Study of oxygen fugacity influence on redox state of iron in granitoidic melts

M V Volovetsky¹, V S Rusakov², O A Lukanin¹ and A A Kargaltsev¹

¹ Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences 19, Kosygin Str, 119991 Moscow, Russia
² Lomonosov Moscow State University, Department of Physics, Vorobyovy Gory, 119899, Moscow, Russia

E-mail: volovetsky@gmail.com

Abstract. A series of experiments has been carried out on two granitoid melt compositions under the wide range of oxygen fugacities. Room temperature $^5$Fe Mössbauer spectroscopy has been used to study the structural and oxidation state of Fe in granitoid composition glasses. Samples were produced in a series of melting experiments at temperatures from 1120 to 1420 ºC and oxygen fugacities from $10^{-0.7}$ (air) to $10^{-12}$ (CCO buffer) bars. The analysis has shown that Fe$^{3+}$/Fe$^{2+}$ ratio in the melt considerably decreases with fO$_2$ decreasing and/or temperature increasing. Dependence of Fe$^{3+}$/Fe$^{2+}$ ratio on fO$_2$ is linear in logarithmic scale with slope 0.18-0.24. Ferrous iron occupies octahedral and probably five-fold positions and is regarded as a network-modifier. Ferric iron coordination depends on iron redox state. Its structural role changes from network-modifier to network-former.

1. Introduction

Iron is an important natural probe that is present in more than one oxidation state in silicate minerals and glasses. The redox state of iron influences differentiation trends in crystallizing silicate melts. Besides, ferric and ferrous cations play different role in the structure of melt, so ferric-ferrous ratio influences the physical properties of melts.

The redox state of iron in melts depends on some external and internal parameters: temperature, oxygen fugacity and composition. The iron oxidation reaction in silicate melts can be expressed by the reaction:

$$4\text{FeO} + \text{O}_2 = 2\text{Fe}_2\text{O}_3$$

with the equilibrium constant

$$K = [a_{\text{FeO}}]([\text{O}_2])^{1/4}/[a_{\text{FeO}_{1.5}}],$$

where $a_i$ are the activities of the species and fO$_2$ – oxygen fugacity.

If we suppose activity coefficients to be equal and take logarithms of both sides of the equation (2) we find

$$\log(\text{FeO}/\text{FeO}_{1.5}) = -0.25 \log(f\text{O}_2) + \log(K)$$

³ To whom any correspondence should be addressed.
Thus in the case of ideal mixing ferric and ferrous components relation between logarithms of Fe redox ratio and oxygen fugacity is expressed by the straight line with the slope of 0.25.

The knowledge of influence of external and internal parameters on ferric-ferrous equilibrium in silicate melts could give an opportunity to reconstruct the conditions of acid rocks forming. This question has been investigated by many authors. However no one of the proposed equations describes experimental results well in a wide range of compositions, temperatures and fO$_2$ [1]. Moreover most of them did not consider acid melts in a wide range of temperatures and oxygen fugacities [2].

2. Samples and experimental methods

Two series of samples were prepared for melting experiments: 1) pantellerite glass – P9 (71% SiO$_2$); 2) melted granite – I2 (73% SiO$_2$) (table 1). P9 series have larger alkali and Fe content. Such compositions were chosen because of their resemblance to acid volcanic glasses and tektites compositions. Tektites are natural silicate glasses which were formed under very high temperature (≥2000 °C) and probably low oxygen fugacity [3].

| Conditions (T, t, log(fO$_2$)) | Sample | SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | FeO | MmO | MgO | CaO | Na$_2$O | K$_2$O | Cl | ZrO$_2$ | Total |
|-------------------------------|--------|--------|--------|-------------|-----|-----|-----|-----|--------|-------|----|-------|-------|
| Initial P9                   | 68.28  | 0.36   | 7.39   | 7.82        | 0.31| 0.07| 0.34| 6.61| 4.17   | 0.81  | 0.33| 96.48 |
| 1120 °C, 46h, -0.7 | P9-N2   | 70.00  | 0.36   | 7.71   | 7.60 | 0.28 | 0.09 | 0.37 | 6.05   | 4.13  | 0.70 | 0.36  | 97.64 |
| 1420 °C, 15h, -5.7 | P9-37   | 63.69  | 0.35   | 20.77  | 4.05 | 0.36 | 0.22 | 0.35 | 3.52   | 3.85  | 0.12 | 0.31  | 97.81 |
| Initial I2                   | 70.46  | 0.06   | 15.28  | 3.41        | 0.14| 2.06| 4.07 | 3.95 | 99.48 |
| 1240 °C, 20h, -7.0 | I2-N15  | 73.53  | 0.06   | 14.15  | 2.98 | 0.14 | 1.62 | 3.76 | 3.87   | 100.13|
| 1420 °C, 7h, -5.7 | I2R-29  | 74.22  | 0.06   | 13.03  | 2.84 | 0.13 | 1.55 | 2.06 | 3.77   | 97.70 |

Starting materials were melted in a vertical muffle furnace under different T-fO$_2$ conditions: T = 1120-1420 °C and -log(fO$_2$) = 7.0-12. Oxygen fugacity was imposed by different gas mixings: 1) pure air; 2) air+N$_2$; 3) CO$_2$+H$_2$. About 500 mg of ground starting materials was used for one experiment. Alumina crucibles were used as a sample containers. Run durations were 2-15 hours at temperature about 1420 C° and up to 50 hours at lower temperatures. Samples were quenched by immersing them into water after they have been drawn from the furnace.

