A review of Mössbauer data on inorganic glasses: the effects of composition on iron valency and coordination

M. DARBY DYAR

Department of Earth, Atmospheric, and Planetary Sciences
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Abstract

Over the last twenty years, the technique of $^{57}$Fe Mössbauer spectroscopy has been widely used to characterize the structural role of iron in a broad range of glass compositions. This overview of previous work on iron-bearing glasses covers both geological and ceramic research on Fe-bearing Na–Si–O, borate, phosphate, and more complex silicate systems. Mössbauer work on multi-component synthetic compositions is reviewed in terms of the effects of each separate cation on Fe$^{3+}$/Fe$^{2+}$ ratios and iron site occupancies.

Introduction

Many geoscientists are unaware of the wealth of experimental data on iron partitioning in glass systems which covers both valences and site occupancies of Fe cations. The technique of Mössbauer spectroscopy has proven to be a useful tool for studying glasses since it provides not only Fe$^{3+}$/Fe$^{2+}$ analyses, but also gives structural information on site characteristics as well. Reviews by Kurkjian (1970), Coey (1974), and Wong and Angell (1976) give excellent summaries of glass/Mössbauer research; however, a considerable volume of data has been published since then. Because iron partitioning in silicate glasses is particularly relevant to petrology and material science problems, a current review of Mössbauer data on silicate (and related) glasses seems timely.

Iron partitioning in a glass is dependent on several factors: duration, temperature, and pressure of the precursor melt's equilibration; quenching conditions (cooling rate and sample size); temperature and pressure of the glass during the (Mössbauer) measurement; and the composition of the sample. Of these, only the latter effect has been extensively studied. However, the other factors may be equally important. Recent work by Naney and Swanson (1984) demonstrates that equilibrium conditions (particularly duration) dramatically affect Fe$^{3+}$/Fe$^{2+}$ ratios, especially in high-silica compositions where redox kinetics proceed far more slowly than was previously thought. A handful of studies (e.g., Mysen and Virgo, 1978) have observed increases in Fe$^{3+}$/Fe$^{2+}$ with increasing $T$$_{equilibration}$ in quenched glasses. Similarly, the work of Mo et al. (1982) and Mysen et al., (1982) suggests the Fe$^{3+}$/Fe$^{2+}$ will decrease with increasing $P$$_{equilibration}$. However, it is impossible to determine the extent to which the quenched glasses in these studies actually represent the equilibrated $T$ and $P$ conditions because the changes which occur between melt and glass are not well understood (Lin, 1983). In fact, quenching conditions may exert a controlling influence on iron partitioning and valency (Dyar and Birnie, 1984; Dyar, 1984a); rapid quenching rates favor lower cation coordination (and Fe$^{2+}$), slower quenches (e.g., samples cooled in air or gas) favor higher coordination and Fe$^{3+}$.

There have been a few in situ measurements on the effects of temperature and pressure on glasses. Low temperature Mössbauer measurements (commonly 4.2 K and 77 K—liquid helium and liquid nitrogen, respectively) are often used to study paramagnetism in glasses; studies such as Kurkjian and Buchanan (1964) show that low temperature measurements greatly increase spectral resolution. High temperature Mössbauer work on glasses is rare, but in situ data on the sodium trisilicate system from Gosselin et al. (1967) and Hong (1978) show that increasing temperature decreases both isomer shift and quadrupole splitting. Also in the same system, Lewis and Drickamer (1968) observed that isomer shift increases with increasing pressure (up to 200 kbar) as compression causes a minimum in electron density at the nuclei of the Fe atoms.

All of the factors listed above are probably secondary to the main variable controlling iron partitioning: composition. Thus this paper will concentrate on a somewhat simplified case, examining closely the effects of composition only on iron valency and coordination. The results have been broken down into three groups for simplification: phosphate, borate, and silicate glasses. Tabulated compositions, isomer shifts, quadrupole splittings, and line widths are drawn from over forty papers. Mössbauer parameters (where necessary) have been recalculated relative to the center of an iron foil spectrum, so that all the listed values may be directly compared. Emphasis will be focussed on the question of how each compositional variable, alone or in combination, affects iron partitioning. The resulting overview is not a simple picture, but it gives a much more comprehensive summary of glass/melt processes to those who would try to appraise the thermodynamic characteristics of phase equilibria.
Overview of previous work

The first indication of the usefulness of the Mössbauer effect to glass research was the study done by Pollack et al. (1962), which demonstrated that glass is sufficiently rigid to enable resonant absorption of nuclear gamma rays to occur. Chemists were quick to study alkali-iron-silicate glass, an important raw material for the young semiconductor industry. Iron was observed in +2 and +3 valence states, as Johnston (1964) and Baak and Hornyak (1961) found through wet-chemical analyses. The Mössbauer technique introduced the ability to determine iron site occupancies and gain insight into the structural characteristics of the materials being studied. Typical ranges of isomer shifts in glasses (reported relative to a metallic Fe standard) as a function of coordination number and valency are given in Table 1.

Mössbauer spectroscopy was quickly adopted for a wide range of glass studies. Phosphate glasses were analyzed by several workers in the 1960's, yielding remarkably consistent values for six-fold coordinated Fe$^{3+}$ and Fe$^{2+}$. Borate glass research, which experienced major growth in the 1970's, shows predominantly four-fold Fe$^{3+}$ and six-fold Fe$^{2+}$. Most recently, more complex silicate glasses have been studied by many workers. It is convenient to review the glass literature based on these three subdivisions, which involve increasingly complicated compositions and structures.

