Effects of quench methods on Fe^{3+}/Fe^{2+} ratios: A Mössbauer and wet-chemical study[1]

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Abstract

The effect of quenching method on Fe^{3+}/Fe^{2+} ratios in three silicate glasses has been studied using natural rock compositions (the USGS rock standards basalt BCR-1 and rhyolite RGM and an andesite K-2B from Dennison volcano, Alaska). Samples were equilibrated at high temperatures and then quenched into an air jet, a 4% H_2–96% Ar jet, or a brine and ice bath. The glasses were analyzed by both Mössbauer spectroscopy and a microcolorimetric technique to compare the results from these commonly used methods for Fe^{3+}-Fe^{2+} determinations. Because the glasses were low in Fe^{3+} content, both analytical methods determined Fe^{3+} estimates by difference, resulting in relatively large uncertainties (3% for Mössbauer spectroscopy and up to 8% for colorimetry). Within these uncertainties, estimates of Fe^{3+}/Fe^{2+} ratios determined by Mössbauer spectroscopy and microcolorimetry are the same. None of the quenching methods used was observed to produce significantly different partitioning of Fe^{2+} among tetrahedral and octahedral structural sites in the basalt glasses. The highest cooling rate (brine and ice bath) yielded the largest tetrahedral Fe^{2+} values. No observable effects of quenching rate were measured with the other glass compositions investigated.

Introduction

Oxidation-reduction equilbria involving Fe are of fundamental importance in studies of magmatic liquids because of the different structural settings occupied by Fe^{3+} and Fe^{2+} in a silicate melt. Fe^{2+} is often considered to be a network modifier, whereas Fe^{3+} may act either as a modifier or as a network former (Mysen et al., 1984). The proportions of Fe^{3+} and Fe^{2+} in a melt are affected by the composition, pressure, temperature, and oxygen fugacity of the system. Some important petrogenetic processes that may be significantly influenced by the Fe^{3+}/Fe^{2+} ratio of the melt are crystallization sequence (Hill and Roeder, 1974), liquid fractionation (Osborn, 1959), and liquid immiscibility (Naslund, 1983). Clearly the ability to determine Fe^{3+}/Fe^{2+} ratios in a consistent manner is important to the study of magmatic processes.

Much of our understanding of magmatic systems is based on experimental studies. Therefore it is necessary to develop an understanding of the *experimental* processes that affect the Fe^{3+}/Fe^{2+} ratio. Determinations of Fe^{3+} and Fe^{2+} in silicate glasses are typically done either by Mössbauer spectroscopy or by wet-chemical techniques. It is important to show that these two analytical techniques yield equivalent results in order to compare experimental results from studies that use either of these analytical methods; such work has been done on various simplified compositions by Mysen and Virgo (1978) and Mysen et al. (1985a, 1985b). Another potential problem in Fe^{3+}-Fe^{2+} studies of glasses is the possibility that changes occur during the quench from the liquid to the glassy state. Previous studies of synthetic analogues of lunar glasses have shown that quenching techniques may have a profound effect on Fe site partitioning and the Fe^{3+}/Fe^{2+} ratio of some synthetic glasses (Dyar and Birnie, 1984; Dyar, 1984a). The presence or absence of Fe^{3+} in these low-Ti synthetic glasses can be predictably altered by manipulation of quench medium. It seems essential to evaluate these effects in a series of glasses produced by melting natural rocks.

The aims of this study are (1) to determine if quenching media affect Fe partitioning in glasses quenched from "natural" compositions and (2) to compare the results of Mössbauer spectroscopy with those of wet chemistry (microcolorimetry) in USGS samples with complex compositions, in order to evaluate the strengths and limitations of each method.

Experimental procedure

Quenching experiments with three silicate liquids derived by melting natural volcanic rocks were conducted at 1343°C and

TABLE 1. Glass compositions

	Rhyolite*	Andesite†	Basalt§
SiO_2	73.43	62.91	54.50
Al_2O_3	13.76	15.63	13.61
Fe_2O_3	0.50	1.92	3.68
FeO	1.24	3.95	8.80
MgO	0.29	2.70	3.46
CaO	1.16	5.80	6.92
Na_2O	4.19	3.45	3.27
K_2O	4.34	1.83	1.70
TiO_2	0.26	0.62	2.20
P_2O_5	0.05	0.12	0.36
MnO	0.04	0.11	0.18
Total	99.26	99.04	99.68

* USGS rock standard RGM-1 (Tatlock et al., 1976).
† Kienle et al. (1983).
§ USGS rock standard BCR-1 (Flanagan, 1967).

TABLE 2. Comparison of Mössbauer with microcolorimetry

Sample	Quench media	% Fe^{3+} (Möss.)*	% Fe^{3+} (M.c.)†
Basalt BCR-1	Brine and ice bath	2–8	6–8
Basalt BCR-1	H_2-Ar jet	6–12	9–12
Basalt BCR-1	Air jet	4–10	8–9
Andesite K-2B	Brine and ice bath	8–14	10–15
Andesite K-2B	H_2-Ar jet	7–13	11–12
Andesite K-2B	Air jet	6–12	9–11
Rhyolite RGM-1	Brine and ice bath	6–12	22–31
Rhyolite RGM-1	H_2-Ar jet	4–10	16–16
Rhyolite RGM-1	Air jet	5–11	19–20

* Fe^{3+} values are determined by *difference* between upper and lower velocity peaks in the Mössbauer spectra. Ranges given represent an absolute error of approximately ±3%.
† Values represent the ranges for duplicate analyses. Accuracy of individual measurements is about ±6% (relative).

log oxygen fugacity ($\log f_{O_2}$) = −7.83. Starting materials consisted of crushed basalt (USGS standard rock BCR-1, Flanagan, 1967), andesite (K-2B, Kienle et al., 1983), and rhyolite (USGS standard rock RGM-1, Tatlock et al., 1976). Compositions are given in Table 1.

