peak is related to the structural environment surrounding the Fe ions (their coordination and symmetry), this peak provides remarkable insights into the variations in iron's geochemical role in melts and glasses (Wilke et al. 2004 and references therein).

MAGMA REDOX AND MOBILITY: VISCOSITY AND PARTIAL MOLAR VOLUME EFFECTS

The significant effect of redox state on a melt's physical properties has long been demonstrated. The first study to clarify the effects of iron valence state on viscous flow behaviour in a multicomponent system involved Fe-rich (~19 mol% FeO) lunar material analogues (Cukierman and Uhlmann 1974). Several experimental studies followed, confirming the effect of the Fe redox ratio on viscous flow and the effect of bulk composition and iron content on the redox ratio itself. These studies attempted to explain the observed correlation between Fe redox state and a magma's physical properties by taking into account structural changes (in terms of oxygen coordination), suggesting that while Fe^{2+} , similar to alkaline earth cations, acts as a network modifier, Fe^{3+} partially behaves as a structural analogue of Al^{3+} (Fig. 2). Dingwell and Virgo (1987) demonstrated the correlation between viscosity, Fe redox state, Fe^{3+} coordination environment(s), and the degree of polymerization of the melt (NBO/T) (Fig. 3). Their data suggest that the f_{O_2} effect on viscosity is related to the different oxygen coordination of the Fe species and that there is an intermediate $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio where Fe^{3+} species are stabilized as complexes with 4-fold and 6-fold coordination (Dingwell and Virgo 1987 and references therein).

In addition to the influence on melt viscosity, the occurrence of ferrous and ferric species with different coordinations (which have different structural roles) has consequences for melt density and compressibility. The dependence of partial molar volume of the two Fe oxides on bulk composition was extensively debated in the 1980s (e.g., Mo et al. 1982; Lange and Carmichael 1987 and references therein) in order to calculate the dependence of the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ redox fraction on pressure. To calculate the density and compressibility of magmatic liquids at one bar, there are well-known

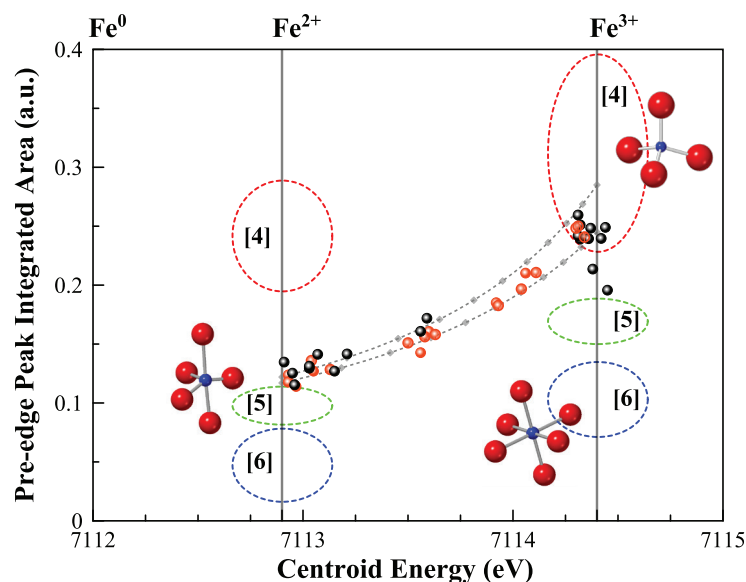


FIGURE 2 Iron pre-edge peak centroid energy (in electron volts, eV) plotted against its integrated area (in arbitrary units, a.u.). This variogram is based on the study of the Fe pre-edge peak of several minerals (modified after Giuli et al. 2012 and references therein). Example 4-, 5- and 6-coordinated Fe species are shown. The energy of metallic Fe is 7,112 eV, and the dashed ovals represent different Fe coordination environments. Red and black circles are data for glasses [from Wilke et al. (2004) and Cicconi et al. (2015)] (± 0.05 eV). Grey lines and diamond symbols are mixing lines between ferrous and ferric end-members. Iron reduction is accompanied by an increase in its average oxygen coordination.

