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 nucleii 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 continous 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_6 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.

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

Fe^{2+}:	IV	0.90-0.95 mm/sec
	VI	1.05-1.10 mm/sec
	VIII	1.20-1.30 mm/sec
Fe^{3+}:	IV	0.20-0.32 mm/sec
	VI	0.35-0.55 mm/sec

* 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.

Early Mössbauer measurements of $Fe_3(PO_4)_2 \cdot 8H_2O$ and $FePO_4 \cdot 4H_2O$ glasses by Kerler and Neuwirth (1962) observed characteristic iron doublets with isomer shifts (δ or I.S.) of 1.251 mm/sec (Fe^{2+}) and 0.291 mm/sec (Fe^{3+}), 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 ferric isomer shifts of 0.37-0.40 mm/sec for Fe_2O_3–$NaPO_3$ glass, and 0.26-0.39 mm/sec for Fe_3O_4–$NaPO_3$ 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_2O_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_2O_3–Fe_2O_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 ($\delta = 0.327$; quadrupole splitting, $\Delta = 0.947$ mm/sec, typical of four-coordinated iron) and a widely varying ferrous peak (average $\delta = 1.057$, $\Delta = 2.137$ 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 2. Phosphate glasses

Reference	Composition	Fe^{3+} oct I.S.	Q.S.	Fe^{2+} oct I.S.	Q.S.	Fe^{2+} oct I.S.	Q.S.	Γ
Kerler and Neuwirth 1962	$Fe_3(PO_4)_2 \cdot 8H_2O$					1.25	2.80	0.60
	$FePO_4 \cdot 4H_2O$	0.29	0.63					0.54
Kurkjian and Buchanan, 1964	$Fe(PO_3)_3$	0.50	0.88			1.15	2.16	0.64
Kamo et al., 1967	$Fe_3O_4 \cdot NaPO_3$	0.32	–			1.25	2.76	
		0.35	–			1.60	3.16	
		0.43	–			1.42	2.94	
		0.44	–			1.47	2.98	
		0.46	–			1.58	3.20	
Hirayama et al., 1968	$MgO \cdot P_2O_5$					1.21	2.24	
						1.13	2.30	
		0.38	0.85			1.16	2.30	
						1.05	2.36	
	$CaO \cdot 2P_2O_5$					1.11	2.22	
		0.40	0.80			1.07	2.15	
Taragin et al., 1972	$16.7Al_2O_3 \cdot 69.7P_2O_5 \cdot 4.5Na_2O \cdot 9.1Fe_3O_4$	0.41	0.80			1.19	2.10	0.64, 0.53
Motran et al., 1973	"iron calcium phosphate glass"	0.35	0.73			1.11	2.28	
Menil et al. 1979	$Fe_{0.02}Na_{0.98}P_{0.81}O_{2.10}F_{0.89}$	0.45	0.36	1.22	2.25	1.24	1.50	0.46, 0.44, 0.55
	$Fe_{0.03}Na_{0.97}P_{0.76}O_{1.98}F_{0.90}$	0.43	0.36	1.19	2.23	1.18	1.48	0.54, 0.50, 0.60
	$Fe_{0.08}Na_{0.92}P_{0.79}O_{2.29}F_{0.51}$	0.42	0.45	1.18	2.47	1.21	1.65	0.49, 0.43, 0.40
	$Fe_{0.19}Na_{0.81}P_{0.58}O_{1.73}F_{0.68}$	0.42	0.44	1.23	2.41	1.25	1.68	0.38, 0.42, 0.58
	$Fe_{0.39}Na_{0.61}P_{0.36}O_{1.22}F_{0.92}$	0.42	0.53	1.23	2.52	1.28	1.86	0.38, 0.38, 0.63
	$Fe_{0.60}Na_{0.40}P_{0.40}O_{1.20}F_{1.53}$	0.44	0.71	1.22	2.70	1.26	1.89	0.53, 0.41, 0.56

trend which is common in many silicate glasses: Fe^{2+}/Fe^{3+} ratios decreased systematically as total iron (1972) and Burzo and Ardelean (1979a and 1979b) confirmed that the proportion of Fe^{3+} increases linearly with increasing iron content, as does quadrupole splitting, but partitioning of ferric iron *between* octahedral and tetrahedral sites (Fe^{3+} is both four- and six-coordinated in xFe_2O_3, $1 - x$ ($PbO \cdot 3B_2O_3$) 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 Δ as is observed.

Nishida et al. (1980a,b; 1981a,b,c,d) added K and/or Cl to the B–Fe–O system and obtained similar trends. Isomer shift *decreases* with the addition of K_2O 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. K_2O 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 SiO_4 units are formed, isomer shift decreases. Similarly, the presence of Cl^- ions in the bulk glass results in the formation of FeO_3Cl tetrahedra; as a "superstructure" of FeO_3Cl and FeO_4 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 $B_2O_3 \cdot MgO \cdot Fe_2O_3 \cdot Na_2O \cdot SnO_2$ systems, decreases in symmetry occured systematically as smaller, increasingly highly charged cations were introduced into the glass, increasing

in charge-to-radius ratio in the order $Na^+ < Mg^{2+} < Fe^{3+} < Sn^{4+}$. Largest isomer shifts resulted from ions with Sn^{4+} 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 Pb^{2+}, Eissa et al. (1980) with Na^+, and Burzo et al. (1982) with Ca^{2+}. The concept of charge-to-radius ratios may be an important one to consider in models of glass structures, particularly where Fe^{3+} and Fe^{2+} 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) Fe^{3+}/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