Samples were prepared using the "Pt loop" technique described by Donaldson et al. (1975). Approximately 100 mg of powdered rock was pressed into a pellet 5 mm in diameter and 3 mm thick. Samples were attached to loops of Pt wire (0.20-mm diameter) using a filament wire heater, before being suspended in the hot zone of a CO_2-CO gas-mixing, vertical tube furnace. The mass of Pt in contact with the sample was approximately 9 mg (mass ratio of sample to Pt ~10). Two 100-mg pellets were used in each experiment to assure that an adequate amount of Fe was available for Mössbauer spectroscopy. Each 100-mg pellet was suspended from a separate wire in the furnace; however, in one case the two pellets became fused together. The furnace design is similar to that described by Williams and Mullins (1981). Two bare-wire Pt-$Pt_{90}Rh_{10}$ thermocouples were used to monitor furnace temperature. One of these thermocouples measured temperature on the O_2 reference side of a Ca-stabilized zirconium oxide cell (Williams and Mullins, 1976). The zirconia electrolyte was used to monitor oxygen fugacity in the hot zone of the furnace. The second thermocouple was placed in a multibore Al_2O_3 insulator employed to suspend samples in the furnace. This hot junction was less than 1 cm from the sample. Temperature profiling with samples attached to the support rod revealed that both vertical and radial gradients were less than 1.5°C/cm in the furnace hot zone. Thermocouples in their normal experimental configuration were calibrated frequently against the melting points of Ag (961.93°C), Au (1064.43°C), and Ni (1455°C). Temperature measurements are precise to ±0.2°C and are believed to be accurate to better than ±3.0°C. Thermocouple drift between calibrations was always observed to be less than ±5°C.

The solid electrolyte f_{O_2} sensor was calibrated by observing the formation and disappearance of an oxide coating on pieces of Ni foil suspended in the normal sample position. The emf values observed over the temperature range 1000 to 1300°C deviated from the predicted output (Sato, 1971) by less than ±10 mV (±0.1 $\log f_{O_2}$ units).

Each silicate melt composition was subjected to three quenching methods: (1) withdrawal of the silicate liquid droplet from the furnace into the path of a filtered air jet; (2) dropping the sample (without exposure to air) into a NaCl brine; and (3) withdrawal from the furnace into a filtered 4% H_2–96% Ar gas jet. On the basis of theoretical calculations by Birnie and Dyar (1986), the former two conditions correspond to cooling rates of approximately 70°C/s and 300°C/s (heat-transfer data were not collected for the case of a 4% H_2–96% Ar jet). The H_2-Ar jet was used to minimize the potential for surface oxidation during quenching. Subsequent chemical analysis (Table 2) revealed no significant oxidation or reduction relative to air quenching.

Mössbauer spectroscopy

Mössbauer spectra were recorded on a constant acceleration ASA spectrometer using a 70–80 mCi ^{57}Co source in a Pd matrix. Velocity was calibrated relative to the spectrum of Fe foil, using current peak positions provided by the Mössbauer Effect Data Center (John G. Stevens, pers. comm., 1984). Mössbauer spectra were fit to a sum of Lorentzian-Gaussian combined line shapes (see Dyar, 1984a, for details) by means of a Gauss nonlinear regression procedure, using the capability to constrain any set of parameters or linear combination of parameters as provided by the program STONE (Stone et al., 1984). Assignments of Fe^{2+} to either fourfold or sixfold coordination are based on ranges of isomer shifts in glasses as a function of coordination number; these ranges represent the consensus of over 150 papers on Mössbauer spectroscopy of glasses, as reviewed by Dyar (1985). In general, Fe^{2+} isomer shifts of 0.90–0.95 mm/s correspond to fourfold coordination; isomer shifts of 1.05–1.10 mm/s relate to sixfold coordination.

Curve-fitting procedures

The interpretation of the Mössbauer spectrum of a glass is a controversial procedure requiring patience and a thorough understanding of the factors that affect the line shape of a spectrum. In a crystalline substance where the Fe atoms are not influenced by matrix effects (such as in a metallic Fe foil), the Mössbauer spectrum will exhibit peaks with an undistorted line shape that closely approximates a Lorentzian curve (Bancroft, 1973). The Lorentzian shape corresponds to the basic nuclear resonant transition process that has a Breit-Wagner form. Similarly, an ^{57}Fe cation in a perfect (Fe end member) mineral structure will also be excited by a very small range of gamma-ray energies, so its spectral profile will also be approximated by a Lorentzian line shape.