Phosphate glasses: a simple system

Phosphate glass may be formed by isolated PO$_4$ tetrahedra (Kanazawa et al., 1969), or polymeric chains of PO$_4$ tetrahedra which bond to neighboring tetrahedra by means of a bridging oxygen ion (Nelson and Exarhos, 1979). Due to charge balance considerations these PO$_4$ units can’t be linked together in a continuous three dimensional network; P must have a double bond to one of the O atoms (Taragin et al., 1972). If Al is present it will form AlO$_4$ octahedra surrounded by rings of PO$_4$ tetrahedra (Pavlushkina et al., 1981); Fe may also fit into a similar structure in the interstices between PO$_4$ chains. From such a crystal structure, it would seem likely to expect iron to be octahedrally coordinated; Mössbauer work has been instrumental in proving this.

Early Mössbauer measurements of Fe$_3$(PO$_4$)$_3$·8H$_2$O and FePO$_4$·4H$_2$O glasses by Kerler and Neuworth (1962) observed characteristic iron doublets with isomer shifts (δ or I.S.) of 1.251 mm/sec (Fe$^{3+}$) and 0.291 mm/sec (Fe$^{2+}$), which they considered octahedral. This work was corroborated by the magnetic susceptibility measurements of Bamford (1962) on similar compositions. Kurkjian and Buchanan (1964) and Kurkjian and Sigety (1968) also observed octahedral iron of both +2 and +3 charge in phosphate glasses, with I.S. = 1.15 and 0.50 mm/sec, respectively. Kamo et al. (1967) reported ferromagnetic shifts of 0.37-0.40 mm/sec for Fe$_2$O$_3$-NaPO$_4$ glass, and 0.26-0.39 mm/sec for Fe$_3$O$_4$-NaPO$_4$ glass. The latter composition also had ferrous sites with I.S. = 1.18-1.58 mm/sec. Mössbauer parameters for octahedral iron in ferrous and ferric valency were also found by Frischat and Tomandl (1971), Vaughan et al. (1973), Beltran-Porter et al. (1980), and Nishida et al. (1981a). Additional references are given in Table 2.

There is some evidence for tetrahedral iron in phosphate glasses with very low (<2 mol.%) Fe$_2$O$_3$ contents. Electron spin resonance (ESR), optical, and X-ray diffraction studies by Bishay and Makar (1969) observed both divalent and trivalent four-coordinated iron; electrical conductivity measurements by Motran et al. (1973) and EPR studies of Menil et al. (1980) also suggest the presence of some minor concentration of tetrahedral iron. Such small amounts of tetrahedral occupancy (<1%) would not be detected by Mössbauer spectra.

In summary, the relatively simple iron-phosphate glass system has been thoroughly examined through Mössbauer spectroscopy. A survey of literature values is listed in Table 2. In general, both Fe$^{2+}$ and Fe$^{3+}$ have been reported in octahedral coordination, though other analytical methods have observed small amounts of tetrahedral iron.

Borate and borosilicate glasses: a more complicated system

Physicists and ceramists have also been very interested in borate systems, which are of great importance to the fiberglass industry. The systematics of B$_2$O$_3$-Fe$_2$O$_3$ glass containing Pb, Ge, K, Cl, and Si are fairly well understood (for a more comprehensive review, see Dannheim and Frey, 1978). The following summary highlights the trends which may be applicable to studies of natural melts in the earth sciences.

An early Mössbauer study of complex borosilicate glasses was made by Taragin and Eisenstein in 1970. They observed iron site partitioning similar to that in sodium silicates: relatively sharp, easily-resolved ferric peaks (δ = 0.327; quadrupole splitting, Δ = 0.947 mm/sec, typical of four-coordinated iron) and a widely varying ferrous peak (average δ = 1.057, Δ = 2.137 mm/sec). Similar results were obtained by Jach (1973 and 1974), Raman et al. (1978a and b), Prasad et al. (1982), and Kamal et al. (1982). Later workers were able to resolve ferric iron in both octahedral and tetrahedral coordination (See Table 3).

Taragin and Eisenstein were also the first to observe a

---

Table 1. Ranges of isomer shifts in glasses as a function of coordination number

<table>
<thead>
<tr>
<th>Phase</th>
<th>SI (mm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>IV: 0.90-0.95, V1: 1.20-1.30, VIII: 1.20-1.30</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>IV: 0.20-0.32, V1: 0.35-0.55</td>
</tr>
</tbody>
</table>

* Quadrupole splittings vary widely for glasses and can not be considered diagnostic for any specific coordinations. Isomer shifts are relative to the midpoint of the metallic Fe spectrum.
trend which is common in many silicate glasses: Fe²⁺/Fe³⁺ ratios decreased systematically as total iron (1972) and Burzo and Ardelean (1979a and 1979b) confirmed that the proportion of Fe³⁺ increases linearly with increasing iron content, as does quadrupole splitting, but partitioning of ferric iron between octahedral and tetrahedral sites (Fe³⁺ is both four- and six-coordinated in xFe₂O₃, 1 - x (PbO, 38203) glasses) is not affected. It seems that adding iron to the system forces a restructuring and deformation of the glass structure, which would tend to increase A as is observed.