Reference	Composition	x	Fe^{3+} tet I.S.	Q.S.	Fe^{3+} oct I.S.	Q.S.	Fe^{2+} oct I.S.	Q.S.	Γ
Taragin and Eisenstein, 1970	"complex borosilicate glass"		0.30	0.69			1.03	2.08	
Tricker et al., 1974	$B_2O_3+CaO+Fe_2O_3$						0.61	1.01	
Bukrey, et al., 1974	$Na_2O \cdot Li_2O \cdot B_2O_3 \cdot Fe_2O_3$		0.284	0.525					0.612
			0.291	0.520					0.597
			0.293	0.515					0.601
			0.305	0.486					0.666
Raman et al., 1975	$xNa_2O 6Fe_2O_3 \cdot (94-x)B_2O_3$ mol. %	10			0.370	0.879			0.686
		12			0.352	0.811			0.611
		15			0.348	1.023			0.865
		20			0.349	0.472			0.799
		25	0.271	0.958					0.797
		28	0.271	0.957					0.776
		30	0.238	0.948					0.862
		35	0.238	0.960					0.836
Kang and Moon, 1976	B_2O_3+5 mol.% Fe_2O_3				0.326	1.00			
					0.376	1.38			
Raman et al., 1978	$xCaO:(69-x)B_2O_3:25Na_2O:6Fe_2O_3$	20	0.283	0.983					0.745
		25	0.285	0.978					0.737
		40	0.293	0.925					0.713
	$xNa_2O:(82-x)B_2O_3:15Al_2O_3:3Fe_2O_3$	15	0.341	1.085					0.782
		20	0.344	0.999					0.749
		25	0.299	1.011					0.743
		30	0.258	0.991					0.767
		35	0.237	0.980					0.755
	$xAl_2O_3:(72-x)B_2O_3:25Na_2O:3Fe_2O_3$	5	0.295	0.994					0.796
		10	0.290	1.034					0.781
		15	0.299	1.011					0.743
		20	0.280	1.012					0.750
		25	0.268	1.001					0.767
	$xLi_2O:(94-x)B_2O_3:6Fe_2O_3$	12			0.366	1.085			0.737
		15			0.359	1.090			0.769
		18			0.339	1.141			0.782
		22			0.334	1.065			0.746
		25			0.324	1.056			0.778
		28			0.322	1.097			0.742
		32			0.314	0.986			0.714
		35			0.325	0.964			0.784
		38			0.316	0.969			0.756
		41			0.311	0.936			0.774
	$xK_2O:(94-x)B_2O_3:6Fe_2O_3$	9			0.386	1.078			0.790
		12			0.355	1.023			0.713
		15			0.345	1.043			0.857
		18			0.337	1.004			0.878
		22	0.317	0.915					0.833
		25	0.272	0.862					0.789
		28	0.241	0.917					0.731
		32	0.240	0.905					0.685
		35	0.226	0.832					0.657
Sekhon and Kamal, 1978	$PbO \cdot 2B_2O_3 \cdot x$ wt.% Fe_2O_3	5			0.335	1.150			0.80
		7.5			0.335	1.050			0.71
		10.0			0.360	1.100			0.82
		12.5			0.410	1.200			0.81
		15.0			0.385	1.150			0.75
		20.0			0.410	1.050			0.80
Horie et al., 1978	$BaO-Fe_2O_3-B_2O_3$		0.25	0.93					
			0.29	0.70					
Nishida et al., 1981b	$xK_2O(100-x)(B_2O_3,SiO_2)7Fe_2O_3$	12	0.31	1.03					0.78
		15	0.28	1.02					0.77
		18	0.28	1.01					0.73
		20	0.25	0.92					0.66
		25	0.23	0.81					0.54
		30	0.23	0.79					0.53
		35	0.23	0.80					0.52
		40	0.22	0.78					0.49
Nishida et al., 1981d	$20K_2O:80B_2O_3 0.33Fe_2O_3$		0.32	1.06					1.22
Bonnenfant, et al., 1982	$(Fe_2O_3)_{30}-(BaO)_{45}-(B_2O_3)_{25}$		0.25	1.01					0.60
Bahgat et al., 1983	$B_2O_3 \cdot Na_2O \cdot MgO \cdot Fe_2O_3 \cdot SnO_2$		0.170	0.550					