However, in a glass the site geometries are much more variable than those in a regular crystalline material. Each glass con-

sists of many individual sites that may be defined as purely six-fold or purely fourfold coordination sites. Although no individual site is constrained to a particular symmetry, charge-balance considerations suggest that each site should approach a reasonable approximation of a regular octahedron or tetrahedron. This collection of sites is in no way crystallographically constrained to be equivalent; in fact, each individual site can be considered unique in terms of cation-to-anion distances and anion-cation-anion bond angles. The randomized structure of a glass matrix probably permits each site to be unique. Therefore, the Mössbauer spectrum of such a randomly ordered glass will represent the overlap of several Lorentzian line shapes arising from many individual sixfold and foldfold coordinated sites, resulting in a distribution of line shapes that has a "pseudo-Gaussian" component. Accordingly, such a line shape can be fitted with a curve shape, which compromises between the Lorentzian character of the individual sites, and the summed collection of the many types of sites, which may be fitted as a pseudo-Gaussian component.

Various other techniques for fitting combinations of distributions have evolved in the literature over the past twenty years (most recently, Eibschutz et al., 1981; Eibschutz and Lines, 1982; and Keller, 1981). These techniques have been applied to silicate glasses by Danckwerth (1982; Danckwerth and Virgo, 1982; and Danckwerth et al., 1982) to assess the effect of composition on the line shape of a Mössbauer spectrum. This approach uses a distribution model of multiple elementary doublets to represent the Gaussian-like distribution of Lorentzian line shapes. However, this method is based on hypothetical nearest-neighbor effects in a glass, which are more likely to be second order. Furthermore, the precision of the Mössbauer technique itself is insufficient to distinguish accurately between such closely overlapping lines (Bancroft, 1969/1970). Therefore the Mössbauer measurements in this paper will use an unconstrained combination of Lorentzian and Gaussian line shapes to fit glass spectra.

For the sake of consistency, the sequence used to fit the nine Mössbauer spectra represented in this study was standardized to prevent human bias in the fits. The following steps were used to fit each spectrum: (1) Fit two peaks, constraining widths, areas, and percentage Gaussian content of each peak to be the same. (2) Fit two peaks, constraining widths and percentage Gaussian content of each peak to be the same. (3) Fit two peaks, constraining (only) percentage Gaussian content of the two peaks to be the same. (4) Fit two peaks with no constraints on the fit, allowing peak position, width, area, and percentage Gaussian content to vary independently. (5) Add a third peak, repeating fits 1 to 4 with three peaks. (6) Add a fourth peak, repeating fits 1 to 4. In these cases, peaks are constrained in doublets; for example, the widths of peaks 1 and 4 are constrained to be the same, and widths of peaks 2 and 3 are also so constrained. Areas and percentage Gaussian content are also constrained in pairs until the late stages of the fit when each peak is allowed to vary independently.

All of the above fits were tried on each Mössbauer spectrum. Iterations of each fit or model were continued repeatedly until a given fit either converged (goodness-of-fit fell below a preset standard convergence criterion) or diverged at least five times. In some cases, up to 200 iterations were necessary to achieve convergence. Results to be presented in this paper represent the maximum number of peaks for which it was possible to obtain a converged fit with the minimum number of constraints. Note that the line shape of each peak (a combination of Lorentzian and Gaussian) is always allowed to vary independently in the late stages of each fit. This is important because line shape does

have an effect on goodness-of-fit parameters in glass samples; as shown in Burns and Dyar (1983), there always exists an optimal combination of Lorentzian and Gaussian curve shapes that will minimize χ^2. By allowing the Gaussian contribution to the line shape to vary for each fit, consistently satisfactory statistics are uniformly achieved.

Dissolution

Portions of the samples used for Mössbauer studies were analyzed by a wet-chemical technique. A modified version of the micro-analytical colorimetric method developed by Wilson (1960) for Fe^{2+} determination in silicate minerals and rocks was used in this study. A weighed aliquot of powdered glass (25 to 40 mg) was placed in a 12×75 mm polypropylene test tube together with 1 mL of concentrated hydrofluoric acid (48%) and 0.1 to 0.3 mL of $0.139M$ V^{5+} (as NH_4VO_3 in $1M$ H_2SO_4) solution. The V^{5+} was added to provide an excess of the amount needed for the reaction

$$VO_2^+ + 2H^+ + Fe^{2+} = VO^{2+} + H_2O + Fe^{3+}. \quad (1)$$
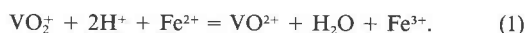
The test tube was then capped, and the contents were agitated before allowing it to stand for 15–20 h at room temperature. During dissolution, all Fe^{2+} is quantitatively oxidized by V^{5+} as shown in the reaction above. A measure of the predissolution Fe^{2+} content of the rock is retained by V^{4+}, which proxies for the Fe^{2+} in solution. After dissolution, 3 mL of $10N$ H_2SO_4 was added to the contents of the test tube to dissolve any fluoride precipitates that may have formed. The resulting solutions were diluted with H_2O to a total volume of 25 mL.

Fe^{2+} determination

Aliquots for colorimetric analysis were taken from the 25 mL of solution using transfer pipettes with disposable tips. Crystalline boric acid was added to the aliquot (0.5–1.0 g: enough to maintain a saturated solution) together with 2 mL of 0.25% 1,10 phenanthroline indicator solution (1.01 g in 100 mL of CH_3OH diluted with H_2O to 400-mL total volume). Boric acid was used as a substitute for the beryllium sulfate used in Wilson's (1960) procedure. This solution was continuously stirred while adding saturated (ammonium) acetate buffer to bring the strongly acid solution to pH 5, promoting development of the colored Fe^{2+}-phenanthroline complex. This procedure takes advantage of the pH sensitivity of Reaction 1. Raising the pH reverses Reaction 1. Complete oxidation of V^{4+} (recall that V^{4+} quantitatively proxies for Fe^{2+}) is accompanied by reduction of an equivalent quantity of Fe^{3+}, regenerating the Fe^{2+} content of the rock. The pH was readjusted to 4 using $6N$ HCl before transferring to a 25-mL volumetric flask and diluting with H_2O to volume. The absorbance (optical density) of this solution was measured at 525 nm using a Bausch and Lomb Spectronic 710 spectrophotometer. This analysis was repeated using a separate aliquot of solution.