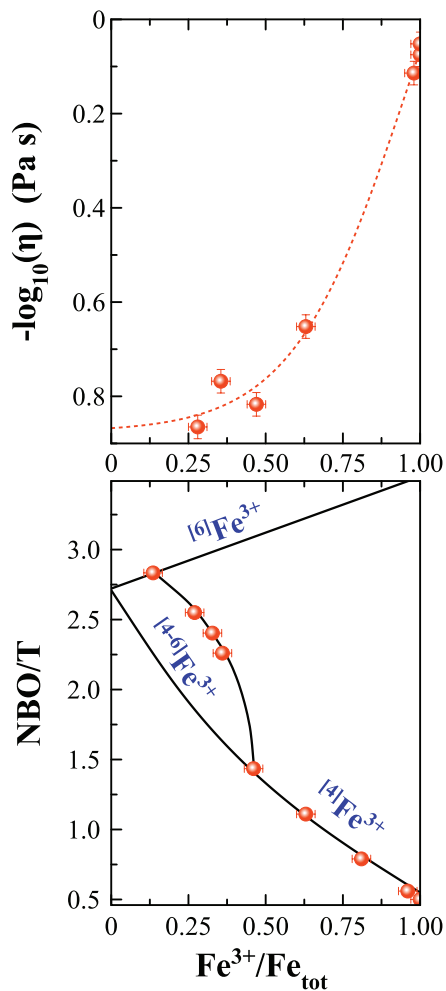


FIGURE 3 (UPPER GRAPH) Non-linear relationship between viscosity (η) and Fe redox fraction ($T = 1,200^\circ\text{C}$). There is an increase in melt viscosity with increasing $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ redox fractions, particularly important at $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ values higher than 0.5. This is related to the transformation of ferrous network-modifier species to ferric ones that behave as network formers ($^{14}\text{Fe}^{3+}$). (LOWER GRAPH) Non-linear relationship between Fe^{3+} coordination with NBO/T in the melt and Fe redox. At low $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ fractions, ferric ions stabilize with higher coordination(s), causing only small variations in the NBO/T parameter and melt viscosity. Numbers in square brackets beside Fe symbols are the coordination numbers. DATA FROM DINGWELL AND VIRGO (1987).

models e.g., Lange and Carmichael (1987) and Kress and Carmichael (1991). However, to derive the partial molar volume of FeO, these models rely on data from simplified systems that do not take into account the complexity of the Fe^{2+} structural environment. Early studies (Mo et al. 1982) and more recent studies (Guo et al. 2013) indicated that Fe^{2+} species have partial molar volume values ranging between 12 and 17 cm^3/mol , with a strong composition dependence that suggests changes in Fe^{2+} coordination with magma chemistry. The partial molar volume of Fe_2O_3 ranges between 40.7 ± 0.8 and 42.1 ± 0.3 cm^3/mol , at $1,400^\circ\text{C}$ (Mysen and Richet 2005; Liu and Lange 2006 and references therein). From high-temperature experiments in peralkaline silicate liquids, Liu and Lange (2006) reported a temperature- and composition-independent partial molar volume of 41.5 ± 0.3 cm^3/mol .

Evidently, the redox of aluminosilicate melts affects melt viscosity and density, which represent their resistance to, and potential for, movement in the Earth. However, despite variations of the aluminosilicate melt properties

being important for geological processes, an even more important phenomenon is influenced by redox processes within the melt. Crystallization.