Table 4. Silicate glasses

Reference	Composition								Fe³⁺ tet		Fe³⁺ oct		Fe²⁺ tet		Fe²⁺ oct		
	SiO_2	TiO_2	Al_2O_3	FeO	MgO	K_2O	CaO	Na_2O	I.S.	Q.S.	I.S.	Q.S.	I.S.	Q.S.	I.S.	Q.S.	Γ
Kurkjian and Buchanan, 1964	3x							1x							1.24	2.01	0.75
Belyustin et al., 1965				16%				16%			0.37	0.85			1.12	2.00	
Gosselin et al., 1967	3x			0.078				1x			0.39	0.74			1.14	2.13	1.05, 0.62
				0.233							0.37	0.87			1.17	2.16	1.04, 0.71
				0.779							0.38	0.85			1.05	2.10	1.17, 0.75
				8.27							0.31	0.87			1.05	2.08	0.63, 0.52
				19.75					0.25	0.88					0.99	2.22	0.56, 0.48
				3.245					0.26	0.60					1.05	2.11	0.67, 0.71
				8.270							0.34	0.72			1.01	2.13	0.78, 0.58
				19.750							0.37	0.81			1.09	2.17	0.66, 0.65
Lewis and Drikamer, 1968								1x	0.27	0.91							
Boon, 1971	1x			1x				1x							1.09	2.86	
															1.01	1.91	
Paragamin et al., 1972	1x			1x				1x	0.35	1.5							
Varnek, 1973	74	0	5	1	1	1	17	1					0.987	1.02	1.03	1.95	0.52
	38	6	20	18	1	10	1	6					0.86	1.48	0.98	1.88	0.66
	35	0	20	18	10	10	1	6					0.88	1.70	1.02	2.20	0.48
	80	0	10	1	1	1	1	6					0.79	1.39	1.12	1.94	0.59
	36	6	20	18	1	1	17	1					0.87	1.61	1.07	2.04	0.73
	35	0	20	11	1	10	17	6					0.97	1.29	1.07	2.05	0.59
Morinaga et al., 1976	1x						1x	1x	0.29	0.77							
											0.31	0.84					
											0.35	0.88					
											0.43	0.85					
									0.22	0.80							
Levy, 1976	1x			1x			1x	1x					0.95	2.50			
Hirao et al., 1979	4			0.15				0.85	0.28	0.78							
	4			0.25				0.75	0.27	0.78							
	4			0.50				0.50	0.24	0.73							
	4			0.58				0.42	0.25	0.75							
	4			0.65				0.35	0.25	0.77							
Nolet et al., 1979	43.39	12.07	8.21	8.43	19.02			8.20							1.06	1.97	0.78
													0.95	1.28	1.08	2.40	0.39, 0.49,
															1.03	1.84	0.48
de Grave et al., 1980	70.0	–	1.9	4.5	5.1	2.2	9.7	6.6	0.245	–	0.295	–	0.965	–	1.035	–	
Komatsu and Soga, 1980	1x			1x				1x	0.25	0.76							
Levitz et al., 1980	47.9		26.46		9.78		15.22	0.3	0.28	1.34							
	3x				1x		1x		0.29	1.33							
									0.26	1.22							
	3x		15.05		1x		1x		0.27	1.25							
	73.1			0.92	4.27		2.07	3.62	0.26	1.35							
Dyar and Burns, 1981	45.5	0.4	7.9	19.9	17.2		8.6				0.40	0.44	0.81,	2.26,			0.30, 0.52,
													0.77	1.80			0.56, 0.47,
																	0.45, 0.57
Danckwerth, et al., 1982	1x			0.25				1x	0.26	–							
	1x			0.25				0.75	0.25	–							
	1x			0.50				0.50	0.27	–							
	1x			.75				0.25	0.29	–							
	1x			1x					0.32	–							
Seifert et al., 1982	1x		1x	1x					0.29	1.40	0.36	1.55					
Virgo et al., 1982a	1x			1x				1x	0.23	0.73							
									0.20	0.93							
									0.22	0.81							
									0.25	0.97							
Virgo et al., 1982b	9x			5 wt.%				1x	0.31	0.85							
	5x			5				1x	0.32	0.85							
	5x			10				1x									
	3x			5				1x	0.25	0.87							
	2x			2.2				1x	0.33	0.85							
	2x			5.0				1x	0.32	0.87							
	2x			8.8				1x	0.29	0.84							
	2x			13.4				1x	0.24	0.85							
	1.5x			5.0				1x	0.24	0.93							
									0.28	0.82							
Burns and Dyar, 1983	45.5	0.4	7.9	19.9	17.2		8.6								1.014	1.916	0.79
	45.6	3.9	8.8	11.3	21.0		8.9								1.029	1.924	0.95
Dyar and Birnie, 1984*	45.5	0.4	7.9	19.9	17.2		8.6						0.978	1.894	1.229	2.242	
													0.996	1.878	1.243	2.315	
													0.938	1.151	1.023,	2.641,	
															1.321	1.152	
													0.961	1.552	1.028,	2.195	
											0.542	0.890	0.986	2.005	1.0068	2.668	

* Fe variations caused by changes in quench media

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 $Na_2O \cdot 3SiO_2$ 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, Γ, 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 Jach and Nabation, 1977a,b) observed similar δ and Δ 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., 1982a,b) have reproduced the above results for iron in $Na_2O \cdot 3SiO_2$ glasses. The general concensus 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 corroborates the Mössbauer conclusions. Using magnetic susceptibility measurements, Bamford (1962) found both Fe^{3+} and Fe^{2+} 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_{oct}^{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 $Fe^{3+}/\Sigma Fe$ seems to increase with iron content.

(2) The δ and Δ parameters for both types of iron are slightly spread, and linewidths are broad suggesting that Fe may occur in two sites for each valency.

(3) 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 sixfold 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; Bandyopadhyay 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 (Mysen 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_2O_3–SiO_2–CaO glasses to examine iron partitioning. They found that partitioning between different sites of the same ion (Fe_{oct}^{3+} and Fe_{tet}^{3+}) was *not* affected by the amount of Ca in the equilibrated melt; however, increasing CaO content clearly increases $Fe^{2+}/\Sigma Fe$ ratios. Replacement of CaO by Na_2O created no significant changes in $Fe_{oct}^{3+}/Fe_{tet}^{3+}$ 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 ($CaFe^{3+}O_2$) with trivalent iron. However, the addition of even more stable Na (and $Na_2Fe^{3+}O_2$ complexes) to a melt may gradually dissociate the Ca complexes in favor of Na complexes. Later work by Mysen et al. (1981) and Danckwerth et al. (1982) reproduced these results. Mössbauer spectra of the system $Na_2Si_2O_5$–$CaSi_2O_5$ with added Fe_2O_3 show the expected increase in I.S. from Na to Ca systems, reflecting the additional contribution from Fe_{oct}^{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 $Fe^{2+}/\Sigma Fe$ ratios.

(2) When Na_2O 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_2O_3-bearing melts, little Mössbauer work on iron-bearing melts has been attempted. Wood and Hess (1980) have shown that the addition of Al_2O_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 can interact. Mysen et al. (1981) suggested that Fe^{3+} generally acts as an octahedral network modifier, 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 $MgO-Al_2O_3-SiO_2-FeO$ system and observed both ferric 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 $Fe^{3+}/\Sigma Fe$ 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_2O 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_2O helps to homogenize and stabilize the environments around FeO_4 tetrahedra, other ions such as Cl can more easily find their way to substitute for O as FeO_3Cl 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_2O 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 on K_2O-bearing in glasses leads to the following simple trends: (1) I.S. decreases as K_2O is increased. (2) $Fe^{2+}/\Sigma Fe$ increases as K_2O 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_2O_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 phos-phate 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+}_{oct} and Fe^{3+}_{oct} 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 ceramist's viewpoint. Woods and Fine (1969) observed that glasses with a nominal composition of $MgFe_2O_4$ 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 $Fe_2O_3 = 1.0$ wt.%, and 0.34–0.44 mm/sec when $Fe_2O_3 = 5.0$ 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 extra-terrestrial 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 superceeded 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^{3+}/Fe^{2+} 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; Coey, 1974; 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. Bandyopadhay 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^{2+} 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_3O_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 $\delta = 0.89$–0.96 and $\Delta = 1.84$–1.93 mm/sec, and Fe^{3+} with $\delta = 0.20$–0.21 and $\Delta = 0.51$–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 ét al. 1980; Bandyopadhay 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 geochemists 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., Lauer, 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 $Fe^{2+}/\Sigma Fe$ ratios in a glass. This tabulation may be useful to qualitatively evaluate glass samples with different $Fe^{2+}/\Sigma Fe$ 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,