Total Fe determination

Another aliquot was taken from the dissolved sample and treated in the same manner with one exception. Before adding the boric acid and indicator solution as described above, an excess amount of V^{4+} solution (0.1 to 0.3 mL as $VOCl_2$) was added to the sample. When the pH is adjusted with the acetate buffer, enough V^{4+} is present to reduce all of the Fe in solution to Fe^{2+} (Reaction 1). The solution is then treated in the same manner as described for Fe^{2+} analysis. This analysis was also repeated using a separate aliquot of solution. The Fe^{3+} content of the rock is determined by difference: $Fe_{tot} - Fe^{2+} = Fe^{3+}$.
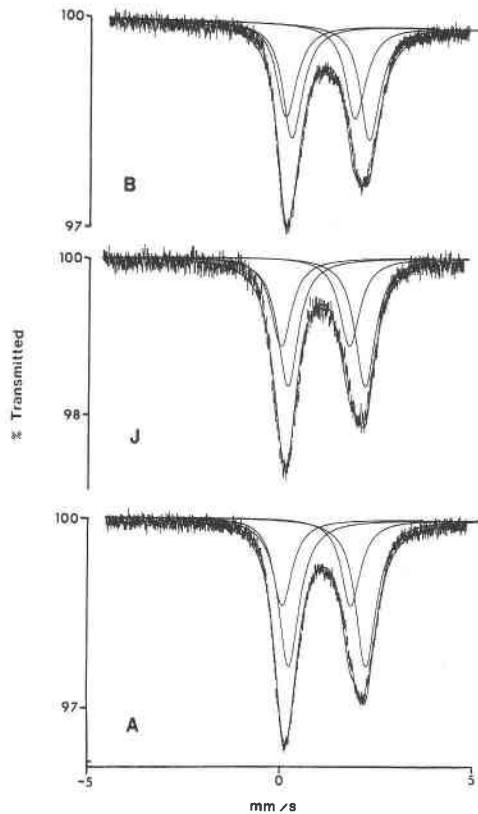
Fig. 1. Mössbauer spectra of the basalt composition equilibrated at 1343°C and log $f_{O_2} = -7.83$ and then quenched into an air jet (A), H_2-Ar jet (J), and a brine and ice bath (B). Note the change in relative peak areas between samples; the doublet with the higher (Fe^{2+} in sixfold) isomer shift is largest in the air-quenched sample. This is in keeping with the theory that Fe has a preference for higher coordination sites in denser (slowly cooled) glasses.

Fig. 2. Mössbauer spectra of the andesite composition equilibrated at 1343°C and log $f_{O_2} = -7.83$ and then quenched into the three media. The fits shown represent only three peaks because a satisfactory four-peak fit could not be obtained. The resolved middle peak (the upper-velocity mate of the Fe_{tet}^{2+} doublet) probably has a lower-velocity mate in the spectrum that cannot be resolved owing to its close superposition on top of the lower-velocity Fe_{oct}^{2+} peak. Note that the H_2-Ar jet–quenched sample (J) has a significantly smaller middle peak than the other two quenches, suggestive of a possible contribution from Fe^{3+} that may have resulted from the larger volume of this sample when it was quenched.

RESULTS

Mössbauer spectra: Changes with quench media

Mössbauer spectra of all nine samples were taken: three different compositions, each quenched into three different media. Results are shown in Figures 1 to 3; Mössbauer parameters are tabulated in Table 3. All values in Table 3 are referenced to the midpoint of a metallic Fe-foil spectrum. Standard deviations as listed refer only to the errors in the curve-fitting procedure (relating to counting statistics). The total error in these measurements, considering the sum of counting statistics, long-term drift, peak overlap, and uncertainty in the model, is probably more than 0.02 mm/s for isomer shift (IS), 0.06 mm/s for quadrupole splitting, and 1–2% for percentage area data (see Dyar, 1984b, for details). Experimental reproducibility of Mössbauer measurements has also been tested by Dyar (1984b); such errors are generally less than 0.016 mm/s for IS, 0.060 for QS, and 1.02% for areas. These errors must be considered when evaluating the Mössbauer results.
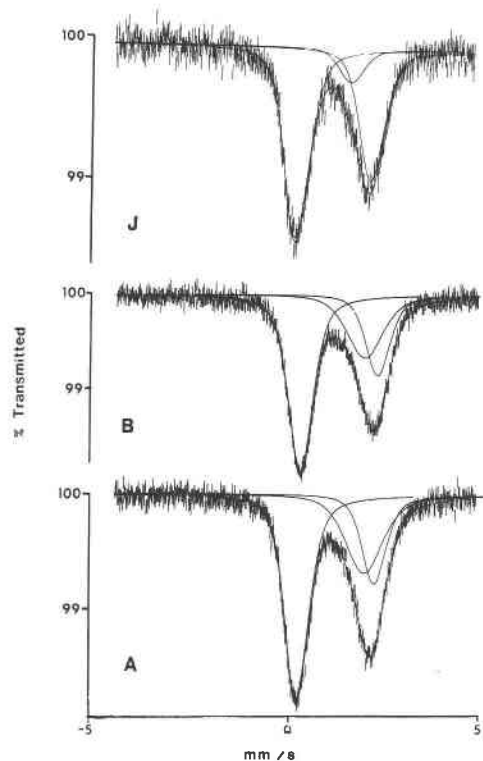
It is important to note that for each glass composition, a different number of peaks was fit. Mössbauer spectra of the basalt composition could be fit with four peaks; one doublet for Fe_{oct}^{2+} and one for Fe_{tet}^{2+}. In the andesite spectra, it was impossible to obtain a converged four-peak fit, perhaps because the two lower-velocity peaks are so closely superposed. Therefore the andesite spectra shown in Figure 2 illustrate three-peak fits: one lower-velocity peak (representing two superposed peaks) and two high-velocity peaks. The assumption that the lower-velocity peak is really two peaks is justified because the computed Mössbauer parameters of peaks 1 and 3 (e.g., IS = 0.94 mm/s and QS = 1.63 mm/s) and peaks 1 and 2 (IS = 1.11 mm/s and QS = 1.97 mm/s) fall in reasonable ranges for fourfold and sixfold coordinated Fe^{2+}.

