Fe in magma – An overview

Max Wilke

Institut für Geowissenschaften, Universität Potsdam, Germany

Abstract
The strong influence of physical conditions during magma formation on Fe equilibria offers a large variety of possibilities to deduce these conditions from Fe-bearing phases and phase assemblages found in magmatic rocks. Conditions of magma genesis and their evolution are of major interest for the understanding of volcanic eruptions. A brief overview on the most common methods used is given together with potential problems and limitations. Fe equilibria are not only sensitive to changes in intensive parameters (especially T and $f\mathrm{O}_2$) and extensive parameters like composition also have major effects, so that direct application of experimentally calibrated equilibria to natural systems is not always possible. Best estimates for pre-eruptive conditions are certainly achieved by studies that relate field observations directly to experimental observations for the composition of interest using as many constraints as possible (phase stability relations, Fe-Ti oxides, Fe partitioning between phases, Fe oxidation state in glass etc.). Local structural environment of Fe in silicate melts is an important parameter that is needed to understand the relationship between melt transport properties and melt structure. Assignment of Fe co-ordination and its relationship to the oxidation state seems not to be straightforward. In addition, there is considerable evidence that the co-ordination of Fe in glass differs from that in the melt, which has to be taken into account when linking melt structure to physical properties of silicate melts at T and P.

Key words *iron – silicate melt – redox conditions*

1. Introduction

Fe is the most abundant 3d-transition element in geological systems and its heterovalent nature is the source of a highly variable geochemical behavior depending mostly on the redox regime during geological processes. In the case of magmatic systems, the valence-state of Fe has strong effects on the stability of Fe-bearing phases as well as on the physical properties of the melt phase itself. The stability of Fe-bearing phases has direct consequences on the overall chemical variation trend of a given magmatic fractionation series as is well documented by the difference of tholeiitic and calc-alkaline magmatic suites. Tholeiitic series show a significant increase in Fe-content during early stages of differentiation whereas in calc-alkaline series this enrichment is suppressed by the early crystallization of Fe-Ti oxides, which is strongly influenced by the prevailing redox regime (Wilson, 1989; Toplis and Carroll, 1995). Silicate magmas or melts containing significant amounts of Fe show considerable dependence in their physical properties on the prevailing redox conditions. *E.g.*, the viscosity of andesitic melt containing 8 wt% FeO_t varies by about 2 orders of magnitude in the high viscosity range depending on the Fe oxidation state ($\mathrm{Fe}^{3+}/\Sigma\mathrm{Fe}=0.2\text{-}0.6$) (*e.g.*, Liebske *et al.*, 2003). Due to the significant effect of Fe oxidation state on the resulting products of magma genesis it is possible to deduce the redox conditions during magma formation, *i.e.* in the case of volcanic rocks, the pre-eruptive conditions.

The aim of this communication is to give a brief overview on the possible methods for extracting information on the redox conditions of magmas and to point out some of the possible

Mailing address: Dr. Max Wilke, Institut für Geowissenschaften, Universität Potsdam, Postfach 601553, 14415 Potsdam, Germany; e-mail: max@geo.uni-potsdam.de

sources of error for such redox estimates. In addition, the structural role of Fe in silicate glass and melt at high temperature is discussed.

1.1. *Redox conditions and volatiles*

Knowledge of the redox regime of volcanic systems is a key parameter needed to understand volatile budgets of magmas involved in volcanic activities. The major volatile component affected by the redox regime is sulfur. The sulfur species found in the gas phase is strongly related to the redox conditions. As the solubility of S in the melt is, of course, related to the S species present, a strong dependence on the redox conditions is observed having a minimum at intermediate redox conditions (*e.g.*, Carroll and Webster, 1994). Depending on the oxygen fugacity, S is incorporated into the melt as S^{2-} or SO_4^{2-} species. Moreover, at reduced conditions Fe and S in the melt directly interact as manifested by the strong correlation of S and Fe concentrations in synthetic and natural samples. This led to the hypothesis of FeS species being present in the melt (Carroll and Webster, 1994). When S saturation is reached at reducing conditions Fe-sulphide phases precipitate from the melt. At oxidizing conditions, in contrast, especially in the presence of water anhydrite may precipitate from the melt (Carroll and Rutherford, 1987).