Table 5. Effects of individual cations on iron partitioning

Cation	C.N.	Cation Charge / Ionic Radius	Effect of Increasing the Proportion of this Cation
P^{5+}	4	29.41	none
Al^{3+}	4	7.69	decrease $Fe^{2+}/\Sigma Fe$
	6	5.66	
Ti^{4+}	6	6.61	increase $Fe^{2+}/\Sigma Fe$ at low f_{O_2}
Fe^{3+}	4	6.12	decrease $Fe^{2+}/\Sigma Fe$
	6	3.64	
Mg^{2+}	4	4.08	slightly increase $Fe^{2+}/\Sigma Fe$
	6	2.78	
	8	2.25	
Fe^{2+}	4	3.17	decrease $Fe^{2+}/\Sigma Fe$
	6	3.28	
Ca^{2+}	6	2.00	increase $Fe^{2+}/\Sigma Fe$
	8	1.79	
	12	1.48	
Na^{+}	4	1.01	increase $Fe^{2+}/\Sigma Fe$
	6	0.98	
	8	0.86	
K^{+}	6	0.72	increase $Fe^{2+}/\Sigma Fe$
	8	0.66	
	12	0.63	

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 $Fe^{2+}/\Sigma Fe$, 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 also 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

References

Adams, J. B. and Charette, M. D. (1975) Effects of maturation on the reflectance of the lunar regolith Apollo 16—a case study. the Moon, 13, 293–299.

Baak, T. and Hornyak, E. J. (1961) Iron-oxygen equilibrium in glass: effect of platinum on Fe^{2+}/Fe^{3+} equilibrium. Journal of the American Ceramic Society, 44, 541–544.

Bahgat, A. A., Shaisha, E. E., and Fayek, M. K. (1983) Coordination of Fe^{3+} and Sn^{4+} in the vitreous compound $B_2O_3 \cdot Na_2O \cdot MgO \cdot Fe_2O_3 \cdot SnO_2$. Physics and Chemistry of Glasses, 24, 5–7.

Bamford, C. R. (1962) A study of the magnetic properties of iron in relation to its colouring action in glass. Part 4. Iron in sodium phosphate glasses. Physics and Chemistry of Glasses, 3, 54–47.

Bandyopadhyay, A. K., Zarzycki, J., Auric, P., and Chapperl, J. (1980a) Magnetic properties of a basalt glass and glass ceramics. Journal of Non-Crystalline Solids, 40, 353–368.

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

containing iron having different redox ratios. Journal of Materials Science, 15, 2081–2090.

Bandyopadhyay, A. K., Ribes, M., Pernot, F., and Zarzycki, J. (1982) Mössbauer and ESR studies on mixed transition metal oxide glasses. Physics and Chemistry of Glasses, 23, 31–36.

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, 545–533.

Bell, P. M., Mao, H. K., and Weeks, R. A. (1976) Optical spectra and electron paramagnetic resonance of lunar and synthetic glasses: a study of the effects of controlled atmosphere, composition and temperature. Proceedings of the Seventh Lunar Science Conference, 2543–2559.

Beltran-Porter, D., Olazcuaga, R., Fournes, L., Menil, F., and LeFlem, G. (1980) Magnetic and Mössbauer resonance examination of the orthophosphate α-$Na_3Fe_2(PO_4)_3$ and a derived vitreous phase. Revue de Physique Appliquee, 15, 1155–1160.

Belyustin, A. A., Ostanevich, Y. M., Pisarevskii, A. M., Tomilov, S. B., Bai-shi, U., and Cher, L (1965) The Mössbauer effect in alkali-iron silicate glasses. Soviet Physics-Solid State, 7, 1163–1169.

Bishay, A. M. and Makar, L. (1969) Role of iron in calcium phosphate glasses. Journal of American Ceramic Society, 52, 605–609.

Boon, J. A. (1971) Mössbauer investigations in the system Na_2O–FeO–SiO_2. Chemical Geology, 7, 153–169.

Bonnenfant, A., Friedt, J. M., Maurer, M., and Sanchez, J. P. (1982) Magnetic and structural properties of iron-based oxide glasses, Fe_2O_3–BaO–B_2O_3 from ^{57}Fe Mössbauer spectroscopy. Journal de Physique, 43, 1475–1487.

Bowker, J. C. (1979) Statistical models and Mössbauer spectroscopy of slags. Ph.D. thesis, Carnegie-Mellon University, Pittsburgh, PA.

Bukrey, R. R., Hooper, H. O., Kenealy, P. F., and Beard, G. B. (1972) A Mössbauer study of the structure and magnetic properties of iron in alkali borate glasses. Bulletin of the American Ceramic Society, 51, 371.

Bukrey, R. R., Kenealy, P. F., Beard, G. B., and Hooper, H. O. (1974) Mössbauer effect study of the structure and magnetic properties of the $Na_2O \cdot Li_2O \cdot B_2O_3 \cdot Fe_2O_3$ glass system. Physics Review, B, 9, 1052–1061.

Brawer, S. A. and White, W. B. (1977) Raman spectroscopic investigation of the structure of silicate glasses (II). Soda-alkaline earth-alumina ternary and quaternary glasses. Journal of Non-Crystalline Solids, 23, 261–278.