Although the pronounced asymmetry shown in the rhyolite spectra (Fig. 3) suggests that four-peak (two doublet) fits would be appropriate, it was not possible to obtain a converged fit for either three- or four-peak
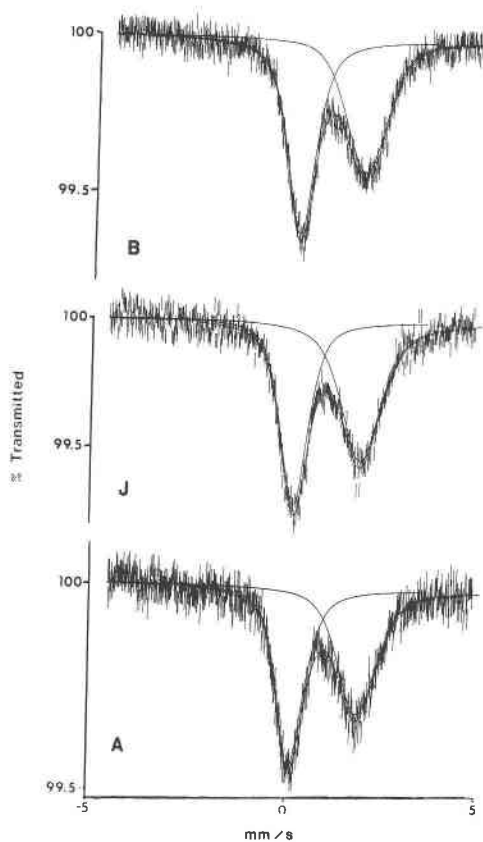
Fig. 3.   Mössbauer spectra of the rhyolite composition equilibrated at 1343°C and log $f_{O_2} = -7.83$ and then quenched into the three media. Because of the low Fe concentration of this composition, Mössbauer spectra were difficult to obtain, and resolution was relatively low. No significant structural variations were observed as a function of quench media. Only a single doublet could be fit to these spectra; three- and four-peak fits could not be resolved.

models. In our experience this often happens when Fe is distributed in a wide variety of sites; in such cases, distinct peaks are impossible to resolve and only a broad "envelope" doublet can be fit. Such a fit is physically meaningful because the obvious asymmetry in shape implies that a *range* of Fe sites, rather than a few discrete site types, is present.

Both χ^2 and MISFIT values are also tabulated for each fit given in Table 3. For a 512-channel spectrum (approximately 502 to 509 degrees of freedom, depending on the constraints used), χ^2 ranges from 391 to 1047. However, χ^2 values over such a large range suggest that χ^2 is being unduly influenced by the magnitude of baseline counts; good values of χ^2 can be very misleading because they may represent fits with large error bars on the data. Therefore a value for MISFIT (Ruby, 1973) is listed, allowing evaluation of different spectra irrespective of the magnitude of their baselines. MISFIT is optimal when it is close to zero. The error on the MISFIT parameter can be called the "uncertainty" of the fit; it measures the

uniqueness of the fitting results and is also optimal when closest to zero. It is generally desirable to keep both MISFIT and its "uncertainty" below 1.

There is *no* significant variation in values of isomer shift and quadrupole splitting (Table 3) in each of the compositions studied, with one exception. The andesite glass quenched in the 4% H_2–96% Ar jet does show distinctively different values for isomer shift and quadrupole splitting in the second doublet. The lower isomer shift suggests that the second doublet may contain a contribution from Fe^{3+}. As discussed in Dyar and Birnie (1984), Fe^{3+} is sometimes present in slowly cooled samples, even when equilibrated at low oxygen fugacities. This implies that the andesite quenched in H_2-Ar cooled more slowly than its counterparts in air and brine and ice. Why should this be? Recall that in the furnace setup, it is sometimes possible for the two 100-mg pellets to become fused together; this makes a larger volume of melt to be quenched. Because cooling rate is controlled by the rate at which heat can diffuse out of the sample and be carried away by the quench medium, a larger volume of sample will cool more slowly than a sample half its size. The Mössbauer data are consistent with the fact that the andesite as quenched by the H_2-Ar jet was actually two pellets fused together. This accounts for the observed lower isomer shift and quadrupole splitting in this sample.

