EFFECT OF COMPOSITION ON THE VALENCE OF IRON IN BASALTIC LIQUIDS,
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The relative concentrations of ferric and ferrous cations in rock melts
are of primary importance in planetary igneous petrology for determining equi-
librium redox conditions and for interpreting phase equilibria in systems con-
taining iron. Factors well known to control the ferric and ferrous concentra-
tions in silicate melts are temperature and oxygen fugacity (fO2). The Fe3+/
Fe2+ ratio of melts at particular conditions of temperature and fO2 cannot yet
be accurately predicted by thermodynamic equations because of insufficient
data regarding the effects of all components on the activity coefficients of
assumed iron species in the melt. The relative concentrations of iron cations,
as well as those of other multivalent elements, in different rock melts equi-
librated at identical temperature, fO2, and pressure depend also upon composi-
tion of the liquid. We have investigated the effects on the ferric-ferrous
ratio of varying individual components in a basaltic liquid. In addition to
establishing a more quantitative relation between the ferric-ferrous ratio and
the equilibrium fO2 of natural melts, the data seem to have bearing upon liq-
uid structures.

The effect of melt composition on the ferric-ferrous ratio has been de-
termined by adding major oxide components to natural tholeiitic basalt #401
(Table 1). Sample powders were compressed into pellets, fused to a looped
platinum wire, and suspended in a vertical quench-type furnace having an fO2
controlled by a mixture of CO2 and H2 gas. The sample-holding technique (1)
virtually eliminated a critical problem of iron loss due to crucible-melt
interaction and minimized time required for gas-melt equilibrium (about 6
hours - see figure 1). Experiments were conducted at about liquidus tempera-
ture (1200°C) and at a temperature well above the liquidus (1360°C). Oxygen-
fugacity values of 10^-8 and 10^-6 atm, respectively, were chosen to approximate
conditions in terrestrial magmas at these temperatures, as measured by Sato
and Wright (2). Sample weights were restricted to approximately 100 mg and
necessitated precise methods of chemical micro analyses. Ferrous iron was
determined by a volumetric titration technique similar to that described by
Wilson (3). The ferric-ferrous ratio in all experimental runs was obtained
by subtraction of the value for ferrous iron from that of total iron deter-
mined by electron-microprobe analyses. The average error of ferric-ferrous
values determined for all experimental runs was 0.03 mole% FeO. This
error was primarily caused by inhomogeneity, (mole% FeO)

because duplicate or triplicate ferrous analyses of all experimental runs
had an average error of only 0.07 wt%.

In order of decreasing significance, the addition of oxides of potassium,
sodium, silicon, aluminum, or calcium produces an increase in the ferric iron
content of the melt at 1200°C. Limited data on titanium oxide addition show
no measurable effect on the ratio at 1200°C and 1360°C. For all added com-
ponents except titanium, the resultant change in the ferric-ferrous ratio is
considerably less at 1360°C than at 1200°C. Table 2 lists results of all
experimental runs. Data illustrating the variation of the ratio as a func-

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tion of potassium oxide in the melt are presented in figure 2. The data for additions at 1200°C are sufficient to allow an accurate $f_{O_2}$ prediction scheme for unoxidized terrestrial basalt liquids of known composition, based on component differences relative to #401 basalt composition.

The effect of temperature on the variation in iron valence due to composition change may be a reflection of structural changes in the melt. At higher temperatures, minimal changes in the valence of iron are induced by component variation. At near liquidus temperatures, the ferric/ferrous ratio is more sensitive to liquid composition, thereby implying significant structural control of the acceptance of ferric or ferrous iron.

The "alkali effect" controlling the ratio of ferric and ferrous iron in basaltic liquids is consistent with results of many investigations into multivalent cation variations in simple synthetic glasses (4,5,6,7). These studies indicate concentrations of iron, manganese, chromium, and cerium into their oxidized states as concentration of alkalis increases. Results of this investigation are also consistent with findings in Roeder's (8) study of iron activity in basaltic liquids in equilibrium with metallic iron at liquidus temperatures. These findings show that increased concentrations of alkali, alumina, and/or silica decrease the amount of FeO dissolved in the melt and cause the precipitation of metallic iron. It is evident that these components cause ferrous iron to become less stable in the melt. At higher $f_{O_2}$'s similar to terrestrial conditions, this process results in an increase of ferric iron, and at very low $f_{O_2}$'s, it may result in direct precipitation of metallic iron from the melt.

Schreiber (9) presented data on the differences in $Cr^{3+}/Cr^{2+}$ and $Ti^{4+}/Ti^{3+}$ ratios of two iron-free model basalt compositions at 1500°C which indicate that enrichment in the melt with CaO enhances oxidation of these species relative to alumina enrichment. These data are in agreement with calculations from our data showing the relative ferric-ferrous variation induced by these components at 1360°C. At present, there are no comprehensive data regarding the effect of individual major components of natural melts on the valence states of chromium and titanium at the lower $f_{O_2}$ values associated with the lunar environment. However, on the basis of the reasonable correlation of the data presented for compositional dependence of the ferric-ferrous ratio with that of other multivalent elements in synthetic systems, it is likely that changes of $Cr^{3+}/Cr^{2+}$ and $Ti^{4+}/Ti^{3+}$ ratios due to bulk composition variation in lunar magmas are analogous to compositionally induced $Fe^{3+}/Fe^{2+}$ changes in terrestrial basaltic liquids.

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Table 1. Composition of #401 Basaltic Glass
(equilibrated at 1200°C; 10^-8 atm FO2)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>46.75</td>
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<tr>
<td>TiO2</td>
<td>1.37</td>
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<tr>
<td>Al2O3</td>
<td>17.10</td>
</tr>
<tr>
<td>FeO</td>
<td>8.55</td>
</tr>
<tr>
<td>MgO</td>
<td>9.35</td>
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<tr>
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<td>Na2O</td>
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<tr>
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<tr>
<td>FeO0.5</td>
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</tr>
<tr>
<td>FeO</td>
<td>.193</td>
</tr>
</tbody>
</table>

Figure 1. Ferric-ferrous ratio (wt%) as a function of time for experimental runs using 401 powder, melted at 1200°C and 10^-8 atm FO2.

Figure 2. Ferric-ferrous ratio variation with mole% KO0.5 in potassium oxide addition melts.

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