Nishida et al. (1980a,b; 1981a,b,cd) added K and/or Cl to the B-Fe-O system and obtained similar trends. Isomer shift decreases with the addition of K₂O or KCl to the system. Narrower linewidths suggest that as potassium is added, the steric configuration around the iron nuclei seems to become more uniform. K₂O also tends to aid in the formation of non-bridging oxygens at levels of ≥20 mol% in borates and 8-10 mol% in borosilicates; as SiO₄ units are formed, isomer shift decreases. Similarly, the presence of Cl⁻ ions in the bulk glass results in the formation of FeOCl tetrahedra; as a “superstructure” of FeOCl and FeO0 tetrahedra is formed in the glass, its overall structure becomes more uniform and the melt is more polymerized. The increased covalency of the Fe-Cl bonds also decreases isomer shift.

A broader range of compositions in simple borate glasses was studied by Bahgat et al. (1983). In their work on B₂O₃ · MgO · Fe₂O₃ · Na₂O · SnO₂ systems, decreases in symmetry occurred systematically as smaller, increasingly highly charged cations were introduced into the glass, increasing in charge-to-radius ratio in the order Na⁺ < Mg²⁺ < Fe³⁺ < Sn⁴⁺. Largest isomer shifts resulted from ions with Sn⁴⁺ as nearest neighbors, and small I.S. was observed in the presence of Na⁺. Other studies show similar trends of decreasing isomer shift with charge-to-radius ratios: Sekhon and Kamal (1979) with Pb²⁺, Eissa et al. (1980) with Na⁺, and Burzo et al. (1982) with Ca²⁺. The concept of charge-to-radius ratios may be an important one to consider in models of glass structures, particularly where Fe³⁺ and Fe²⁺ are both present. This will become evident as Mössbauer data from more complex systems are presented later.

In summary, then, the results from borate and borosilicate glass studies suggest the following:

(1) Both ferric and ferrous ions are often present, even at low oxygen fugacities.
(2) Fe³⁺/total Fe and quadrupole splitting increase with iron concentration.
(3) The addition of K⁺ or Cl⁻, which lead to the formation of non-bridging oxygens, decreases isomer shift.
(4) The coordination of an iron atom in a glass may be a function of the charge-to-radius ratio of its nearest neighbors.

Complex systems: silicate glasses

Although the simpler systems demonstrate some of the major trends of iron coordination in glasses, a more thorough understanding of complex, multication systems is needed to achieve any geological relevance. The wide range of measurements on synthetic systems, summarized in Table 4, clearly illustrates the complex effects which several
Table 3. Borate glasses

<table>
<thead>
<tr>
<th>Reference</th>
<th>Composition</th>
<th>Fe(^{3+}) tet</th>
<th>Fe(^{3+}) oct</th>
<th>Fe(^{2+}) oct</th>
<th>(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taragin and Eisenstein, 1970</td>
<td>&quot;complex borosilicate glass&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tricker et al., 1974</td>
<td>(\text{Ba}_2\text{O}_3\text{CaO}_2\text{Fe}_2\text{O}_3)</td>
<td>0.284</td>
<td>0.293</td>
<td>0.305</td>
<td>0.61</td>
</tr>
<tr>
<td>Bukrey, et al., 1974</td>
<td>(\text{Na}_2\text{O}\cdot\text{Li}_2\text{O}\cdot\text{B}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3)</td>
<td>0.284</td>
<td>0.293</td>
<td>0.305</td>
<td>0.61</td>
</tr>
<tr>
<td>Raman et al., 1975</td>
<td>(\text{xNa}_2\text{O}\cdot\text{Fe}_2\text{O}_3\cdot(94-x)\text{B}_2\text{O}_3) mol. %</td>
<td>0.370</td>
<td>0.348</td>
<td>0.349</td>
<td>0.799</td>
</tr>
<tr>
<td>Kang and Moon, 1976</td>
<td>(\text{Ba}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3)</td>
<td>0.326</td>
<td>0.325</td>
<td>0.326</td>
<td>0.766</td>
</tr>
<tr>
<td>Raman et al., 1978</td>
<td>(\text{xCaO}\cdot(69-x)\text{B}_2\text{O}_3\cdot25\text{Na}_2\text{O}\cdot6\text{Fe}_2\text{O}_3)</td>
<td>0.283</td>
<td>0.293</td>
<td>0.283</td>
<td>0.796</td>
</tr>
<tr>
<td>Sekhon and Kanal, 1978</td>
<td>(\text{PbO}\cdot2\text{B}_2\text{O}_3\cdot\text{K}_2\text{O}\cdot\text{Na}_2\text{O}\cdot\text{Fe}_2\text{O}_3)</td>
<td>0.366</td>
<td>0.345</td>
<td>0.327</td>
<td>0.806</td>
</tr>
<tr>
<td>Horie et al., 1978</td>
<td>(\text{Ba}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3\cdot25\text{Fe}_2\text{O}_3)</td>
<td>0.25</td>
<td>0.29</td>
<td>0.27</td>
<td>0.770</td>
</tr>
<tr>
<td>Nishida et al., 1981b</td>
<td>(\text{xK}_2\text{O}\cdot(100-x)\text{B}_2\text{O}_3\cdot5\text{Li}_2\text{O}\cdot\text{Fe}_2\text{O}_3)</td>
<td>0.31</td>
<td>0.28</td>
<td>0.25</td>
<td>0.770</td>
</tr>
<tr>
<td>Nishida et al., 1981d</td>
<td>(2\text{K}_2\text{O}\cdot8\text{B}_2\text{O}_3\cdot0.33\text{Fe}_2\text{O}_3)</td>
<td>0.32</td>
<td>0.28</td>
<td>0.25</td>
<td>0.770</td>
</tr>
<tr>
<td>Bonnenfant, et al., 1982</td>
<td>(\text{Fe}_2\text{O}_3\cdot3\text{PbO}\cdot(6\text{B}_2\text{O}_3\cdot4\text{Fe}_2\text{O}_3)\cdot25)</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.770</td>
</tr>
<tr>
<td>Sengat et al., 1983</td>
<td>(\text{Ba}_2\text{O}_3\cdot\text{Na}_2\text{O}\cdot\text{MgO}\cdot\text{Fe}_2\text{O}_3\cdot\text{SnO}_2)</td>
<td>0.170</td>
<td>0.170</td>
<td>0.170</td>
<td>0.770</td>
</tr>
</tbody>
</table>
Table 4. Silicate glasses