Relative peak positions in the different spectra remain generally constant within the resolution of the technique. However, there *is* significant variation in peak areas, especially for the basaltic glasses. The ratio of $Fe^{2+}_{oct}/Fe^{2+}_{tet}$ increases as the quench medium changes from brine and ice to H_2-Ar to air. Heat-transfer coefficients probably increase as the quench medium changes from brine and ice to H_2-Ar to air (Birnie and Dyar, 1986). There appears to be a link between preference for sixfold coordination and the slower quenches in gas jets. This is not surprising in light of the known relationship between molar volume and cooling rate: rapid quenches result in higher molar volumes, contrasting with slower quenches that yield denser glasses (Kingery et al., 1976). This effect is observed in high-pressure mineral phases such as garnets: cations seek higher coordination under higher pressure. Therefore the basalt glass behaves predictably when quenched into the three media: more sixfold Fe is observed in the slowest quenches (densest glasses). Unfortunately, our sample size is too small to allow us to measure such densities directly; however, as stated above, the effect is well known from studies of other amorphous materials (Kingery et al., 1976).

This phenomena also explains why the presence of FE^{3+} can be anticipated in the large-volume andesite sample quenched into H_2-Ar. This "slowest-cooled" sample would be the densest glass measured. In such glasses it is hypothesized that size considerations force some of the Fe^{2+} to become oxidized to a smaller Fe^{3+} ion, in order to better fit in a denser glass. This effect has been observed with $Fe^{2+} \rightarrow Fe^{3+}$ in synthetic analogues of lunar glasses (Dyar, 1984a).

TABLE 3. Mössbauer parameters for glasses

Sample	Quench medium	~Fe^{2+}_{oct}			~Fe^{2+}_{tet}			χ^2	% MISFIT
		IS 1	QS 1	% Area	IS 2	QS 2	% Area		
Basalt glass	Brine and ice	1.16	2.00	54	0.89	1.77	46	906	0.29
	(S.D.)	(0.007)	(0.009)	(1.6)	(0.008)	(0.010)	(1.6)		(0.29)
	H_2-Ar jet	1.14	1.99	59	0.86	1.75	41	1047	0.47
	(S.D.)	(0.006)	(0.008)	(1.5)	(0.009)	(0.011)	(1.5)		(0.04)
	Air jet	1.13	1.98	64	0.84	1.76	36	1013	0.25
	(S.D.)	(0.004)	(0.005)	(1.1)	(0.007)	(0.009)	(1.1)		(0.02)
Andesite glass*	Brine and ice	1.11	1.97	27	0.94	1.63	73	391	−0.17
	(S.D.)	(0.007)	(0.013)	(2.5)	(0.019)	(0.037)	(2.2)		(−0.03)
	H_2-Ar jet	1.08	1.92	10	0.80	1.35	90	667	0.41
	(S.D.)	(0.007)	(0.016)	(2.6)	(0.031)	(0.064)	(2.2)		(0.07)
	Air jet	1.09	1.97	29	0.96	1.71	71	404	−0.15
	(S.D.)	(0.009)	(0.016)	(2.2)	(0.014)	(0.029)	(2.0)		(−0.03)
Rhyolite glass	Brine and ice	1.04	1.66	100				593	0.17
	(S.D.)	(0.007)	(0.008)	(1.2)					(0.04)
	H_2-Ar jet	1.05	1.71	100				862	0.65
	(S.D.)	(0.006)	(0.008)	(1.0)					(0.06)
	Air jet	1.05	1.70	100				473	−0.19
	(S.D.)	(0.008)	(0.011)	(1.7)					(−0.06)

* Because of poor statistics on four-peak fits, three-peak fits are tabulated. Doublet 1 pairs peaks 1 and 2; doublet 2 pairs peaks 1 and 3.

The overall results on the basaltic glass experiments agree with past work; quench methods have a consistent effect on coordination and, less frequently, a small effect on redox state. However, this does *not* imply that cations move faster than electrons during a quench; in fact it is unlikely that the cations are moving at all. Rather the coordination changes are probably caused by subtle rearrangements of oxygens as they are packed around the cations during the densification process as the glass cools. As discussed earlier, it is really rather arbitrary to try to sharply differentiate between fourfold and sixfold coordination in a glass because there is really a continuum of different types of sites with varying cation-to-anion distances within polyhedra. Only a very slight structural rearrangement (such as would be caused by densification) can result in enough of a change that the electronic configuration of a given cation may no longer (or may suddenly) be affected by a neighboring anion. Thus, for glasses, a coordination change requires relatively less energy than a redox state change (which involves movement of an electron over the relatively great distance from one cation to another).

No significant change in percentage area data is observed in the other andesite and rhyolite glasses, probably because the diffusion kinetics of these glasses with high silica content are much more sluggish. In such samples there is little structural rearrangement on quenching, and therefore cation-coordination changes are not observed.