CRYSTALLIZATION OF SILICATE MELTS

It is mandatory to consider the appropriate f_{O_2} conditions when determining magma phase equilibria relationships and chemistry. Different f_{O_2} conditions will control the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ redox fraction in the melt, the composition of the Fe-bearing phases nucleating and crystallizing, and the composition of the residual melt (which will typically be enriched in silica and depleted in iron). Redox conditions of the system are also responsible for shifts of phase equilibria: they can influence the differentiation history and magma rheological evolution and also the crystallization of the Fe-bearing phases that will control the oxygen fugacity conditions of the melt (see Cicconi et al. 2020 this issue). Hill and Roeder (1974) studied basaltic compositions and showed that, depending on the imposed f_{O_2} , the crystallization of chromite is hampered in favour of clinopyroxene phases at higher temperatures, and in favour of Ti-magnetite + pyroxene + plagioclase at lower temperatures. Equilibrium crystallization experiments have been performed to constrain phase relations and the stability of Fe–Ti oxides, for example by Toplis and Carroll (1995) on synthetic anhydrous Fe-rich basalts in a range of f_{O_2} covering 4 log units (FIG. 4A). Their data show that the appearance temperature of magnetite–ulvöspinel (Fe_3O_4 – Fe_2TiO_4) and ilmenite–hematite (FeTiO_3 – Fe_2O_3) solid solutions depend strongly on the f_{O_2} conditions of the magma. Moreover, depending on redox conditions, the onset of clinopyroxene crystallization varies between $\sim 1,385$ K and $1,413$ K. When water was added, the differentiation history of hydrous ferrobasalt was significantly modified: there was i) a strong decrease of the liquidus temperatures of the mineral phases, ii) changes in the crystallization sequence, iii) variations in Ca/Fe and Mg/Fe partitioning between clinopyroxene and melts, and in the forsterite content in olivine (Botcharnikov et al. 2008).

In addition to phase stability, the prevailing f_{O_2} conditions of a magma will influence the abundance, shape and size of the crystals, which in turn will affect the overall rheology of the magma. FIGURE 4B shows that crystallization kinetics depend on f_{O_2} , with higher crystal nucleation/growth rates for oxidized than for reduced melts. To explore the effect of f_{O_2} on lava rheology, dynamic undercooling experiments, and high-temperature viscosity measurements of a trachybasalt from Etna volcano (Italy), were performed in air and under reducing conditions (close to the FMQ buffer) by Kolzengurg (2018). The onset of crystallization was shifted to much lower temperatures under the reducing conditions, whereas oxidized magmas had a lower crystallization tendency. The crystallization of small nano- and micro-crystal phases (nanolites or microlites) may be particularly effective in influencing magma viscosity. In recent years, the influence of particle size and shape on the rheology of magmas has been extensively investigated. Liebske et al. (2003) reported that although the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ redox fractions largely affected the viscosity of andesitic melts, the occurrence of Fe crystals exercised a decisive influence over magma rheology. Recently, it has been proposed that the crystallization of sub-micron Fe crystals (nanolites), and the consequent relative enrichment in silica and depletion in iron of the residual melt, could be an important mechanism to drive changes in magma rheology and volatile exsolution. This then can profoundly affect the dynamics of volcanic eruptions (Di Genova et al. 2017).

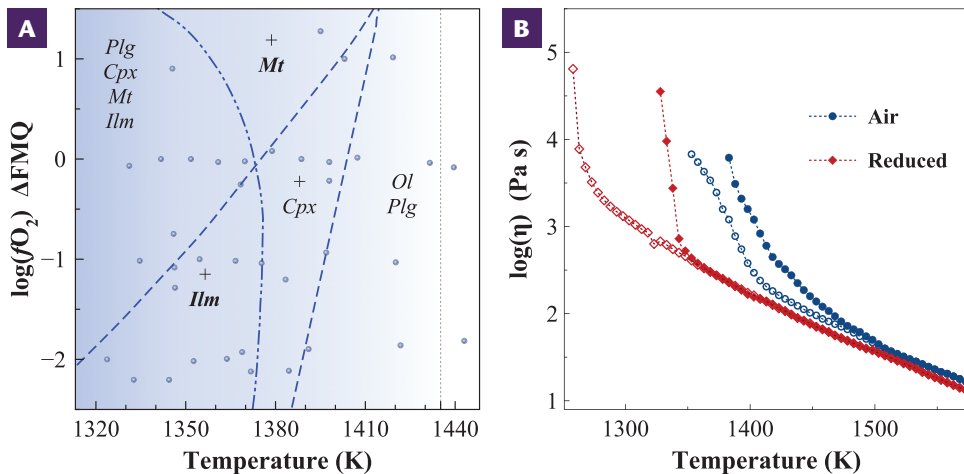
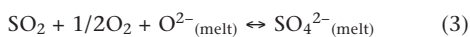
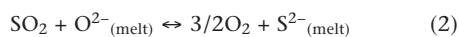