<table>
<thead>
<tr>
<th>Reference</th>
<th>SiO2</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>FeO</th>
<th>MgO</th>
<th>Fe2+tet</th>
<th>Fe2+oct</th>
<th>Fe3+</th>
<th>Fe3+</th>
<th>Fe2+</th>
<th>Fe2+</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kurkjian and Buchanan, 1964</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.24</td>
<td>2.01</td>
<td>0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beljajev et al., 1965</td>
<td>165</td>
<td>165</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gosselin et al., 1967</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.37</td>
<td>0.95</td>
<td>1.12</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lewis and Drikerer, 1968</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.27</td>
<td>0.91</td>
<td>1.09</td>
<td>2.66</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gosselin et al., 1967</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.35</td>
<td>1.5</td>
<td>0.987</td>
<td>1.02</td>
<td>1.03</td>
<td>1.95</td>
<td>0.52</td>
</tr>
<tr>
<td>Hirdo et al., 1979</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.95</td>
<td>2.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nolet et al., 1979</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.28</td>
<td>0.74</td>
<td>1.17</td>
<td>2.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>de Grave et al., 1980</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.77</td>
<td>0.31</td>
<td>0.84</td>
<td>0.35</td>
<td>0.88</td>
<td>0.43</td>
</tr>
<tr>
<td>Komatsu and Soga, 1980</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.77</td>
<td>0.35</td>
<td>0.89</td>
<td>0.43</td>
<td>0.89</td>
<td>0.43</td>
</tr>
<tr>
<td>Levitz et al., 1980</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.77</td>
<td>0.35</td>
<td>0.89</td>
<td>0.43</td>
<td>0.89</td>
<td>0.43</td>
</tr>
<tr>
<td>Dyar and Burns, 1981</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.77</td>
<td>0.35</td>
<td>0.89</td>
<td>0.43</td>
<td>0.89</td>
<td>0.43</td>
</tr>
<tr>
<td>Danckwerth et al., 1982</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.77</td>
<td>0.35</td>
<td>0.89</td>
<td>0.43</td>
<td>0.89</td>
<td>0.43</td>
</tr>
<tr>
<td>Seifert et al., 1982</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.77</td>
<td>0.35</td>
<td>0.89</td>
<td>0.43</td>
<td>0.89</td>
<td>0.43</td>
</tr>
<tr>
<td>Virgo et al., 1982a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.77</td>
<td>0.35</td>
<td>0.89</td>
<td>0.43</td>
<td>0.89</td>
<td>0.43</td>
</tr>
<tr>
<td>Virgo et al., 1982b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.77</td>
<td>0.35</td>
<td>0.89</td>
<td>0.43</td>
<td>0.89</td>
<td>0.43</td>
</tr>
<tr>
<td>Burns and Dyar, 1983</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.77</td>
<td>0.35</td>
<td>0.89</td>
<td>0.43</td>
<td>0.89</td>
<td>0.43</td>
</tr>
<tr>
<td>Dyar and Birnie, 1984</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.77</td>
<td>0.35</td>
<td>0.89</td>
<td>0.43</td>
<td>0.89</td>
<td>0.43</td>
</tr>
</tbody>
</table>

* Fe variations caused by changes in quench rates
of the most abundant elements have on glass structure. These systems are perhaps best discussed by addressing each cation separately.

**Sodium trisilicate glass** was the first composition to be extensively studied by early Mössbauer workers, as its spectrum was easy to resolve and did not appear to be influenced by composition. Kurkjian and Buchanan (1964) fit a series of Na$_2$O : 3SiO$_2$ glasses with a doublet having an isomer shift of 1.24 mm/sec and quadrupole splitting of 2.01 mm/sec, which was considered typical of Fe$^{2+}$ in octahedral coordination. They also observed a linewidth, $\Gamma$, of 0.75 mm/sec (about three times the natural linewidth of Co$^{57}$ in Pd), which they attributed to distortion of the glass sites. Subsequent workers (Tomandl et al., 1967; Hirayama et al., 1968; Mulay, 1972; Labar and Glenn, 1973/1974; Levy et al., 1976; and Jacq and Nabatoin, 1977a,b) observed similar $\delta$ and $\Delta$ for Fe$^{2+}$ and also observed tetrahedral and octahedral Fe$^{3+}$ in other Na–Si compositions; as the quality of spectra and fitting techniques (more sophisticated models of line shapes) improved, two different types of Fe$^{2+}$ octahedral sites were resolved (Boon, 1971). Later work (Gosselin et al., 1967; Virgo et al., 1982b) shows that the ratio of Fe$^{2+}$/Fe$^{3+}$ seems to decrease when total iron increases.

