Magma, the largest repository and carrier of Earth's redox processes

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ABSTRACT

Magma is the most important chemical transport agent throughout our planet. In this contribution we provide a brief overview of the interplay between magma redox, major element chemistry, crystal and volatile content, and of the influence of redox on properties that drive the dynamics of igneous systems. Given the almost infinite conditions of temperature, pressure, and chemical compositions relevant to igneous petrology, we focus on the concepts and methods that redox geochemistry uses for understanding magma formation, ascent, evolution and crystallization. Particular attention is paid to the strong and complex interplay between melt structure and chemistry, and on the influence of the overall redox conditions on melt properties, crystallization mechanisms and 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 1200 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, fO_2 (see *Introduction, 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 fO_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 building the network structure .

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 (*e.g.* the average elemental abundance is 6.3%). Since 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 magma 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, sulphur species deserve a

special mention since the oxidation of sulphide to sulphate involves 8 electrons, and for any increment of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox ratio, there is an eight-fold increment for sulphur species ($\text{S}^{6+}/\text{S}^{2-}$; see [Introduction, this issue](#) and [Moretti and Stefansson, this issue](#)). Despite the large electron transfer, the effectiveness of the sulphide to sulphate ratio as a buffer of the redox potential is limited by the abundance of sulphur in melts, which is significantly lower than iron in most commonly encountered natural magmas.

COMPOSITION & STRUCTURE: WHO CONTROLS WHAT?

The effect of melt composition/structure upon properties is a hot topic in geoscience, but also in the technological world. Indeed, understanding the structural role of cations allow us to predict how variations in concentration affect 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 building the silicate network is silicon, bonded to four oxygens to form SiO_4 tetrahedral units. A three-dimensional network is formed as 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+} , or Al^{3+} , help to build the network; (ii) network *modifiers* (*e.g.* metal cations like Na^+ , K^+ , Mg^{2+} , Ca^{2+}) 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 with a net charge deficit, such as AlO_4 where Al^{3+} replaces Si^{4+} . Thus, in aluminosilicate melts, the

overall role of metal cations depends on aluminum concentration in the network. From the redox perspective, iron plays different roles depending on its oxidation state ([Mysen and Richet 2005](#); [Cicconi et al. 2015 and references therein](#)): Fe^{2+} acts as a network-modifier, whereas Fe^{3+} plays a more complex role that will be discussed later. Given the abundance of iron in melts, $\text{Fe}^{3+}/\text{Fe}^{2+}$ exchanges 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, Ce. These elements have different structural roles in silicate melts, present distinct oxidation states and coordination numbers, some of which are uncommon even in minerals (*e.g.* five-fold coordinated $^{[5]}\text{Ni}^{2+}$, [\(Galoisy and Calas 1993\)](#). 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, determines the oxygen fugacity of the system. Conversely, in open systems, controls on $f\text{O}_2$ arise through exchanges 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 involving either macroscopic oxide components [1a] or convenient ionic species [1b]:

A lot of experimental work has been carried out to rationalise the impact of temperature, pressure, composition and $f\text{O}_2$ on the equilibrium Fe oxidation state in magmas, and several simple, empirical models have been proposed, *e.g.* ([Kress and Carmichael 1991](#); [Borisov et al. 2018](#)). Further complications arise from the complex relationships between real species (*e.g.*, ionic complexes of iron, which in

turn depend on how they are measured) and components (the corresponding oxides). This distinction between species and 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 BO, NBO and free oxygens making the melt structural framework and, particularly, to the activity of free/non-network oxygens (aO^{2-}). 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 key to solving the compositional dependence of redox equilibria in melts 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 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. Since a greater network-modifying ion activity results in increasing melt depolymerization, this parameter can broadly be related

to the ratio of non-bridging oxygens (NBO) per tetrahedral cations (T) in glasses and melts (NBO/T).

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. Fe 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 behavior 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 modifiers cations (increasing melt basicity). This trend can be better visualized when calculating the Fe redox ratio using the Kress and Carmichael (1991) algorithm (Figure 1A). When changing magma composition from phonolite to rhyolite to basalt/andesite, alkali content decreases strongly. Since alkalis have basicity values much higher than network-forming cations, they contribute strongly to increasing the overall basicity of the melt, and thus 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 molar alkali content, induces a stabilization of Fe^{2+} , whereas in metaluminous (alkalis=Al) or peraluminous (alkalis<Al) systems, increasing molar alkali content drives a strong stabilization of Fe^{3+} (Dickenson and Hess 1982) (Figure 1B). At constant alkali/Al (or silica) ratio, 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 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 average Fe valence and coordination environment is very important to understand its influence on magma properties. X-ray Absorption Spectroscopy (XAS) is an element-selective technique 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 their 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 (*i.e.* Fe K-edge pre-edge peak) can provide further insights into Fe speciation (and local symmetry), and many experimental data show that Fe^{2+} ions have higher average coordination number. This can be appreciated in studies of 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 (Figure 2). Since the area under the pre-edge peak is related to the structural environment surrounding Fe ions (coordination, symmetry), it provides remarkable insights into variations of iron's geochemical role in melts and glasses (Wilke et al. 2004 and references therein).