Burns, R. G. and Dyar, M. D. (1983) Spectral chemistry of green glass-bearing 15426 regolith. 14th Proceedings, Lunar and Planetary Sciences Conference, 82–83.

Burns, R. G. and Dyar, M. D. (1981) Coordination chemistry of iron in natural and synthetic glasses. (abstr.) Geological Society of America Abstracts with Programs, 420.

Burzo, E. and Ardelean, I. (1979a) Mössbauer effect study of iron cations in lead borate glasses. Physics and Chemistry of Glasses, 20, 15–20.

Burzo, E. and Ardelean, I. (1979b) On the iron valence states in B_2O_3–PbO–GeO_2 glasses. Solid State Communications, 31, 75–78.

Burzo, E., Ungur, D, and Ardelean, I. (1982) Effect of composition on valence states of iron cations in some borate glasses. Nuclear Instruments and Methods in Physics Research, 199, 189–191.

Charette, M. P., McCord, T. B., Pieters, C., and Adams, J. B. (1974) Application of remote spectral reflectance measurements

to lunar geology classification and determination of titanium content of lunar soils. Journal of Geophysical Research, 79, 1605–1613.

Chavez-Rivas, F., Regnard, J. R., and Chappert, J. (1980) Mössbauer study of natural glasses: Lipari and Teotihuacan obsidians. Journal de Physique, Colloque, C-1, 41, 275–276.

Coey, J. M. D. (1974) Amorphous solids: a review of the applications of the Mössbauer effect. Journal de Physique, 35, C6-89–C6-105.

Danckwerth, P. A., Virgo, D., and Mysen, B. O. (1982) The structural state of Fe in alkaline vs. alkaline-earth silicate systems. Carnegie Institute of Washington Yearbook, 81, 344–347.

Dannheim, H. and Frey, T. (1978) Mössbauer investigation of the incorporation of tin and iron in sodium borate glasses. In L. D. Pye, V. D. Frechette, and N. J. Kreidl, Eds., Borate Glasses: structure, properties, applications, p. 227–238. Plenum Press, New York.

de Grave, E., van Iseghem, P., de Batist, R., and Chambaere, D. (1980) Mössbauer spectroscopic study of some complex M_2O–MO–M_2O_3–SiO_2 glasses. Journal de Physique, 41, C-1, 269–271.

Delano, J. W. (1979) Apollo 15 green glass: chemistry and possible origin. Proceedings of the Tenth Lunar and Planetary Science Conference, 275–300.

Dyar, M. D. and Birnie, D. P. (1984) The effects of quench media on iron partitioning and ordering in a lunar glass. In L. D. Pye, J. A. O'Keefe and V. D. Frechette, Eds., Natural Glasses, North-Holland Publishing Company. Journal of Non-Crystalline Solids, 67, 397–412.

Dyar, M. D. and Burns, R. G. (1981) Coordination chemistry of iron in glasses contributing to remote-sensed spectra of the moon. Proceedings of the Lunar and Planetary Science Conference, 12B, 695–702.

Dyar, M. D. (1984a) Experimental methods for quenching structures in lunar-analog silicate melts: variations as a function of quench media and composition. 15th Proceedings, Lunar and Planetary Science Conference, Journal of Geophysical Research, 89, C233–C239.

Dyar, M. D. (1984b) Precision and interlaboratory reproducibility of measurements of the Mössbauer effect in minerals. American Mineralogist, 69, 1127–1145.

Eissa, N. A., Sanad, A. M., Youssef, S. M., El-Henawii, S. A., and Gomaa, S. Sh. (1980) Mössbauer effect study of oxidation and coordination sites of iron in some sodium borate glasses. Acta Physica Academiae Scientiarum Hungaricae, 48, 403–408.

Fenstermacher, J. E. (1980) Optical absorption due to tetrahedral and octahedral ferric iron in silicate glasses. Journal of Non-Crystalline Solids, 38 and 39, 239–244.

Fox, K. E., Furukawa, T., and White, W. B. (1981) Luninescence of Fe^{3+} in metaphosphate glasses: evidence for four- and six-coordinated sites. Communications of the American Ceramic Society, C-42.

Fox, K. E., Furukawa, T., and White, W. B. (1982) Transition metal ions in silicate melts. Part 2. Iron in sodium silicate glasses. Physics and Chemistry of Glasses, 23, 169–178.

Frischat, G. H. and Tomandl, G. (1971) Mössbauer investigation of silicate and phosphate glasses with small additions of Fe_2O_3. Glastechnisch Berichte, 44, 173–177.

Galant, E. J. (1966) Optical properties and structural elements of silicate glasses containing titanium. In E. A. Porai-Koshits, Ed., Structure of Glass, p. 160–163. New York Consultants Bureau, New York.

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

(1981) A thermodynamic appraisal of experimental solid–liquid phase equilibria in natural silicate liquids. (abstr.) Geological Society of America Annual Meeting Abstracts with Programs, 458.

Ghiorso, M. S., Carmichael, I. S. E., Rivers, M. L., and Sack, R. O. (1983) The Gibbs Free Energy of mixing of natural silicate liquids; an expanded regular solution approximation for the calculation of magmatic intensive variables. Contributions to Mineralogy and Petrology, 84, 107–145.

Gosselin, J. P., Shimony, U., Grodzins, L., and Cooper, A. R. (1967) Mössbauer studies on iron in sodium trisilicate glasses. Physics and Chemistry of Glasses, 8, 56–61.

Hess, P. C. (1977) Structure of silicate melts. Canadian Mineralogist, 15, 162–178.

Hirao, K., Soga, N., and Kunugi, M. (1979) Mössbauer and ESR analyses of the distribution of Fe^{3+} in leucite type iron silicate glasses and crystals. Journal of the American Ceramic Society, 62, 109–110.

Hirao, K., Komatsu, T., and Soga, N. (1980) Mössbauer studies on some glasses and crystals in the $Na_2O-Fe_2O_3-SiO_2$ system. Journal of Non-Crystalline Solids, 40, 315–323.