Recent workers (Hirao et al., 1980; Komatsu and Soga, 1980; and Virgo et al., 1982b,a) have reproduced the above results for iron in Na$_2$O : 3SiO$_2$ glasses. The general consensus is that Fe$^{3+}$ exists in at least one (probably two) distinct tetrahedral site which is not seen at low $P_{O_2}$. The proportion of Fe$^{2+}$ increases at low oxygen fugacities. Seifert et al. (1978) observed Fe$^{2+}$ peaks with what they called "intermediate" isomer shifts ranging from 0.888 to 0.991 mm/sec, with linewidths between 0.539 and 0.811 mm/sec. Such broad linewidths may indicate the presence of more than one Fe$^{2+}$ site as well.

It should also be stressed that other analytical techniques have produced data which corroborate the Mössbauer conclusions. Using magnetic susceptibility measurements, Bamford (1962) found both Fe$^{2+}$ and Fe$^{3+}$ in octahedral coordination in sodium silicate glasses. Optical absorption due to Fe$^{2+}$ and octahedral and tetrahedral Fe$^{3+}$ was observed by Fenstermacher (1980) in sodium silicate glass. Fox et al. (1981, 1982) combined optical absorption, luminescence and Raman spectroscopy to identify three coordination environments; Fe$^{2+}$ and Fe$^{3+}$ in two distinct tetrahedral arrangements. Finally, Park and Chen (1982) used extended X-ray absorption fine structure (EXAFS) measurements to conclude that Fe$^{3+}$ is in octahedral coordination in dilute concentrations in sodium disilicate glasses.

The extensive literature on sodium in iron-bearing silicate melts (see Table 4) leads to the following conclusions:

1. Both ferrous and ferric iron are present; the proportion of Fe$^{3+}$/Fe$^{2+}$ seems to increase with iron content.
2. The $\delta$ and $\Delta$ parameters for both types of iron are slightly spread, and linewidths are broad suggesting that Fe may occur in two sites for each valency.

Mössbauer data show that Fe$^{3+}$ fills both octahedral and tetrahedral sites, though the EXAFS data of Park and Chen (1982) shows only octahedral Fe$^{3+}$.

**Calcium** is a network modifier which tends to prefer six-fold or higher coordination sites in glass. It is frequently used in bulk glass compositions for studies of effects of other cations (e.g., Varret and Naudin, 1979; Bandypadhyay et al., 1982; Neumann et al., 1982; Tomozawa et al., 1982; and Schreiber et al., 1980) because calcium tends to be fairly stable in complexes with iron (Waff, 1977), and is a useful charge-balancer for many other common cations (Myessen et al., 1981). However, the influence of Ca itself has been well studied through use of $^{57}$Fe Mössbauer spectroscopy. Levy et al. (1976) used Fe$_2$O$_3$-SiO$_2$–CaO glasses to examine iron partitioning. They found that partitioning between different sites of the same ion (Fe$^{2+}$ and Fe$^{3+}$) was not affected by the amount of Ca in the equilibrated melt; however, increasing CaO content clearly increases Fe$^{2+}$/Fe$^{3+}$ ratios. Replacement of CaO by Na$_2$O created no significant changes in Fe$^{2+}$/Fe$^{3+}$ ratios, but substitution of Na for Ca did have a substantial effect on Fe$^{3+}$/Fe$^{2+}$ ratios, which increased with increasing temperature and/or decreasing basicity. Both I.S. and Q.S. were also affected by this compositional dependence.

Iwamoto et al. (1978 and 1979) varied the Ca component in Ca–Fe–Si–O glasses and found similar trends. Fe$^{3+}$/Fe$^{2+}$ ratios consistently increase with increasing CaO content and $P_{O_2}$. This corroborates the work of Waff (1977) who postulates that when no Na is present, Ca forms highly stable complexes (CaFe$^{3+}$O$_4$) with trivalent iron. However, the addition of even more stable Na (and Na$_2$Fe$^{3+}$O$_5$ complexes) to a melt may gradually dissociate the Ca complexes in favor of Na complexes. Later work by Myessen et al. (1981) and Danckwerth et al. (1982) reproduced these results. Mössbauer spectra of the system Na$_2$Si$_2$O$_7$–CaSi$_2$O$_5$ with added Fe$_2$O$_3$ show the expected increase in I.S. from Na to Ca systems, reflecting the additional contribution from Fe$^{3+}$ as Na complexes preferentially over Ca.

The effects of Ca on silicate melts, based on Mössbauer data, can be summarized as follows:

1. Addition of Ca alone to a Si–Fe–O system caused increased Fe$^{2+}$/Fe$^{3+}$ ratios.
2. When Na$_2$O is present, it controls iron partitioning and the effect of Ca content on Fe$^{3+}$/Fe$^{2+}$ is diminished.

**Aluminum** can play a dual role as either four-fold network former or six-fold network modifier in a melt. Although a large number of other analytical techniques, including Raman (Brawer and White, 1977), Radial Distribution Function (Taylor and Brown, 1979, 1980), and electronic absorption spectra (Khalilov et al., 1978), have been applied to Al$_2$O$_3$-bearing melts, little Mössbauer work on iron-bearing melts has been attempted. Wood and Hess (1980) have shown that the addition of Al$_2$O$_3$ causes a decrease in critical temperature, phase separation, and liquidus temperature; Al does not seem to affect site partitioning preferences of TiO$_2$, MgO, and CaO. Although
the addition of Al seems to increase polymerization by creating more network-forming complexes, the partitioning of iron may not be directly affected.

Al and Fe can be correlated in peralkaline melts, where Na, K, Al, and Fe interact. Mysen et al. (1981) suggested that Fe\(^{3+}\) generally acts as an octahedral network modifer, except when Na + K > Al and Fe\(^{3+}\) is forced to be four-fold.