2. Fe-redox equilibria exploited for redox estimates

2.1. *Coexisting Fe-Ti oxides*

Oxygen thermobarometry using Fe-Ti oxides is mainly based on the exchange equilibrium

$$Fe_2TiO_4 + Fe_2O_3 = Fe_3O_4 + FeTiO_3$$
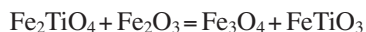
which is strongly dependant on temperature and oxygen fugacity (*e.g.*, Lindsley, 1991). Due to the massive amount of work performed on the stability relations in the Fe-Ti-O system Fe-Ti oxides provide pretty accurate estimates of temperature and oxygen fugacity (*e.g.*, Andersen

and Lindsley, 1988; Ghiorso and Sack, 1991). However, application of this method to volcanic rocks is often restricted by the lack of Fe-Ti oxides in the eruption products or by uncertainties on the co-existence of oxides found in volcanic rocks. Therefore, often only a fragmentary image of the temperature-fO_2 history of the magma is achieved (*e.g.*, Martel *et al.,* 1999).

2.2. *Partitioning of Fe between melt and plagioclase*

Although plagioclase contains only minor amounts of Fe, the incorporation of Fe is strongly dependent on oxygen fugacity. Fe^{3+} may easily replace Al in the tetrahedral site. Fe^{2+} may be incorporated by replacement of Ca on the *A* site or by a coupled exchange of Fe^{2+} and Si *versus* 2Al on the tetrahedral site. The incorporation of Fe^{3+} is favored, so that the Fe-partitioning between melt and plagioclase is sensitive to the prevailing redox conditions (Sato, 1989; Phinney, 1992; Wilke and Behrens, 1999; Sugawara, 2000, 2001). As plagioclase is usually found throughout all volcanic rocks this method can be readily applied in many cases.

Plagioclase usually shows strong zoning and each zone grew from the melt at a given set of *P*, *T* and fO_2 (fig. 1). If melt (glass) inclusions are present as well in each of the zones even the evolution of conditions may be deduced. Since the partitioning is also influenced by temperature, melt composition and volatile content accurate estimates are only possible if the dependence of partitioning is calibrated for the system of interest. A more rigorous model for the Fe-partitioning between melt and plagioclase was suggested by Sugawara (2000, 2001).

The model was parametrized on partitioning data from several compositions at various *P*, *T* and fO_2 in the system SiO_2-Al_2O_3-FeO-MgO-CaO-Na_2O and thus provides a good basis for direct application to similar natural systems. However, Sugawara (2001) also showed that the accuracy of the *P-T-fO_2* estimates can be significantly improved by considering exchange equilibria among more than two phases,

Fig. 1. Microscopic image of a chemically zone plagioclase phenocrysts (Plg) in a highly vesicular pumice sample from the Minoan Tuff (Santorini, Greece). Inclusions in the plagioclase host represent quenched melt (Gls) trapped at various stages during crystal growth and thus provides information on the compositional development of the erupted magma (Large black spot: Vesicle filled with resin above Plg-crystal). Bottom side of image 1.2 mm, crossed polarizers).

e.g., by inclusion of pyroxene or olivine instead of using only melt and plagioclase (Sugawara, 2001).

2.3. *Fe-oxidation state in volcanic glass*

Another possibility to estimate redox conditions is the direct use of the Fe oxidation state found in volcanic glass (*e.g.*, Helgason *et al.*, 1992a,b). Depending on the nature and size of the sample several analytical techniques provide access to the Fe oxidation state of volcanic glass. Bulk methods like wet chemical analysis and Mössbauer provide quite precise data (error of $Fe^{3+}/\Sigma Fe \pm 0.03-0.1$). However, samples have to be homogeneous and free of crystal inclusions which is seldom the case. Methods with spatial resolution that also provide insight into the Fe oxidation state of volcanic glass in heterogeneous samples include Micro-Mössbauer spectroscopy (50-100 μm spot size) (Mc-

Cammon *et al.*, 1991), Micro-XANES (*X*-ray Absorption Near Edge Structure, 3-30 μm spot size) (Bajt *et al.*, 1994; Delaney *et al.*, 1998; Bonnin-Mosbah *et al.*, 2001; Dyar *et al.*, 2002; Schmid *et al.*, 2003), EELS (Electron Energy Loss Spectroscopy, *e.g.*, van Aken *et al.*, 1998) or high resolution *X*-ray emission analysis using the electron microprobe (spotsize ≥ 1 μm) (Höfer *et al.*, 1994; Fialin *et al.*, 2001). These methods also enable the investigation of glass inclusions within crystals and thus provide insight into the history of redox conditions during magma evolution. While oxidation-state estimates from Micro-Mössbauer spectroscopy may be as precise as those performed by usual Mössbauer spectroscopy provided the Fe-content is high enough (approximately 5 wt% FeO).