FIGURE 4 (A) Phase equilibria for anhydrous Fe-rich basalt as a function of temperature and redox conditions. The range of f_{O_2} covers 4 log units, from >2 log units below to 1.5 log units above the fayalite–magnetite–quartz (FMQ) buffer. Lines outline the stability fields of mineral phases. Abbreviations: Ol = olivine; Plg = plagioclase; Cpx = Ca-rich clinopyroxene; Mt = magnetite–ulvöspinel solid solution; Ilm = ilmenite–hematite solid solution. Plagioclase and liquid phases are always present below the liquidus (vertical solid line $\sim 1,430$ K). The appearance of Ilm or Mt strongly depends on the f_{O_2} conditions of the magma. Small circles indicate the experimental data of TOPLIS AND CARROLL (1995). (B) Evolution of apparent viscosity (Pascal second) of crystallizing trachybasalt melts at varying cooling rates (empty symbols = $3^\circ\text{C}/\text{min}$; solid symbols = $0.5^\circ\text{C}/\text{min}$) performed in air (blue) or under reducing (red) conditions. Dynamic undercooling experiments are representative of non-equilibrium conditions typical of the ascent of magmas in conduits. MODIFIED AFTER KOLZENBURG ET AL. (2018).

VOLATILES IN MAGMA AND f_{O_2} CONDITIONS

The amount of volatiles dissolved in melts, their speciation (i.e., the form they take when incorporated in the liquid), and the mechanisms of their exsolution and diffusion are key parameters in driving volcanic eruptions. The most abundant gas species in magmatic systems are H_2O and CO_2 , followed by sulfur species (H_2S and SO_2), halogens, nitrogen, and the noble gases. The dissolution/exsolution behaviour of these volatiles is strongly dependent on the stability of the different gaseous molecular species. For example, carbon can be stable as CH_4 , CO , CO_2 , depending on P - T - X - f_{O_2} . Consequently, there is a link between magma redox and the speciation of the dissolved volatile elements, and a consequent feedback between degassing and magma f_{O_2} (see Moretti and Stefansson 2020 this issue, and references therein).

In addition to C–H–O species, sulfur may also be abundant in magmatic gases. In magmas, dissolved sulfur can be stable both as sulfide and sulfate (Fincham and Richardson 1954), depending on the f_{O_2} conditions. The proportion of the different species greatly affects sulfur solubility (Moretti and Ottonello 2005; Baker and Moretti 2011 and references therein). A rapid change in sulfur oxidation state occurs within about 2.0–2.5 orders of magnitude of the oxygen fugacity as defined by the nickel–nickel oxide (NNO) oxygen buffer (Fig. 5) such that sulfur solubility is governed by two concomitant equilibria:



The total amount of sulfur solubilized in a melt is given by the sum of the oxidized (sulfate) and the reduced (sulfide) species (Fig. 5A). When the total amount of dissolved sulfur in the melt (S wt%) is normalized to the fugacity of SO_2

in the gas, the theoretical slopes of 3/2 and 1/2 (t.s. in Fig. 5B) are observed for the equilibria in Equations (2) and (3), respectively. Equation (3) dominates at higher f_{O_2} conditions, whereas under progressively reducing conditions, Equation (2) becomes important. The absolute value of f_{O_2} at which one equilibrium predominates over the other (which determines the relative predominance of sulfate or sulfide species) changes by 2 orders of magnitude depending on P , T and magma composition (including dissolved volatile content, particularly H_2O) (see Figure 3 in Moretti and Stefansson 2020 this issue).

The compositional dependence reflects the shift in melt structure, and, hence, solvent properties (Moretti and Ottonello 2005; Baker and Moretti 2011 and references therein).