Hirayama, C., Castle, J. G., and Kuriyama, M. (1968) Spectra of iron in alkaline earth phosphate glasses. Physics and Chemistry of Glasses, 9, 109–114.

Hong, C. Y. (1978) The Mössbauer effect study of Fe ion in soda glass system. New Physics (Korean Physical Society), 18, 120–126.

Horie, O., Syono, Y., and Nakagawa, Y. (1978) Mössbauer study of amorphous $BaO-Fe_2O_3-B_2O_3$ system. Solid State Communications, 25, 423–426.

Iwamoto, N., Tsunawaki, Y., Nakagawa, H., Yoshimura, T., and Wakabayashi, N. (1978) Investigation of calcium-iron-silicate glasses by the Mössbauer method. Journal of Non-Crystalline Solids, 29, 347–356.

Iwamoto, N., Tsunawaki, Y., Nakagawa, H., Miyago, M., Yoshimura, T., and Wakabayashi, N. (1979) Study of calcium-iron-silicate glasses by Mössbauer spectroscopy. Journal de Physique, 40, C2–151.

Jach, J. (1973) Mössbauer study of an iron-containing borate glass. Journal of Nonmetals, 1, 155–158.

Jach, J. (1974) A Mössbauer study of the devitrification of an iron containing borate glass. Journal of Nonmetals, 2, 89–93.

Jach, J., and Nabation, D. (1977a) A Mössbauer study of the reaction between Fe and sodium disilicate glass. Semiconductors and Insulators, 3, 23–32.

Jach, J., and Nabation, D. (1977b) Mössbauer study of an iron-containing sodium disilicate glass. Semiconductors and Insulators, 3, 33–41.

Johnston, W. D. (1964) Oxidation-reduction equilibria in iron-containing glass. Journal of the American Ceramic Society, 47, 198–201.

Kamal, R., Sekhon, S. S., Kishore, N., Mendiratta, R. G. (1982) Mössbauer spectra in the $xNa_2O \cdot (1 - x - y)B_2O_3 \cdot yFe_2O_3$ glass system. Journal of Non-Crystalline Solids, 53, 227–233.

Kamo, M., Takashima, Y., and Ohashi, S. (1967) The Mössbauer of the iron–sodium metaphosphate systems. Bulletin of the Chemical Society of Japan, 40, 2812–2815.

Kanazawa, T., Nakai, A., and Kawazoe, H. (1969) Structure and properties of $CaO-MgO-P_2O_5-SiO_2$ glass. Journal of the Chemical Society of Japan, Industrial Chemistry Section, 72, 2211–2216.

Kang, S. G., and Moon, Y. S. (1976) Mössbauer effect study of the iron ion in borate glasses. Sae Mulli, 16, 7–11.

Kerler, W. and Neuwirth, W. (1962) Messungen des Mössbauer-Effekts von Fe^{57} in zahlreichen Eisenverbindungen bei verschiedenen Temperaturen. Zeitschrift für Physik, 167, 176–193.

Khalilov, V. Kh., Pivorarov, S. S., Zakharov, V. K., Bokin, N. M., Prokhorova, T. I., Klimashina, E. V., and Gorovaya, B. S. (1978) Absorption spectra and structural state of Fe^{3+} ion in vitreous silicas and quartz. Fizika i Khimiya Stekla, 4, 180–184.

Komatsu, T. and Soga, N. (1980) ESR and Mössbauer studies of crystallization processes of sodium iron silicate glass. Journal of Chemical Physics, 72, 1781–1785.

Kurkjian, C. R. (1970) Mössbauer spectroscopy in inorganic glasses. Journal of Non-Crystalline Solids, 3, 157–194.

Kurkjian, C. R. and Buchanan, D. N. E. (1964) Mössbauer absorption of Fe^{57} in inorganic glasses. Physics and Chemistry of Glasses, 5, 63–70.

Kurkjian, C. R. and Sigety, E. A. (1968) Coordination of Fe^{3+} in glass. Physics and Chemistry of Glasses, 9, 73–83.

Labar, C. and Glenn, P. (1973/1974) A spectroscopic determination of ferrous iron content in glasses. Journal of Non-Crystalline solids, 13, 107–119.

Lauer, H. V. (1977) Effect of glass composition on major element redox equilibria: $Fe^{2+}-Fe^{3+}$. Physics and Chemistry of Glasses, 18, 49–52.

Lauer, H. V. and Morris, R. V. (1977) Redox equilibria of multivalent ions in silicate glasses. Journal of The American Ceramic Society, 60, 443–451.

Levitz, P., Calas, G., Bonnin, D., and Legrand, A. P. (1980) Geological significance of study by Mössbauer spectroscopy of iron-(III) in silicate glasses with multiple compositions. Revue de Physique Appliquee, 15, 1169–73.

Levy, R. A. (1976) Mössbauer resonance of Fe^{2+} and Fe^{3+} cations in silicate glasses. American Institute of Physics Conference Proceedings, United States of America, 29, 158.

Levy, R. A., Lupis, C. H. P., and Flinn, P. A. (1976) Mössbauer analysis of the valence and coordination of iron cations in SiO_2-Na_2O-CaO glasses. Physics and Chemistry of Glasses, 17, 94–103.

Lewis, G. K., Jr. and Drickamer, H. G. (1968) High-pressure Mössbauer studies of ^{57}Fe in silicate and phosphate glasses. Journal of Chemical Physics, 49, 3785–3789.

Lin, T-C. (1983) Transition metal ion electronic spectra in alkali borate and silicate glasses and melts from 25–1000°C. Masters Thesis, Purdue University.

Mao, H. K., Virgo, D., and Bell, P. M. (1973) Analytical and experimental study of iron and titanium in orange glass from Apollo 17 soil sample 74220. Fourth Lunar Science Conference, 397.

Menil, F., Fournes, L, Dance, J.-M., and Videau, J.-J. (1979) Sodium-iron fluorophosphate glasses. Part 2. EPR and Mössbauer resonance study. Journal of Non-Crystalline Solids, 34, 209–221.