Figure 1A – Evolution of the Fe^{3+}/Fe_{tot} ratio with temperature for different melt compositions in air (Rhy: rhyolite, Tra: trackyte, Com: comendite, And: andesite, Bas: basalt); data estimated from the algorithm of Kress and Carmichael (1991). Compositions with higher alkali contents (Pho, Tra, Com) are more oxidized than alkali-poor ones (Bas, And, Rhy), thus following the basicity of the melt. **1B** - Fe^{3+}/Fe_{tot} redox fraction vs. the $K_2O/(K_2O+Al_2O_3)$ molar ratio (data from Dickenson and Hess 1982). At constant temperature, depending on the alkali/Al ratio, the Fe redox ratio shows contrasting behavior.

Figure 2 - Iron pre-edge peak centroid energy plotted against its integrated area. The variogram is based on the study of the Fe pre-edge peak of several minerals (modified after [Giuli et al. 2012](#) and [references therein](#)). The energy of metallic Fe is 7112 eV, and the dashed ovals represent different Fe coordination environments. Circles are data for glasses from [Wilke et al. \(2004\)](#) and [Cicconi et al. \(2015\)](#) (± 0.05 eV). Fe reduction is accompanied by an increase in its average oxygen coordination.

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 behavior 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 Fe redox ratio on viscous flow, but also 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 physical properties by taking into account structural changes (in terms of oxygen coordination), suggesting that while Fe^{2+} , like alkaline earth cations, acts as a network-modifier, Fe^{3+} partially behaves as a structural analogue of Al^{3+} ([Figure 2](#)). [Dingwell and Virgo \(1987\)](#) demonstrated the correlation between viscosity, iron redox state, Fe^{3+} coordination environment(s), and degree of polymerization of the melt (NBO/T) ([Figure 3](#)). Their data suggest that the $f\text{O}_2$ effect on viscosity is related to the different oxygen coordination of 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](#)).

Figure 3: Non-linear relationship between viscosity (η , top panel) and Fe^{3+} coordination change (bottom panel) and Fe redox ratio. 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 behaves as network-formers ($[\text{Fe}^{3+}]$). At low $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios, ferric ions stabilize with higher coordination(s), causing only small variations in the NBO/T parameter and melt viscosity. Data from ([Dingwell and Virgo 1987](#)).

In addition to the influence on melt viscosity, the occurrence of ferrous and ferric species with different coordination (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 models *e.g.* (Lange and Carmichael 1987; Kress and Carmichael 1991); however, to derive the partial molar volume of FeO these models rely on data from simplified systems, without taking into account the complexity of the Fe^{2+} structural environment. Early (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, suggesting 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 1400 °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, redox of aluminosilicate melts affects their viscosity and density, which represent their resistance to and potential for movement in the Earth. However, while variations of the aluminosilicate melt properties are important for geological processes, an even more important phenomenon is influenced by redox processes within the melt, namely crystallization.

CRYSTALLIZATION OF SILICATE MELTS

It is mandatory to consider the appropriate $f\text{O}_2$ conditions when determining magma phase equilibria relationships and chemistry. Different $f\text{O}_2$ 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, thus influencing on one hand the differentiation history and magma rheological evolution; on the other hand, crystallization of Fe-bearing phases will control the oxygen fugacity conditions of the melt (see [introduction, this issue](#)). An early study by [Hill and Roeder \(1974\)](#) on basaltic compositions showed that, depending on the imposed fO_2 , crystallization of chromite is hampered in favor of clinopyroxene phases at higher temperatures, and in favor of Ti-magnetite+pyroxene+plagioclase at lower temperatures. Equilibrium crystallization experiments have been performed to constrain phase relations and Fe-Ti oxides stability, for example by [Toplis and Carroll \(1995\)](#) on synthetic anhydrous Fe-rich basalts in a range of fO_2 covering 4 log units ([Figure 4A](#)). Their data show that the appearance temperature of magnetite-ulvöspinel (Fe_3O_4 - Fe_2TiO_4 ; Mt) and ilmenite-hematite ($FeTiO_3$ - Fe_2O_3) solid solutions depend strongly on the fO_2 conditions of the magma. Moreover, depending on redox conditions, the onset of clinopyroxene crystallization varies between ~1385 and 1413 K. When water is added, the differentiation history of hydrous ferrobasalt is significantly modified, with 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 forsterite content in olivine ([Botcharnikov et al. 2008](#)).