Estimates from Micro-XANES (Fe K-edge) usually have larger errors, *i.e.* an error of $Fe^{3+}/\Sigma Fe$: $\pm 0.1-0.2$ if a general calibration as given by Bajt *et al.* (1994) or Wilke *et al.* (2001) is used. Using specific calibrations for the glass

composition of interest the error can be substantially improved to an error comparable to the one by Mössbauer analysis (Berry *et al.*, 2003). The major advantage of this method is that spectra may also be taken at Fe-content below 1 wt% if the photon flux is high enough.

The use of $L_{\alpha,\beta}$-emission lines with the electron microprobe provides information on the oxidation state with the same spatial resolution as for chemical analyses by this technique and a precision of 10-20 % rel.

However, the application is usually restricted by the total Fe-content (above 3.5 wt%, Fialin *et al.*, 2001). The use of EELS at the Fe *L*-edge may provide data with a precision that may be better than 5% rel. but the volume analysed is only in the 10 nm-range and glasses are potentially not stable under the electron beam which may be overcome by cooling the sample during measurements (Liebscher, pers. comm.).

To be able to deduce the redox conditions from such data, knowledge is needed, of course, on the relationship between Fe oxidation state and temperature, pressure and melt composition.

A considerable amount of effort was put into this field to establish the relationship to the above mentioned parameters using wet chemical analysis of Fe^{2+} in combination with electron microprobe analysis for bulk Fe content or Mössbauer spectroscopy for the determination of the Fe oxidation state (*e.g.*, Johnston, 1964, 1965; Fudali, 1965; Sack *et al.*, 1980; Mysen *et al.*, 1980, 1985; Kilinc *et al.*, 1983; Lange and Carmichael, 1989; Borisov and Shapkin, 1990; Kress and Carmichael, 1991; Moore *et al.*, 1995; Gaillard *et al.*, 2001; Wilke *et al.*, 2002). Sack *et al.* (1980), Kilinc *et al.* (1983) and Kress and Carmichael (1991) used a rather simple empirical equation parametrized on a large dataset of melts equilibrated at various superliquidus conditions to describe the dependence of Fe oxidation state on T, X and P.

Borisov and Shapkin (1990) used a similar approach that differed only in the amount of fitting parameters. As these equations are purely empirical it is not clear to what extent these equations can be extrapolated to melt systems at conditions very different from those used in the parametrization of the equation, especially if

they are extrapolated to significantly lower temperatures or to subliquidus conditions. Despite the uncertainty inherent in this approach, this equation is used in rather complex thermodynamic models predicting magmatic phase relations, such as the program MELTS (Ghiorso and Sack, 1995) or the model used by Sugawara (2000, 2001) for Fe-partitioning between melt and plagioclase. Although these models can certainly be considered major improvements in the modelling of magmatic systems the use of such an empirical equation in such models obviously puts some restrictions on the applicability to systems that strongly differ in either composition or pressure-temperature conditions.

Another approach to model the relationship of Fe oxidation state to intensive and extensive variables only recently introduced to geologically relevant melts is suggested by Ottonello and Moretti (Ottonello *et al.*, 2001; Moretti and Ottonello, 2003; Moretti, 2005).

This model is based on an acid-base model for oxide melts (Fraser, 1975, 1977) which classifies a given metal oxide in terms of its acidic or basic behavior, which directly affects the polymerization reaction between single bonded, double bonded and free oxygens in silicate melts. Basic components produce cationic units whereas acidic components produce anionic units. In the case of Fe, Fe^{3+} shows amphoteric behavior whereas Fe^{2+} shows only basic behavior. The disproportion of Fe^{3+} between anionic and cationic matrix in contrast to Fe^{2+} predicts that the ratio of rational activity coefficients Fe^{3+} and Fe^{2+} components cannot be expected to be 1 or even constant. As shown by the authors, this approach describes well Fe-oxidation states of published datasets of glasses synthesized at known temperature and oxygen fugacity (Ottonello *et al.*, 2001).

The effect of water on the Fe-oxidation state was studied by several authors (Moore *et al.*, 1995; Baker and Rutherford, 1996; Gaillard *et al.*, 2001; Wilke *et al.*, 2002). It may be concluded from these studies that water has no direct influence on the oxidation state other than that it influences the prevailing oxygen fugacity. Recently the influence of water dissolved in the melt was also included in the model of Ottonello and Moretti (Moretti, 2005).