Menil, F., Fournes, L, Dance, J.-M., and Videau, J.-J. (1980) Sodium iron fluorophosphate glasses. Part 2. EPR and Mössbauer resonance study. Journal de Physique, Colloque C1(1), 41, C1–271.

Mo, X., Carmichael, I. S. E., Rivers, M., and Stebbins, J. (1982) The partial molar volume of Fe_2O_3 in multicomponent silicate liquids and the pressure dependence of oxygen fugacities in magmas. Mineralogical Magazine, 45, 237–245.

Morinaga, K., Suginohara, Y., and Yanagase, T. (1976) Oxygen coordination number of Fe ions in $CaO-SiO_2$ and Na_2O-SiO_2 systems. Japanese Institute of Metals Journal, 40, 480–486.

Motran, R. S., Bishay, A. M., and Johson, D. P. (1973) Role of iron and electrical conductivity in iron calcium phosphate glasses. In A. Bishay, Ed., Recent Advances in Science and Technology of Materials. Vol. 1, p. 109–130. Plenum Press, New York.

Mulay, L. N. (1972) Elegance of the static magnetic and Mössbauer techniques in structural studies on glasses containing metal ions. Bulletin of the American Ceramic Society, 51, 370.

Mysen, B. O., Danckwerth, P., and Virgo, D. (1982) The effect of pressure on redox equilibria in melts in the system Na_2O–SiO_2–FeO. Carnegie Institute of Washington Yearbook, 357–360.

Mysen, B. O. and Virgo, D. (1978) Influence of P, T, and bulk composition on melt structures in the system $NaAlSi_2O_6$–$NaFe^{3+}Si_2O_6$. American Journal of Science, 278, 1307–1322.

Mysen, B. O., Seifert, F. and Virgo, D. (1980) Structure and redox equilibria of iron-bearing silicate melts. American Mineralogist, 65, 867–884.

Mysen, B. O., Virgo, D., and Kushiro, I. (1981) The structural role of aluminum in silicate melts—a Raman spectroscopic study at 1 atmosphere. American Mineralogist, 66, 678–701.

Naney, M. T., and Swanson, S. E. (1985) Iron redox kinetics in silicate liquids at one atmosphere. Contributions to Mineralogy and Petrology, in press.

Nelson, B. N. and Exarhos, G. J. (1979) Vibrational spectroscopy of cation-site interactions in phosphate glasses. Journal of Chemical Physics, 71, 2739–2747.

Neumann, E. R., Mysen, B. O., Virgo, D., and Seifert, F. A. (1982) Redox equilibria of iron in melts in the system CaO–Al_2O_3–SiO_2–FeO. Carnegie Institute of Washington Yearbook, 81, 353–355.

Nishida, T., and Takashima, Y. (1980a) Mössbauer spectroscopic study of the formation of non-bridging oxygen in potassium borate glasses. Journal of Non-Crystaline Solids, 37, 37–43.

Nishida, T., Shiotsuki, T., and Takashima, Y. (1980b) Mossbauer study of the fraction of non-bridging oxygens in potassium borate glasses. Journal of Non-Crystalline Solids, 41, 161–170.

Nishida, T., Shiotsuki, T., Takashima, Y. (1981a) Mössbauer and ESR studies of non-bridging oxygens in potassium phosphate glasses. Journal of Non-Crystalline Solids, 43, 115–122.

Nishida, T., Hirai, T., and Takashima, Y. (1981b) Mössbauer spectroscopic study of nonbridging oxygen atoms in potassium borosilicate glasses. Physics and Chemistry of Glasses, 22, 94–98.

Nishida, T., Hirai, T., Takashima, Y. (1981c) Mossbauer spectroscopic study of potassium borate glasses at low temperatures. Journal of Non-Crystalline Solids, 43, 221–228.

Nishida, T., Kai, N., and Takashima, Y. (1983d) Mössbauer and ESR studies of potassium borate glasses containing a small amount of chloride ions. Physics and Chemistry of Glasses, 22, 107–109.

Nolet, D. A., Burns, R. G., Flamm, S. L., and Besancon, J. R. (1979) Spectra of Fe-Ti silicate glasses: implications to remote-sensing of planetary surfaces. Proceedings of the Tenth Lunar and Planetary Science Conference, 1775–1786.

Nolet, D. A. (1980) Optical absorption and Mössbauer spectra of Fe, Ti silicate glases. Journal of Non-Crystalline Solids, 37, 99–110.

Pargamin, L., Lupis, C. H. P., and Flinn, P. A. (1972) Mössbauer analysis of the distribution of iron cations in silicate slags. Metallurgical Transactions, 3, 2093–2105.

Park, J. W. and Chen, H. (1982) The coordination of Fe^{3+} in sodium disilicate glass. Physics and Chemistry of Glasses, 23, 107–108.

Pavlushkina, T. K., Goroagev. B. B., and Artamonora, T. I. (1981) Structure of silicate-phosphate glasses. Thirteenth Conference on Silicate Industry and Silicate Science—Budapest, Section 1, 148–152.

Pollak, H., DeCoster, M., and Amelinckx, S. (1962) Mössbauer effect in amorphous substances. In D. M. J. Compton and D. Sehuen, Eds., Mössbauer Effect. p. 298, Wiley, New York.

Prasad, A., Bahadur, D., Singru, R. M., and Chakravorty, D. (1982) Study of Na_2O–SiO_2–Fe_2O_3–Y_2O_3 glass by Mössbauer and EPR spectroscopy. Journal of Materials Science, 17, 2687–2692.

Raman, T., Nagesh, V. N., Chakravorty, D., and Rao, G. N. (1975) Mössbauer studies in the glass system $Na_2O \cdot B_2O_3 \cdot Fe_2O_3$. Journal of Applied Physics, 46, 972–973.