Mössbauer vs. microcolorimetry: $Fe^{3+}/\Sigma Fe$ ratios

Table 2 shows a comparison between Mössbauer results and microcolorimetric analysis for $Fe^{3+}/\Sigma Fe$ ratios in the samples. It is important to emphasize the difference between Tables 2 and 3. Table 3 shows area data for peaks that were resolved; numbers given there show total *combined* areas of paired peaks. Data in Table 2 show implied Mössbauer results; numbers given represent the

difference in area between the upper- and lower-velocity peaks for each spectrum. This formulation is necessary because the Fe^{3+} peaks were impossible to resolve uniquely in the Mössbauer spectra; this is caused by their broad widths at half-peak heights and by their somewhat Gaussian curve shape (i.e., the peaks have broader shoulders). Both of these features are common in spectra of glasses; they make it difficult to determine Fe^{3+} content directly unless the Fe^{3+} peaks are positioned fortuitously on the shoulders of Fe^{2+} peaks. However, in cases where only small amounts of Fe^{3+} are present, it *is* possible to determine Fe^{3+} content indirectly, by fitting one unconstrained peak to each half of the Mössbauer spectrum. Because Fe^{3+} doublets generally lie in the lower-velocity region of the spectrum, the lower half of the envelope will often have an increased area because of contributions from the masked Fe^{3+} doublet. Therefore it is possible to determine Fe^{3+} content by difference, simply by subtracting the area of the high-velocity peak (where no Fe^{3+} peaks

TABLE 4. Results of microcolorimetry control analysis

	Fe^{2+} as FeO	Fe_{tot} as FeO	Fe^{3+} as Fe_2O_3 (by difference)
	Basalt BCR-1		
USGS	8.80	12.11	3.68
This study	8.75	12.29	3.93
	8.72	12.54	4.25
	8.80	12.42	4.02
	9.08	12.42	3.71
Mean (S.D.)	8.84 (0.16)	12.42 (0.10)	3.93 (0.22)
	Rhyolite RGM-1		
USGS	1.24	1.69	0.50
This study	1.19	1.63	0.49
	1.20	1.62	0.47
	1.24	1.67	0.47
	1.24	1.68	0.49
Mean (S.D.)	1.22 (0.03)	1.65 (0.03)	0.48 (0.01)

lie) from the larger, low-velocity peak (Fe^{2+} plus both Fe^{3+}). Of course, this procedure assumes that the upper- and lower-velocity Fe^{2+} peaks are symmetric; some workers would disagree (e.g., Mao et al., 1973; Mysen and Virgo, 1978; Levitz et al., 1980). However, observed asymmetries are generally <5% of the percentage area data and as such as within the overall error of the measurement (note that the precision of the Fe^{3+} Mössbauer data is $\pm3\%$). Also, unless the symmetry of Fe^{2+} peaks is assumed, it is impossible to obtain Fe^{3+} numbers for these samples. Therefore the difference method has been used to obtain the Mössbauer values in Table 2; note that the estimated uncertainty in these values is large. Perhaps the contribution from Fe^{3+} is also affecting the Mössbauer parameters listed in Table 3; however since the Fe^{3+} peaks cannot be directly resolved, their effects on the Fe^{2+} are difficult to assess.

Microcolorimetry: Experimental errors

Analyses of unreacted standard rocks (USGS BCR-1 and RGM-1) were performed using the methods previously described to provide a check on our analytical technique and an estimate of analytical error. In this manner the total effect of all procedural errors (i.e., weighing, pipette transfer, volumetric glassware, Fe standard solution preparation, nonlinearity of spectrophotometer) and solution-chemistry interferences (i.e., complexing or adsorption of Fe by fluorides, redox of Ti, V, and Mn) can be estimated. Whipple (1974a) provided an extensive discussion of the factors affecting the accuracy of Wilson's (1960) method. The averages of these analyses are shown in Table 4.

The discrepancies between mean values for Fe^{2+} and Fe_{tot} determined for these standard rocks and the accepted USGS values are less than 3%. Individual analyses differ from the accepted values by up to 4%. Fe^{3+} is determined by difference and therefore can be expected to exhibit the largest errors. The mean values for Fe_2O_3 determined in this study are high for BCR-1 (+8%) and low for RGM-1 (+4%). Individual determinations differ by up to 15% and 6%, respectively. Clearly the Fe^{3+} determinations are the least-accurate measurements. This poor precison is of particular concern when ratios of Fe^{3+}/Fe^{2+} or Fe^{3+}/Fe_{tot} are calculated. Errors can be very large for analyses of reduced glasses, as is the case for the glasses synthesized for this study, because the proportion of Fe^{3+} is small. Reducing conditions were desired in this study to produce Fe^{2+}-rich liquids that could be used to test the effects of the quenching phenomena observed by Dyar and Birnie (1984) in analogues of lunar glasses.

DISCUSSION

Given that the errors in both types of measurements are considerable, it is probably fortuitous that the figures in Table 2 actually come so close to agreement when reasonable error limits are applied. The agreement is even more remarkable when the limitations of the techniques are discussed on a broader scale.

In general, there are four basic difficulties to be considered when interpreting the Mössbauer spectra of glasses:

1. The recoil-free fraction for iron in glasses is poorly understood. In some minerals such as garnets, the line strength of Fe^{3+} is approximately 29% greater than that of Fe^{2+} (Whipple, 1974b). In such minerals the Fe^{3+} is held more rigidly in its site, such that more of the Fe^{3+} atoms recoil than do Fe^{2+}. The resultant Mössbauer spectrum appears to have more Fe^{3+} than is actually present. Fortunately, in most minerals, this process is well-understood and can be corrected for. Unfortunately, little is known about the relative recoil-free fractions of Fe^{2+} and Fe^{3+} in glasses.