Starting materials and obtained samples were studied using electron microprobe to investigate chemical changes during the experiments.

Mössbauer samples were prepared by grinding glasses under ethanol to avoid some oxidation prior to analysis, then were mounted in plexiglas holders. Room temperature Mössbauer spectra show broadened, slightly asymmetric quadrupole split doublets. Some spectra show contribution of magnetic phases. Spectra were analyzed in terms of two independent quadrupole splitting distributions corresponding to Fe$^{3+}$ and Fe$^{2+}$ sites. It was supposed that there was the positive correlation of hyperfine parameters (δ and ε) for Fe$^{2+}$. When the contribution of magnetic phases was essential additional distribution function of hyperfine magnetic field was calculated.

3. Results and discussion

Microprobe analysis has shown that some quantity of Na volatilizes during melting. For more viscous I2-series the volatilization was revealed at 1420 °C. But for the P9-series the volatilization of Na has been revealed at any used temperatures. There was a strong influence of alumina crucible on the melts at 1420 °C for these glasses. It led to the enrichment of Al and the non-homogeneity of glass (table 1).

Mössbauer spectra of the most of studied glasses are paramagnetic ones with broad lines and at least two subspectra. Experimental spectra have been analyzed in terms of two quadrupole splitting distributions corresponding to Fe$^{3+}$ and Fe$^{2+}$ sites. Each distribution shows one peak (figure 1).
At the lower temperature and oxidative atmosphere (T=1140 °C, fO$_2$=10$^{-0.7}$ bar) there was observed crystallization of oxide magnetic phases in the samples of I2 series. At the same time there were not any oxide phases in the series P9 in remarkable quantities. The series I2 is more viscous and its liquidus probably lies above 1140 °C.

The rates of redox reactions in investigated melts are strongly dependent on temperature. At T = 1420 °C about 5 hours is enough to attain equilibrium between glass and furnace atmosphere. At the same time at T = 1220 °C we could not reach the equilibrium for 50 hours even for less viscous melt of P9-series.

Oxygen fugacity was varied in the range from 10$^{-0.7}$ (air) to 10$^{-12}$ (near CCO buffer: graphite-CO-CO$_2$) bar. Even in the most oxidative atmosphere some quantity of Fe$^{2+}$ remained. The Fe$_{3+}$/Fe$_{2+}$ ratio in the melt considerably decreases with fO$_2$ decreasing and temperature increasing according to the following equation [4] (figure 2).

\[
\log(\text{Fe}^{3+}/\text{Fe}^{2+}) = a\log(f\text{O}_2) + b/T + c
\]  

(4)

In the figure there are given approximation equations for experimental data. It should be noted that the slope of lines is in the range 0.17-0.24 and is smaller than theoretical value for ideal ferric-ferrous mix (0.25).

![Figure 2](image-url)  

**Figure 2.** Relationship between logarithms of Fe$^{3+}$/Fe$^{2+}$ ratio and fO$_2$. In legends there are given equations of approximation lines.

It is difficult to obtain temperature dependence in a wider range due to kinetic limitations at the bottom side and instrumental limitations at the upper side. Thus we can not reach temperatures of the formation of tektites and volcanic glasses.

To reach extremely reducing conditions we used closed graphite crucible. So fO$_2$ in this system was near CCO buffer. Under these very reducing conditions (about 10$^{-12}$ bar) at temperature 1420 °C...
some quantity of metallic iron segregated in visible spherules and almost all iron in glass was divalent (some quantity of Fe$^{3+}$ remained).

Mössbauer line shifts of ferric iron change from values typical for octahedral oxygen coordination to those for tetrahedral coordination with increasing in its content. The transitional border lies at Fe$^{3+}$ content near 50 at.%Fe (figure 3). Probably there is a coordination transition from octahedral to tetrahedral positions with increasing in ferric iron content. Such transition was noted by Mysen et al. for Na-, Ca-, Mg-alumosilicate glasses [5].

It is worth that shifts of Fe$^{3+}$ in reduced granitoid glasses are the same as in the case of tektites [3]. It points to similar structure and probably similar thermal history.

Mössbauer line shifts of ferrous ions lie in relatively narrow regions. Values for I2 series lie in regions typical for octahedral and five-fold sites. Values for P9 are between regions typical for octahedral and tetrahedral sites. These values are independent of Fe$^{3+}$/Fe$^{2+}$ ratio (figure 3). We assigned these values to distorted octahedral sites. Ferrous iron in silicate is usually regarded as network-modifier and assigned to octahedral positions.

4. Conclusions
Using Mössbauer spectroscopy it has been shown that relation between Fe$^{3+}$/Fe$^{2+}$ ratio and oxygen fugacity is linear in logarithm scales according to the equation (4). However slope of the lines are 0.17-0.21 for I2-series and 0.22-0.24 for P9-series. They deviate from theoretically predicted value 0.25. This deviation may be caused by non-ideality of the mixing ferric and ferrous components.

Ferrous iron occupies octahedral and probably five-fold positions and is regarded as network-modifier. Ferric iron coordination changes from octahedral to tetrahedral with increasing Fe$^{3+}$/Fe$^{2+}$ ratio. This transition occurs at Fe$^{3+}$ content about 50 at.%Fe.

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