At first glance, it would appear difficult to incorporate the oxide components and their activities into the redox equilibrium reactions for sulfur species in addition to iron species. However, the complexity fades when it becomes clear that redox equilibrium reactions, such as those given in Equations (1) to (3), make use of the oxygen electrode: $1/2\text{O}_2 + 2e^- \leftrightarrow \text{O}^{2-}$ (see Cicconi et al. 2020 this issue; Moretti

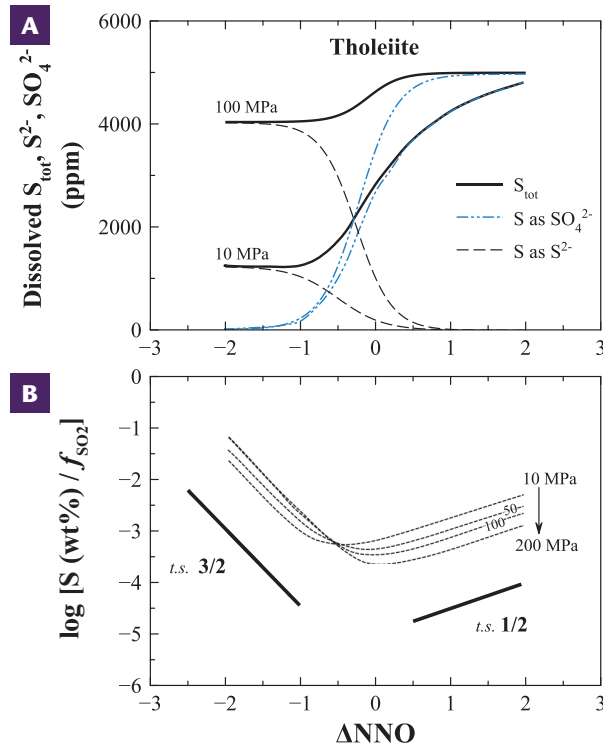


FIGURE 5 (A) The total amount of sulfur solubilized in a melt (here a tholeiitic melt equilibrated with a CO_2 – H_2O – SO_2 – H_2S gas phase at 1,400 K, between 10 and 100 MPa) is given by the sum of oxidized (sulfate) and reduced (sulfide) species. (B) Sulfur solubilized in a tholeiitic melt plotted against $\log f_{O_2}$ (expressed as a change in the nickel–nickel oxide buffer, or ΔNNO); note that we cannot appreciate the stoichiometric constraints imposed by Equations (2) and (3). These constraints can be visualised, however, when the total amount of dissolved sulfur in the melt (S wt%) is normalized to the fugacity of SO_2 (f_{SO_2}) in the gas. Abbreviation: t.s. = theoretical slope. DATA FROM MORETTI'S MODEL (SEE BAKER AND MORETTI 2011 AND REFERENCES THEREIN).

and Stefansson 2020 this issue). This half-reaction is an aspect of redox that is all too often overlooked, yet one that provides the link between redox and acid–base chemistry in melts. It is essentially related to the exchanges that occur between the bridging, non-bridging, and (non-network) free oxygens.

SUMMARY

Magmas are composed of a silicate melt, with or without suspended crystals and gas bubbles. The silicate melt network is built from bonding between anions and cations having different size, valence, coordination environments, bonding strength, and preferred associations. Variations in the relative proportions of those ionic species, and the

activity of the different kinds of oxygen that bond to the redox species, strongly influences melt properties and controls magma crystallization behaviour and differentiation. This ionic composition when allied to volatile solubilities plays a key role in magma transport and exercises a direct influence on the dynamics of volcanic eruptions.

In aluminosilicate melts, the *oxygen electrode* links f_{O_2} directly to the acid–base character of the melt, a connection expressed via the aO^{2-} . This activity measure has the same role as pH in aqueous solutions and provides a robust way to relate redox and acid–base chemistry in melts, and, in turn, to predict physico-chemical properties by including an all-important compositional parameter into redox reactions that involve silicate melts. ■

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