In addition to phase stability, the prevailing fO_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 fO_2 , with higher crystal nucleation/growth rates for oxidized than for reduced melts. To explore the effect of fO_2 on lava rheology, dynamic undercooling experiments, and high-temperature viscosity measurements of a trachybasalt from Etna were performed in air and under reducing conditions (close to the FMQ buffer) by [Kolzenburg \(2018\)](#). The onset of crystallization is shifted to much lower temperatures under reduced conditions, whereas oxidized magmas have lower crystallization tendency. The crystallization of small nano- and micro-crystals

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 while the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ redox fractions largely affect the viscosity of andesitic melts, the occurrence of Fe-crystals exercises 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, and thus the dynamics of volcanic eruptions ([Di Genova et al. 2017](#)).

Figure 4A: Phase equilibria for anhydrous Fe-rich basalt as a function of temperature and redox conditions. The range of $f\text{O}_2$ covers 4 log units, from >2 log units below to 1.5 log units above the FMQ buffer. Lines outline the stability fields of mineral phases: Ol, olivine; Plg, plagioclase; Cpx, Ca-rich clinopyroxene; Mt, magnetite-ulvospinel solid solution; Ilm, ilmenite-hematite solid solution. Plagioclase and liquid phases are always present below the liquidus (vertical solid line ~ 1430 K). The appearance of Ilm or Mt strongly depends on the $f\text{O}_2$ conditions of the magma. Small circles indicate the experimental data of [Toplis and Carroll \(1995\)](#). **4B:** Evolution of apparent viscosity of crystalizing 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 $f\text{O}_2$ 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 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 noble gases. The dissolution/exsolution behavior 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- $f\text{O}_2$. Consequently, there is a link between magma redox and the speciation of the

dissolved volatile elements, and a consequent feedback between degassing and magma fO_2 . (see [Moretti and Stefansson, 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 sulphide and sulphate ([Fincham and Richardson 1954](#)), depending on the fO_2 conditions. The proportion of the different species greatly affects sulfur solubility ([Moretti and Ottonello 2005; Baker and Moretti 2011 and references therein](#)), and a rapid change in sulfur oxidation state occurs within about 2-2.5 orders of magnitude of the oxygen fugacity defined by the NNO oxygen buffer (Figure 5) sulphur solubility is governed by two concomitant equilibria:

such that the total amount of sulphur solubilized in a melt is given by the sum of oxidized (sulphate) and reduced (sulphide) species (Figure 5A). When the total amount of dissolved sulphur in the melt (S wt.%) is normalized to the fugacity of SO_2 in the gas, the theoretical slopes 3/2 and 1/2 (t.s. in Figure 5B), respectively for reactions [2] and [3], are respected. Equilibrium [3] dominates at higher fO_2 conditions, whereas under progressively reducing conditions, equilibrium [2] becomes important. The absolute value of fO_2 at which one equilibrium predominates over the other (hence determining the relative predominance of sulphate or sulphide 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 & Stefansson](#)). 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 sulphur species, as well as for iron species. However, the complexity fades when it becomes clear that redox

equilibrium reactions, such as those reported in reaction [1] to [3] make use of the *oxygen electrode*, $\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightleftharpoons \text{O}^{2-}$ (see [introduction](#) and [Moretti and Stefannson, 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, essentially related to exchanges occurring between bridging, non-bridging, and (not-network) free oxygens.

Figure 5: The total amount of sulphur solubilized in a melt (here a tholeiitic melt equilibrated at 1400 K, 10 and 100 MPa with a $\text{CO}_2\text{-H}_2\text{O-SO}_2\text{-H}_2\text{S}$ gas phase) is given by the sum of oxidized (sulphate) and reduced (sulphide) species. When plotted versus $\log f\text{O}_2$ (expressed as ΔNNO) (**5A**), we cannot appreciate the stoichiometric constraints imposed by reactions [2] and [3], which instead can be visualized when the total amount of dissolved sulphur in the melt (S wt.%) is normalized to the fugacity of SO_2 ($f\text{SO}_2$) in the gas (**5B**). Data from Moretti's model (see [Baker and Moretti 2011](#) and [references therein](#)).

OUTLOOK

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 species, and the activity of the different kind of oxygen bonded to the redox species, strongly influences melt properties, and controls magma crystallization behaviour and differentiation, as well as volatile solubilities, thus playing a key role in magma transport in the Earth, and exercising direct influence on the dynamics of volcanic eruptions.

In aluminosilicate melts, the *oxygen electrode* links directly $f\text{O}_2$ to the acid-base character of the melt, conveyed via the $a\text{O}_2^-$. This 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 physic-chemical properties by including an all-important compositional parameter into redox reactions involving silicate melts.

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