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THE STRUCTURAL ROLE OF FERRIC IRON IN SILICATE MELTS

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Iron is the major cation involved in oxidation-reduction processes in magmatic silicate liquids. The molecular structural configurations assumed by ferric and ferrous iron are important in determining their activities in these liquids. They, in turn, affect both crystal-fractionation trends and the compositions of precipitated iron-titanium phases on cooling.

In discussing the structural characteristics of iron in silicate melts, it is useful to consider the general structural model which has emerged through investigation in the past two decades. In explaining many physical properties of these liquids, it has been useful to regard acid cations such as Si^{4+} as "network-formers" (in four-fold oxygen coordination), and basic cations such as Na, K. Ca, Mg, Fe^{2+} as "network-modifiers" (in six-fold or higher coordination). On the basis of simple geometric packing arguments, aluminum has an ionic radius intermediate between that preferring four- and six-fold coordination. It can thus assume either structural role. To exist in tetrahedral coordination, however, it must have an "associated" charge balancing cation (i.e. Na, K, $Ca_{1/2}$, $Mg_{1/2}$, etc.). This simplistic structural model finds extensive support in studies of alumino-silicate melts in which singularities in physical properties have been observed when the ratio of Al^{3+} to monovalent+½divalent cations = 1 (i.e. stochiometric composition). Such singularities occur in refractive indices (Schairer & Bowen 1956), and electrical conductivity (Isard 1959). The viscosity model of Bottinga & Weill (1972), which is also based on this structural model, has been very successful in accurately predicting the viscosities of silicate melts over a wide range of composition and temperature. The high-pressure extension of this model (Waff 1975) has successfully predicted a viscosity decrease in magmas with increased pressure, as verified by Kushiro *et al.* (1966). It also offers a consistent explanation of the electrical conductivity data of Waff & Weill (1975) for magmatic liquids.

Fe^{3+} is amphoteric with Al^{3+}, having the same charge and nearly the same ionic radius (0.51Å versus 0.64Å). It is well-known to exhibit isomorphic behavior with Al^{3+} in some crystalline solids. On this basis, one might expect Fe^{3+} to behave analogously with Al^{3+} in silicate melts. Waff & Weill (in prep.) have measured ferric-ferrous ratios of a wide compositional variety of glasses quenched from silicate melts which were equilibrated at known temperatures and oxygen fugacities. It was generally observed that at any given $f(O_2)$ and T, ferric-ferrous ratios increased with (1) increasing total iron concentration, and (2) increasing alkali concentration. The latter occurs only above a "critical concentration" of approximately 9 mole % ($Na_{1/2}O$ + $K_{1/2}O$). This threshold or "critical concentration" for the alkali shift is thought to be due to take-up of alkalis first by Al^{3+} in four coordination, and then by Fe^{3+} in four coordination, since all melts considered had Al_2O_3 contents between 14 and 21%. The threshold may vary with composition, but such variation was not discernible in the data. This may be due to the relatively narrow range of Al_2O_3 concentrations. In all the above samples there was an excess of mono- and divalent cations to balance charge for Al^{3+} and Fe^{3+}. No other significant dependence of ferric-ferrous ratios was observable. Mössbauer spectra were taken of some of these samples by Waff *et al.* (unpublished data). Spectra taken of glasses quenched from 1400°C and $\log f(O_2) = -0.68$ showed isomer shifts and quadruple splittings for ferric iron which were characteristic of four-fold coordination. At the very least (depending on the method of data analysis), a substantial fraction (on the order of half) of the ferric iron must be four-coordinated. Since high alkali concentration increases the ferric-ferrous ratios, it is believed that $(Na,K)Fe^{3+}O_2$ complexes are more tightly bound and, therefore, more stable than $(Ca,Mg)_{1/2}Fe^{3+}O_2$ complexes. The data suggest that Ca is the major divalent cation forming stable complexes with Fe^{3+}, at least at 1400°C.

It is instructive to consider the effects of the analogous aluminates on viscosity. $NaAlO_2$ complexes are apparently stable in silicate melts to temperatures in excess of 1800°C. On the other hand, $Ca_{1/2}AlO_2$ added stochiometrically to a silicate melt of intermediate silica content increases viscosity at lower temperatures, but decreases viscosity at temperatures above approximately 1500°C (cf. Bottinga & Weill 1972). The change is gradational and can be interpreted in terms of thermal dissociation of $Ca_{1/2}AlO_2$. This structural complex is a network-former and increases viscosity. As temperature is elevated, it becomes progressively more thermally dissociated according to the reaction $2Ca_{1/2}AlO_2 = CaO+Al_2O_3$. The products of this reaction act as network modifiers, and decrease viscosity. At sufficiently high temperatures the equilibrium fraction of $CaO+Al_2O_3$ would exceed $2Ca_{1/2}AlO_2$. The net effect of adding $Ca_{1/2}AlO_2$ to the melt would then be to produce a decrease in viscosity, as is observed. If Fe^{3+} behaves analogously with Al^{3+}, then it is expected that $(K,Na)\text{-}Fe^{3+}O_2$ complexes would be stable over all magmatic temperatures, whereas $Ca_{1/2}Fe^{3+}O_2$ complexes would be partly dissociated thermally at any given temperature. The dissociated components would produce octahedrally coordinated Fe^{3+}. This explanation of the behavior of ferric iron is consistent with the data of Waff & Weill (in prep.) and with the Mössbauer studies reported by Kurkjian & Sigety (1968), Pargamin *et al.* (1972), and Levy *et al.* (1976).

There is some unresolved difficulty in assignment of tetrahedral and octahedral doublets in Mössbauer spectra for ferric iron in silicate glasses. Kurkjian & Sigety assumed that the isomer shift was diagnostic of the coordination, whereas Levy *et al.* assumed quadruple splitting. Therefore, caution should be exercised in using published tetrahedral to octahedral ferric-iron ratios until more definitive silicate-glass analyses are available. The data of Waff & Weill (in prep.) are not dependent on this ratio, provided that it is large and relatively insensitive to divalent cation concentration.

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