The development of a correct model for predicting the Fe-oxidation state of a given melt composition at P, T and fO_2 of interest is of major importance, of course. However, additional problems in using the Fe-oxidation state of glass to deduce redox conditions arise from the fact that the original oxidation state may not be safely stored in the glass and might be affected by the thermal history of the volcanic glass after the first quench. Burkhard (2001) has shown that the Fe-oxidation state of a basaltic glass from Kilauea, Hawaii, may already change during re-heating at relatively low temperatures just above the temperature of glass transformation, well before the onset of crystallization. This reaction is intrinsically controlled and does not depend on any exchange of oxygen with the surrounding environment. Such a change may also occur in natural samples if relatively thin lava lobes that have not completely cooled down are re-heated by successive lava flows. Burkhard (2003) shows that such a re-heating may even lead to complete crystallization of the formerly vitrified parts of the bottom lava lobe. In more silicic melt compositions such effects are certainly less probable as the difference in eruptive style provides few possibilities for alteration by re-heating and thus the pristine oxidation state may well be preserved. The small effect of the quench rate during the first quench after eruption is confirmed by experimental observations. The Fe-oxidation state was found not to depend on the usual experimentally accessible quench rates (Dyar *et al*., 1987; Wilke *et al*., 2002).

3. Local structural environment of Fe in silicate melts

Although the structural environment of Fe in silicate melts is only of minor interest in the light of redox estimation in magmatic systems, it plays a major role in transport properties of silicate melts. The effect of oxidation state on the viscosity described at the beginning indicates that Fe^{3+} may be considered as a network former and Fe^{2+} as a network modifier.

Although this assignment might well describe the influence of oxidation state on viscosity, it still leaves open the question of the exact local structure around the two possible Fe-species.

Many spectroscopic investigations have been performed to gain further insight into the co-ordination environment of Fe in melt and glass and have produced a variable picture on the co-ordination found for Fe^{3+} and Fe^{2+}. Fe^{3+} is often assigned to be tetrahedrally co-ordinated although octahedrally co-ordinated is also reported (*e.g*., Dyar, 1985; Mysen *et al*., 1985; Virgo and Mysen, 1985; Hannoyer *et al*., 1992; Galoisy *et al*., 2001; Partzsch *et al*., 2003). For Fe^{2+}, assignments are even more variable ranging from octahedral, over trigonal bipyramidal to tetrahedral co-ordination (Waychunas *et al*., 1988; Keppler, 1992; Jackson *et al*., 1993; Rossano *et al*., 1999, 2000). The controversial assignment of co-ordination polyhedra is certainly related to the influence of the bulk composition and/or polymerization of the glasses used, but may be in part also related to the different techniques used. *E.g*., crystal-field spectra usually show strong clear evidence for Fe^{3+} in tetrahedral co-ordination, whereas evidence for higher co-ordinated Fe^{3+} may be superimposed by bands related to Fe^{2+} (Hannoyer *et al*., 1992). The presence of higher co-ordinated Fe^{3+} may then be cross-checked or more easily detected by the use of Mössbauer spectroscopy or *X*-ray absorption spectroscopy (Virgo and Mysen, 1985; Hannoyer *et al*., 1992; Partzsch *et al*., 2003; Wilke *et al*., 2004a). Spectral features are usually assigned to specific co-ordination polyhedra by comparison of the spectra taken on the glass to spectra of model compounds with Fe in well known structural environment, implying that the lack of long-range order has only little effect on the position of spectral bands or features. Beside the lack of long-range order, assignments are probably rendered more difficult by the fact that there is no unique co-ordination polyhedron for Fe.

Instead, the co-ordination polyhedra vary from site to site leading to a distribution of the local structure around Fe in the glass or melt. This site-to-site distribution is probably best reflected in the distribution of hyperfine parameters that can be determined from Mössbauer spectral analysis (Alberto *et al*., 1996; Dunlap, 1997;

Rossano *et al*., 1999; Wilke *et al*., 2002). Thus assignment to distinct co-ordination polyhedra is problematic and would not even describe the situation of Fe in glass or melt adequately, so that most spectroscopic analyses provide only information on the average co-ordination.

3.1. *Difference between melt and glass*

Interpretations on the melt structure based on observations made on glasses assume that the structure found in the glass represents the one that would also be found in the melt.