2. Lack of independent constraints on Mössbauer fitting has also hampered the application of Mössbauer spectroscopy to glasses. In mineralogical applications it is frequently possible to make logical assumptions about a spectrum based on independent evidence from X-ray data and/or crystal-structure refinements. With glasses this is possible only with data produced by the relatively less accessible technique of extended X-ray absorption fine structure spectroscopy. The lack of corroborating evidence for Mössbauer-generated structural assignments also makes the technique vulnerable to overinterpretation, because no other evidence is available to contradict Mössbauer values for site populations.

3. The possible existence of single Fe^{3+} peaks has not yet been considered sufficiently. The quadrupole splitting phenomenon that creates Mössbauer doublets is *not* ubiquitous; it arises partly from the asymmetry of the localized electronic configuration of the ligand environment and partly from the asymmetric electron distribution in orbitals. An Fe atom situated in a perfect cubic symmetry site will have an unperturbed ligand environment; its Mössbauer spectrum will consist of a single peak. It can be postulated that regular Fe^{3+} polyhedral environments *do* exist in glasses; therefore, the presence of singlets in spectra might be suspected. To date, singlet peaks have not been considered in the literature (Dyar, 1985).

4. Samples with low Fe_{tot} concentrations (or small amounts of either Fe^{3+} or Fe^{2+} relative to other species) are often difficult to analyze. A typical Mössbauer apparatus is set up with gamma rays passing through a sample embedded in a matrix material of low atomic number (zero Fe); the amount of sample used is usually based on an ideal situation of 7 mg Fe/cm^2 of the sample holder (Dyar, 1984b). When a sample has very low Fe_{tot} content, it sometimes becomes impossible to pack enough sample in the holder to attain the "ideal situation;" the large amount of mineral also absorbs (and blocks) gamma-ray transmission. When less than 7 mg Fe/cm^2 is used, the quality of the spectrum deteriorates in a predictable manner (Dyar, 1984b) because the sample has to be run longer. This situation can be improved by using a Mössbauer source with a very high gamma-ray flux, so the sample stays on the spectrometer for only a short amount of time (thus optimizing counting statistics while minimizing the contribution of electronic drift). Another possibility for

enhanced resolution is the technique of cooling the sample with liquid He or N_2; however, Dewar flasks are not always available for this type of measurement. It is also possible to dope a synthetic composition with enriched ^{57}Fe to improve spectral quality, but since 100 mCi sources and enriched ^{57}Fe are expensive, such procedures are not always used. Consequently, there can be considerable disagreement between Mössbauer and wet chemistry for low-Fe samples.

Existing wet-chemical (microcolorimetric) techniques provide an economical, yet time-consuming (and destructive) method for measuring Fe^{2+} and Fe^{3+} in homogeneous silicate glasses. The problem presented by determining Fe^{3+} by difference is shared with Mössbauer spectroscopy methods for low-Fe, high-Si compositions of geologic interest. The poor precision of wet-chemical Fe^{3+} measurements is disconcerting, but is of particular concern in reduced specimens containing small amounts of Fe^{3+}. For example, the rhyolite samples studied here show the largest differences in Fe^{3+} values (when compared with Mössbauer results); probably the wet-chemical determinations are responsible for much of this error. In such cases, the Fe^{3+} values or calculated ratios (i.e., Fe^{3+}/Fe^{2+} or Fe^{3+}/Fe_{tot}) can have very high uncertainty (50–100%). This is not a trivial problem in experimental studies requiring reducing conditions. One particular application for which this could present a problem is in the calculation of magmatic f_{O_2} values from volcanic glass compositions. A 10% change in the ratio Fe^{3+}/Fe^{2+} changes the f_{O_2} estimate calculated by the method of Kilinc et al. (1983) by one log unit. It should be emphasized that such pessimism concerning Fe^{3+}/Fe^{2+} ratios is appropriate only in situations where the samples being analyzed have a small amount (about 10% or less) of Fe in the 3+ state.

CONCLUSIONS

Previous work on smaller-dimension glass samples has shown that Fe^{3+}/Fe^{2+} ratios and Fe site occupancies may be significantly affected by quench processes. In this study, the basalt samples again showed a strong correlation between quench rate and Fe^{2+} site occupancies. The brine and ice bath, the most efficient quenching medium tested, yielded samples with up to 46% of the Fe^{2+} in fourfold sites. The 4% H_2–96% Ar jet is slightly less efficient and produced 3–10% less Fe^{2+} in fourfold sites. The air jet is the poorest medium tested, producing glasses with the most Fe^{2+} in sixfold sites. These trends may be predicted from the known relationships among temperature, cooling rate, and molar volume; rapidly (brine and ice) cooled glasses are most random and least dense, whereas slowly (air) quenched samples are relatively more ordered and dense. Changes in site sizes and geometries in the densest glasses may cause the Fe^{2+} to preferentially occupy sixfold sites.

The observed correlation between quench medium and Fe site occupancy is not apparent in the rhyolite and andesite glasses. The rhyolite samples were too Fe poor to enable detailed Mössbauer spectra to be measured satis-

factorily; however the basic fits showed no changes among samples quenched in different media. The H_2–Ar jet–quenched andesite sample showed a significant proportion of lower-coordinated Fe^{2+}, probably owing to an increased Fe^{3+} contribution to the lower-velocity peak of that doublet.

Comparison of results from Mössbauer spectroscopy and microcolorimetric determinations of the Fe^{2+} and Fe^{3+} contents of glasses produced by quenching melts of three "typical" volcanic rock compositions indicates that significant analytical uncertainties are associated with Fe^{3+} values obtained from either method. However, within this analytical uncertainty, the two methods yield the same value.

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