Unfortunately, these conclusions have not yet been fully tested by the Mössbauer effect. Seifert et al. (1982) examined the simple MgO-\(\text{Al}_2\text{O}_3\)-SiO\(_2\)-FeO system and observed both ferrous and ferrous iron. Fe\(^{3+}\) (observed values: \(\delta = 0.29-0.36\) mm/sec, \(\Delta = 1.40-1.55\) mm/sec) appears to favor tetrahedral coordination in this preliminary study. Their early results, based on five data points, indicated a positive correlation between Fe\(^{3+}\)/EFe and Al/(Al + Si), suggesting that Al and Fe\(^{3+}\) play a similar role in the structure.

Potassium almost universally prefers octahedral coordination in melts, and may frequently substitute for Na in Fe-O complexes (Waff, 1977). Nishida et al. (1981a,b,c,d) have conducted an extensive series of experiments on potassium borate, phosphate, and borosilicates, as discussed earlier. Their data show a definite decrease in isomer shift as K\(_2\)O content is increased.

The Fe\(^{2+}\) fraction of a K-bearing melt may also increase with K content, at least in the range from 0–30 mol% (Nishida et al., 1981a). Because the presence of K\(_2\)O helps to homogenize and stabilize the environments around FeO\(_2\) tetrahedra, other ions such as Cl can more easily find their way to substitute for O as FeO\(_2\)Cl tetrahedra. Cl, incidentally, seems to further increase the symmetry around the related Fe nuclei, causing more accentuated decrease in isomer shift when both K and Cl are present.

Mössbauer parameters for K-bearing silicate glasses have also been given by Virgo et al. (1981). Their values for isomer shifts in K\(_2\)O glasses range from 0.27–0.34 mm/sec, rather lower than the 0.41–0.50 mm/sec range seen by Nishida et al. (1981b). The difference is probably a function of the effects of other ions in the systems on which the two different groups worked.

The somewhat borate-oriented research in K\(_2\)O-bearing glasses leads to the following simple trends: (1) I.S. decreases as K\(_2\)O is increased. (2) Fe\(^{2+}\)/\(\Sigma\)Fe increases as K\(_2\)O is increased.

Phosphorus in silicate glasses has been thoroughly investigated by Ryerson and Hess (1980), who used phase equilibria, chromatographic and spectral data to research the role of P\(_2\)O\(_5\) in silicate melts. In pure SiO\(_2\) melts, P occurs as a four-fold network-forming cation; but where other metal cations (such as Fe) are present, P acts to increase the formation of 3-D networks (melt polymerization). Ryerson and Hess suggest that phosphate-metal complexing may aid in the destruction of Si-O-M-O-Si bonds, thus polymerizing the melt. If this is the case, then Mössbauer spectra should show the change in Fe bonding.

These trends observed in Mössbauer spectra of phosphate glasses, as discussed earlier, can be understood in light of the phase equilibria studies. When metals are present in addition to SiO\(_2\), phosphorus takes on six-fold octahedral coordination. This accounts for the observed Fe\(^{2+}\) and Fe\(^{3+}\) in the Mössbauer spectra. The polymerizing effect of P is no doubt strong enough to set up the octahedral network with any metal present in the melt; changes in the iron concentration should not affect melt coordination as long as enough “metal” of any type is present to complex with phosphorus. This nicely explains the observed effects of P on Mössbauer spectra: (1) P forces both ferrous and ferric iron to assume 6-fold coordination. (2) Changes in iron concentration do not affect iron partitioning.

Magnesium and its effects on melt structure have been studied primarily from a ceramicist’s viewpoint. Woods and Fine (1969) observed that glasses with a nominal composition of MgFe\(_2\)O\(_4\) have only Fe\(^{3+}\), whose tetrahedral versus octahedral site occupancy is largely a function of glass equilibration temperature. The only Mössbauer studies of Mg-bearing systems are reported by Virgo et al. (1981), who report that the presence of MgO and CaO in iron-bearing melts results in isomer shifts of 0.46–0.54 mm/sec when Fe\(_2\)O\(_3\) = 1.0 wt.%, and 0.34–0.44 mm/sec when Fe\(_2\)O\(_3\) = 5.0 wt.%. In their glasses, Ca and Mg have little effect on iron partitioning; iron concentration appears to be the principle cause for stabilization of Fe\(^{3+}\) tetrahedra. It seems likely that Mg does not have much of an effect on iron partitioning in melts, except possibly as a stabilizer with Ca in (Ca,Mg\(_{1/2}\))Fe\(^{3+}\)O\(_2\) complexes, as hypothesized by Waff (1977) and discussed earlier.

Titanium is a particularly important element for studies involving remote sensing of reflectance spectra of extraterrestrial bodies; for example, it contributes to the overall spectral profiles of the Moon’s surfaces (Dyar and Burns, 1981). Mare basalt types are even classified by their Ti contents (Charette et al., 1974). Therefore Ti has been the subject of considerable planetary-oriented research which has succeeded simpler “pre-Apollo” studies (e.g., Galant, 1966).

Several lunar glass compositions (and their synthetic analogues) have been studied in great detail (Adams and Charette, 1975; Bell and Mao, 1972; Delano, 1979; Mao et al., 1973; Nolet et al., 1979); the principle objects of analysis have been “Apollo 17 orange,” “Apollo 15 green,” and “Luna 24 brown glass.” Each type has its own distinctive Fe–Ti ratio which drastically influences not only its optical spectrum, but the Fe\(^{2+}\)/Fe\(^{3+}\) ratio and the resultant Mössbauer spectrum as well.