Raman, T., Rao, G. N., and Chakravorty, D. (1978a) Mössbauer effect studies of alkali borate glasses. Journal of Non-Crystalline Solids, 29, 85–107.

Raman, T., Chakravorty, D., and Rao, G. N. (1978b) Mössbauer effect studies of alkali borate glasses. Hyperfine Interactions, 4, 873–878.

Regnard, J. R., Chavez-Rivas, F., Chappert, J. (1981) Study of the oxidation states and magnetic properties of iron in volcanic glasses: Lipari and Teotihuacan obsidians. Bulletin de Mineralogie, 104, 204.

Ryerson, F. J. and Hess, P. C. (1980) The role of P_2O_5 in silicate melts. Geochimica et Cosmochimica Acta, 44, 611–624.

Sack, R. O., Carmichael, I. S. E., Rivers, M., and Ghiorso, M. S. (1980) Ferric-ferrous equilibria in natural silicate liquids at 1 bar. Contributions to Mineralogy and Petrology, 75, 369–376.

Schreiber, H. D., Lauer, H. V., Thanyasiri, T. (1980) Oxidation-reduction equilibria of iron and cerium in silicate glasses: individual redox potentials and mutual interactions. Journal of Non-Crystalline Solids, 38–39, 785–790.

Seifert, F. A., Virgo, D., and Mysen, B. O. (1978) Melt structures and redox equilibria in the system Na_2O–FeO–Fe_2O_3–Al_2O_3–SiO_2. Carnegie Institute of Washington Yearbook, 77, 511–526.

Seifert, F. A., Mysen, B. O., Virgo, D., and Neumann, E. R. (1982) Ferric-ferrous equilibria in melts in the system MgO–Al_2O_3–SiO_2–FeO. Carnegie Institute of Washington Yearbook, 81, 355–356.

Sekhon, S. S. and Kamal, R. (1978) Mössbauer study of the glass system $PbO \cdot 2B_2O_3 \cdot Fe_2O_3$. Journal of Non-Crystalline Solids, 28, 189–192.

Sekhon, S. S. and Kamal, R. (1979) Mössbauer spectra in $xPbO \cdot (1 - x)B_2O_3$ doped with Fe_2O_3. Journal of Non-Crystalline Solids, 33, 169–175.

Takeda, M., Sato, K., Sato, J., and Tominaga, T. (1979) Iron-57 Mössbauer study of naturaly occurring glasses: Japanese obsidians. Revue de Chimie Minerale, 16, 400.

Taragin, M. F. and Eisenstein, J. C. (1970) Mössbauer effect in some complex borosilicate glasses. Journal of Non-Crystalline Solids, 3, 311–316.

Taragin, M. F., Eisenstein, J. C., and Haller, W. (1972) Mössbauer study of Fe^{37} in an aluminophosphate glass. Physics and Chemistry of Glasses, 13, 149–152.

Taylor, M. and Brown, G. E. (1979) Structure of mineral glasses-II. The SiO_2–$NaAlSiO_4$ join. Geochimica et Cosmochimica Acta, 43, 1467–1473.

Taylor, M., Brown, G. E., and Fenn, P. (1980) Structure of mineral glasses-III. $NaAlSi_3O_8$ supercooled liquid at 805°C and the ef-

fects of thermal history. Geochimica et Cosmochimica Acta, 44, 109–117.

Tomandl, G., Frischat, G. H., and Oel, H. J. (1967) Mössbauer effect in iron-alkali-silicate-glass. Glastechnische Berichte, 40, 38–44.

Tomozawa, M., Singer, G. M., MacCrone, R. K., and Warden, J. T. (1982) Mixed valence effect in phase separation of sodium borosilicate glasses. Journal of Non-Crystalline Solids, 49, 165–171.

Tricker, M. J., Thomas, J. M., Omar, M. H., Osman, A., and Bishay, A. (1974) Mossbauer and X-ray photoelectron spectroscopic studies of heat-treated calcium borate glasses containing iron. Journal of Materials Science, 9, 1115–1122.

Varnek, V. A., Verevkin, G. V., and Sokolova, V. K. (1973) Use of Mössbauer spectra to investigate eight-component silicate glasses. Inorganic Materials, Consultants Bureau Translation, 9, 662–664.

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 Appliquee, 14, 613–618.

Vaughan, J. G., Wilson, L. K., and Kinser, D. L. (1973) Mössbauer effect spectroscopy of iron phosphate glasses. Bulletin of the American Ceramic Society, 52, 384.

Virgo, D., Mysen, B. O., and Seifert, F. A. (1981) Relationship between the oxidation state of iron and the structure of silicate melts. Carnegie Institute of Washington Yearbook, 80, 308–311.

Virgo, D., Mysen, B. O., Danckwerth, P., and Seifert, F. A. (1982a) The anionic structure of 1 atm melts in the system SiO_2–$NaFeO_2$. Carnegie Institute of Washington Yearbook, 81, 347–349.

Virgo, D., Mysen, B. O., Danckwerth, P., and Seifert, F. A. (1982b) Speciation of Fe^{3+} in 1-atm Na_2O–SiO_2–Fe–O melts. Carnegie Institute of Washington Yearbook, 81, 349–353.

Waff, H. S. (1977) The structure of ferric iron in silicate melts. The Canadian Mineralogist, 15, 198–199.

Whipple, E. R. (1973) Quantitative Mössbauer Spectra and Chemistry of Iron. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge.

Wong, J., and Angell, C. A. (1976) Glass: structure by spectrosopy, p. 97–128. Marcell Dekker, New York.

Wood, M. I. and Hess, P. C. (1980) The structural role of Al_2O_3 and TiO_2 in immiscible silicate liquids in the system SiO_2–MgO–CaO–FeO–TiO_2–Al_2O_3. Contributions to Mineralogy and Petrology, 72, 319–328.

Woods, K. N. and Fine, M. E. (1969) Nucleation and growth of magnesioferrite in MgO containing 0.9% Fe^{3+}. Journal of The American Ceramic Society, 52, 186–188.