However, the structure found in glass is the one frozen in from the liquid at temperatures around the glass transition, which potentially differs from the melt structure found at higher temperatures. First evidence for differences in the co-ordination of Fe between melt and glass may already be taken from the fact that Mössbauer hyperfine parameters vary as a function of quench rate (Dyar *et al*., 1987; Wilke *et al*., 2002). First direct experimental evidence in the case of Fe was given by Waychunas *et al*. (1988) and Jackson *et al*. (1993). These authors have shown evidence by collecting XANES and EXAFS spectra at ambient conditions and high temperature that the co-ordination of Fe^{2+} found in glass differs from the one found in the melt. An increase in the intensity of the pre-edge feature located 10-20 eV before the main edge and a shortening of the measured Fe-O distance indicates that the co-ordination of Fe^{2+} at melt conditions is lower than that found in glass. Similar observations have been made for other elements like Ti and Ni (Farges and Brown, 1996; Farges *et al*., 1996).

An *in situ* Raman study on Fe-rich sodium-silicate glass and melt by Wang *et al*. (1993) looking to bands that are related to vibrational modes of the polymeric network has evidenced no changes above the temperature of glass transformation for oxidized samples. The high temperature spectrum of the reduced sample, however, indicates a further anionic species present in the melt and a depolymerization of the melt network, which was related by the authors to the ferrous iron in the melt.

New results from further *in situ* measurements using high resolution *X*-ray absorption spectroscopy at the Fe K-edge yielded similar results to those former studies using this technique (Wilke *et al*., 2004b; Wilke *et al*., unpubl.). XANES and EXAFS spectra were taken on $Na_2Si_3O_7$ glass and melt that was doped with 5 wt% Fe_2O_3 at both reducing and oxidizing conditions. At reducing conditions only a very small increase in the pre-edge intensity is observed in contrast to the results by Jackson *et al*. (1993). The change in the pre-edge intensity is much stronger at oxidizing conditions indicating that Fe^{3+} is affected much more strongly. An increase in the pre-edge intensity may be interpreted by a lowering of the coordination number or a change in site geometry, as the pre-edge intensity of tetrahedrally co-ordinated Fe is much higher than the one of octahedrally co-ordinated Fe (Wilke *et al*., 2001). So far, this change seems not to be quenchable and thus indicates an immediate re-arrangement of the local structure at T_g.

Although the structural differences between melt and glass are probably unimportant for defining redox equilibria in silicate melts these differences are certainly important for the understanding of transport properties and their relation to the melt structure.

4. Conclusions

Fe equilibria in magmatic systems provide valuable constraints for the understanding of the development of magmas prior to volcanic eruption or sub-volcanic emplacement. Each of the methods proposed here, however, has its limitations when applied to natural systems, although they always yield at least some rough estimate on the redox regime, of course. For more precise estimates a combination of techniques or Fe equilibria has to be used. As discussed by Sugawara (2001) the use of Fe-partitioning between three or more phases (*e.g.*, plagioclase, olivine and melt) is probably much more reliable than just partitioning between plagioclase and melt. A very important tool to constrain pre-eruptive conditions for a given volcanic site precisely is probably the experimental determination of phase relations as a function of *T*, *P*, fluid and melt composition (*e.g.*, Rutherford and Devine,

1996; Martel *et al*., 1998; Cotrell *et al*., 1999). Beside the determination of phase stability relations such experiments can also be used to calibrate the Fe (exchange) equilibria for the bulk composition of interest, *i.e*. Fe partitioning among phases, Fe oxidation state in glass, etc.

The modelling approaches introduced by Ottonello and Moretti to the volcanologist/ petrologist community provide an important step forward to profound modelling of redox equilibria in melt systems. Such models are certainly needed to model melt-crystal equilibria and to predict the evolution of the composition of magmas during volcanic cycles. An extension of this modelling approach is certainly desirable.

For an understanding of the relationship between melt-transport properties and melt structure a better link between composition and melt structure should be established. Fe is one further example that the local environment in glass may be significantly different from that in the melt. Any model of the melt structure that may be used as an input for the compositional dependence of transport properties should be based on experimental evidence of the molten state.

The simple parameter NBO/T (Non-Bridging Oxygen per Tetrahedron), often used to approximate changes in the melt polymerization with composition, differentiates the given elements only by the network forming or network modifying role, neglecting completely the potentially large difference in the field strength of the ions. A structural model that also accounts for these differences should provide a better basis for modelling compositional dependence of *e.g*., viscosity data.

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