Orange glass typically contains approximately 8.7 wt.% TiO\(_2\) and 22.01 wt.% FeO (Mao et al., 1973). When Ti is present in such high concentrations, the glass takes on an orange color as a result of Ti\(^{3+}\) occurring in samples equilibrated at low oxygen fugacities (Bell et al., 1976). Mössbauer spectral profiles on such Fe–Ti glasses consist of an asymmetric doublet with peaks around zero and 2 mm/sec (Mao et al., 1973; Nolet et al., 1979; Nolet, 1980);
however, computed peak areas are almost identical in the low and high velocity regions, suggesting negligible Fe$^{3+}$. Deconvoluted spectra resolve six-coordinated Fe$^{2+}$ sites with a range of distortions. Isomer shifts vary from 1.02-1.09 mm/sec, with quadrupole splittings from 1.72-2.32 mm/sec. Although tetrahedral Fe$^{2+}$ was assigned in optical spectra of orange glass, Mössbauer spectra were unable to resolve an appropriate tetrahedral Fe$^{2+}$ doublet. Ti is present both as Ti$^{3+}$ and Ti$^{4+}$ in such low fugacity experiments (Nolet, 1980).

The green and brown lunar glasses, however, have considerably lower Ti contents (0.4 and 1.0 wt.% Ti, respectively) (Dyar and Burns, 1981) resulting in very different properties. When only small amounts of Ti are present, the Ti prefers to exist as Ti$^{4+}$, allowing Fe to assume Fe$^{3+}$ (Burns and Dyar, 1981) under oxidizing quench conditions. In such glasses made under low oxygen fugacity “lunar” conditions, both tetrahedral and octahedral ferrous iron can also be resolved in Mössbauer spectra.

In summary, it is clear that Ti can play an important role in controlling iron partitioning at low oxygen fugacities. Specifically, high Ti contents (>2.0 wt.%) reduce the Fe$^{3+}$/Fe$^{2+}$ ratio greatly. When Ti content is very low, however, Fe$^{3+}$ may account for up to 30% of the total iron in the glass (Dyar, 1984a).

Iron content alone may be the most important variable controlling iron partitioning. Several workers (Bandyopadhyay et al., 1980a; De Grave et al., 1980; Kurkjian, 1970; Mysen et al., 1980; and Schreiber, 1980) have noted that Fe$^{3+}$ content increases consistently as total Fe is increased. Bandyopadhyay et al. (1980a) observe a change from octahedral to mixed site iron occupancy when Fe$^{3+}$ content exceeds 45% of the total Fe; Fe$^{2+}$ is normally tetrahedral but may be both octahedral and tetrahedral when Fe$^{3+}$ is more than 55% of the total Fe. Apparently the high Fe content sets up a different set of oxygen coordination sites at that threshold; the changeover is also reflected in lower values of isomer shift and narrower linewidths (De Grave et al., 1980).

**Complex systems: natural terrestrial glasses**

Few Mössbauer studies have been reported on natural terrestrial glasses; not surprisingly the results are highly variable and probably reflect different magma compositions. Takeda et al. (1979) studied a group of natural Japanese obsidians; they found Fe$^{2+}$ in highly distorted octahedra in the glass, accompanied by some magnetic iron oxide phase contained as inclusions in the glass.

Chavez-Rivas et al. (1980) studied Lipari and Teotihuacan obsidians, both with total iron contents below 5 wt.%. Both samples had small (<1%) Fe$\text{O}_4$ amorphous particles; slight asymmetry and broad linewidths (0.7-1.4 mm/sec) were observed. The Lipari samples contained both Fe$^{2+}$ (92 ± 2%) and Fe$^{3+}$ (8 ± 2%); Teotihuacan obsidians were more ferric-rich (55 ± 3%). Regnard et al. (1981) reproduced these results very closely, finding Fe$^{2+}$ with δ = 0.89-0.96 and Δ = 1.84-1.93 mm/sec, and Fe$^{3+}$ with δ = 0.20-0.21 and Δ = 0.51-0.84 mm/sec. Other work on granitic and basaltic glass compositions shows the range of iron valency and coordination which might be expected in such complex compositions (Varnek, 1973; Levitz et al., 1980; Bandyopadhyay et al. 1980b). Clearly terrestrial obsidians have variable Fe$^{3+}$/Fe$^{2+}$ ratios; based on this small sampling, Fe$^{3+}$ and Fe$^{2+}$ are generally present.

**Discussion**

The preceeding review of Mössbauer measurements demonstrates the complexity of compositional effects on iron valency and partitioning. Since the majority of these studies are based on glasses quenched from melts equilibrated in air, just above the liquidus for each composition, the resultant data represent a severely simplified picture. Obviously an understanding of the effects of varying equilibrium conditions (T, P, and duration), quenching procedures, and T and P of the Mössbauer measurements would be necessary to complete the total picture; yet (as discussed earlier) there is not enough Mössbauer work on such effects to allow significant conclusions to be drawn. While recognizing these other factors as (perhaps) secondary influences on the partitioning of iron in quenched glasses, it is possible to draw some conclusions based strictly on the effects of composition.

The search for an ideal expression to equate iron partitioning in glasses with T, P, and composition has tantalized geochimists for several years. Because only data on compositional effects is tabulated, this report does not presume to comment on the relative merits of such endeavors (e.g., Laue, 1977; Lauer and Morris, 1977; Sack, 1980; and Ghiorso et al., 1981 and 1983), but merely to present the Mössbauer data which should be considered in such models. Table 5 shows the conclusions drawn from literature data (summarized from the references in Tables 2-4 and from the discussion of each separate cation's effect on iron partitioning) and suggests the effect which each cation may have on Fe$^{2+}$/ΣFe in a glass. This tabulation may be useful to qualitatively evaluate glass samples with different Fe$^{2+}$/ΣFe ratios, and to suggest the effects which certain cations may have on iron valency.

It is particularly significant that these conclusions are based on Mössbauer (and not wet chemical) determinations, because systematic differences may result from use of the different techniques. A recent comparison of wet chemical vs. Mössbauer determinations of Fe$^{3+}$/Fe$^{2+}$ ratios in tektites (glasses) has been undertaken by the Smithsonian Institution Department of Mineral Sciences and this author. In the two compositions studied to date, the Mössbauer effect determined roughly twice the amount of Fe$^{3+}$ (6% of total iron) in each composition than was found through wet chemical determinations in these low-iron samples, a result which has been commonly observed in tektite studies (R. Fudali, pers. comm., 1984). Either there is an error in the wet chemical procedure (which might be caused by the difficulty of working with low iron compositions) or the Mössbauer measurement is deceptive. The statistical error of the Mössbauer work is probably not large enough to explain the observed difference (Dyar,
1984b). However, it is well known that the recoil-free fraction of Fe\(^{3+}\) in minerals is sometimes larger than that for Fe\(^{2+}\) (Whipple, 1974); in garnets and amphiboles the line strength of Fe\(^{3+}\) is approximately 29% greater than that of Fe\(^{2+}\). In such minerals, the Fe\(^{3+}\) is held more rigidly in its site than the Fe\(^{2+}\), such that the Mössbauer effect absorption is enhanced preferentially for Fe\(^{3+}\). The resultant spectra show enhancement of Fe\(^{3+}\) peaks. Although little is known about the relative recoil free fraction of iron in glasses, it seems possible that the proportion of Fe\(^{3+}\) might be slightly increased due to a larger recoil-free fraction effect, making the Fe\(^{3+}\)/Fe\(^{2+}\) ratio higher than it really should be. This possibility is discussed further by Bowker (1979). Until more is known about this effect, it seems potentially unwise to try to compare wet chemical determinations with Mössbauer results on Fe\(^{3+}\)/Fe\(^{2+}\) ratios in glasses. However, the conclusions presented in Table 5 probably give a reasonable set of assumptions for the interpretation of Mössbauer results.

Another interesting hypothesis brought to light by this review is Bahgat et al.'s (1983) theory that charge-to-radius ratios may control glass structures. This is related to Hess' (1977) conception that the degree of polymerization of a melt is related to the field strength (cation charge divided by the square of the cation radius plus 1.40). Hess suggests that high field strength ions (Fe, Mg) are indicative of higher states of polymerization (glasses with sheet and 3-D networks) than lower field strength ions (Na, K). Table 5 shows that the high charge-to-radius cations (which are roughly proportional to Hess' "field strengths") tend to decrease Fe\(^{2+}/t\)Fe, where low charge-to-radius cations increase Fe\(^{2+}\). Hess also notes that polyvalent cations disrupt this correlation; Mössbauer results on Ti\(^{4+}\) show this also. It is gratifying to note the similarities between the Mössbauer results and the conclusions reached by Hess, which are based on phase and thermodynamic properties.

Finally, it is hoped that the data presented in this review will be used to establish some consistency among future work on Mössbauer spectroscopy of glasses. It is easy to pick out the sources of inconsistencies in the data by scanning Tables 2-4; the numerous redundancies in the literature are readily apparent. Furthermore it is appalling to note that of the 150-200 published papers on Mössbauer spectra of glasses, less than 50 papers bothered to list their experimentally-determined values for isomer shift and quadrupole splitting, choosing instead to draw their conclusions from data which only the authors could directly inspect. However, the tabulated data demonstrate that the Mössbauer technique is undoubtedly a consistent and viable method for determinations of iron coordination in glasses; future work in the diverse applications of Mössbauer spectroscopy in glasses deserves to be placed in the context of what has already been done. Through awareness of the diverse literature in ceramic, chemical, and geological literature, it is optimistically hoped that duplications and discrepancies can be avoided.

Acknowledgments

I am grateful to Roger G. Burns for his thoughtful critique of this manuscript, and to Francis Doughty for his perceptive typing. I thank George Rossman and two anonymous reviewers for their comments, which greatly improved this manuscript. This work was supported by a National Science Foundation grant (Contract No. EAR 84-161613) and a NASA grant (Contract No. NSG-7604), both awarded to Roger G. Burns, and by the Mineralogical Society of America Biennial Crystallographic Research Grant (to M. D. Dyar).

References


Bandyopadhyay, A. K., Auric, P., Phalippou, J., and Zarzycki, J. (1980b) Spectroscopic behavior and internal friction of glasses...


Bell, P. M. and Mao, H. K. (1972) Crystal-field effects of iron and titanium in selected grains of Apollo 12, 14, and 15 rocks, glasses and fine fractions. Proceedings of the Third Lunar Science Conference, 545–553.


Ghiorsu, M. S., Carmichael, I. S. E., Sack, R. O., and Rivers, M. L.


Varret, F. and Naudin, F. (1979) Mössbauer spectra of Fe$^{2+}$ and Fe$^{3+}$ impurities in a soda-lime silicate glass; measurement of the Fe$^{2+}$ content. Revue de Physique Appliquée, 14, 613–618.


*Manuscript received, June 6, 1983; accepted for publication, November 15, 1984.*