QUENCHING EFFECTS ON IRON SITE PARTITIONING IN THE APOLLO 17 ORANGE GLASS COMPOSITION, M. Darby Dyar, Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139

Past studies of the composition and structures in lunar glasses have contributed greatly to our understanding of mare petrogenesis and the structure of the lunar interior (1,2,3). In particular, analyses of the spectral signatures of glasses have proven extremely useful to remote sensing applications in areas of the moon where glass is in significant proportions in the lunar soil. Such studies have also provided information on Fe site occupancies in glasses, which are used to construe oxygen fugacities at the lunar surface (4). Much of this data has been obtained through work on synthetic analogues of lunar glasses. However, recent Mossbauer studies of an Apollo 15 green glass composition (5) have shown that synthetic glasses are extremely sensitive to variations in quenching media (6). Glass structure and Fe^{3+}/Fe^{2+} ratios are strongly controlled by quenching conditions, which may mask the effects of the original glass' formation temperature or oxygen partial pressure. Furthermore, synthetic glasses were often run at low fugacities on Pt wires, (which may result in considerable Fe loss from the sample and misleading phase equilibrium data. These problems suggest that previous investigations of lunar glass structure ought to be reconsidered.

The purpose of this report is to critically consider the effects of quench media on the Apollo 17 orange glass composition: 39.42(wt.)% SiO_2, 22.48% FeO, 9.04% TiO_2, 6.32% Al_2O_3, 7.74% CaO, and 14.97% MgO (7). Aliquots of 30mg each were equilibrated at 1400°C, log f_{O_2} = -11.3, using Fe-alloyed Pt wire loops (8) in a gas mixing furnace. Each identical sample was equilibrated for one hour and then quenched into one of three different quench media: a brine/ice eutectice mixture (-21°C), silicone oil (25°C) or air (25°C). Each experiment was repeated at least three times. ^{57}Fe Mossbauer spectra were measured on all runs; spectra were fit with a combination Lorentzian/Gaussian peak shape (9).

The three quenchants may be ranked in order of efficiency as brine/ice (fastest quench)>silicone oil>air (slowest quench). Because cooling rate is related to molar volume, the fastest quenched glasses will have the least dense structures, and vice versa (6). The iron site occupancies shown by the Mossbauer spectra (Figs. 1-3) follow this trend. The least dense glasses have the lowest Fe^{2+} isomer shifts; the densest (air quenched) glasses have the highest isomer shifts, indicating that iron is favoring higher coordination. Quadrupole splitting also increases in the densest glasses. The fits also show that the proportion of octahedral to tetrahedral iron varies with quench medium.

These results can be compared against the Mossbauer spectrum of lunar sample 74220 (orange glass) examined by Vaughan and Burns (2). The lunar sample can be fit with a four-fold Fe^{2+} doublet and at least one six-fold Fe^{2+} doublet, suggesting a relatively ordered glass comparable to the slowest cooled, air-quenched synthetic glass. A similar result was determined for the Apollo 15 green glass composition (6). More rapid quenching, such as that provided by the brine/ice mixture leads to a glass with a significantly different type and proportion of oct/tet Fe^{2+} sites. Therefore, past studies which employed rapid quench media such as water or liquid Hg may have drawn suspect conclusions regarding the structure of lunar glasses.

This work also underscores the fact that quenched glasses have undergone drastic structural changes upon passing through the glass transition temperature at differing rates. It is doubtful that these quenched glasses are in any way structurally representative of their original melts (10).

QUENCHING EFFECTS ON ORANGE GLASS

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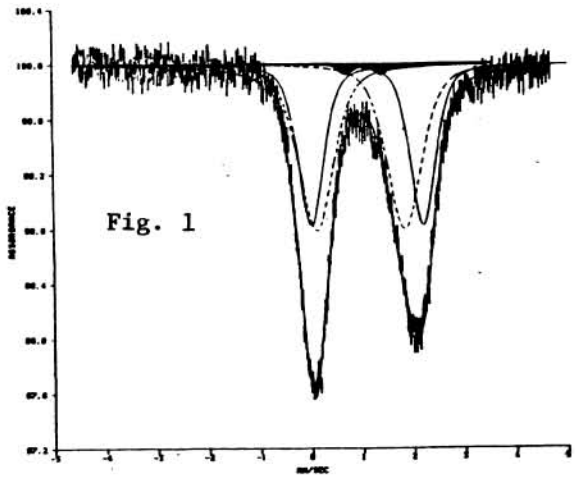

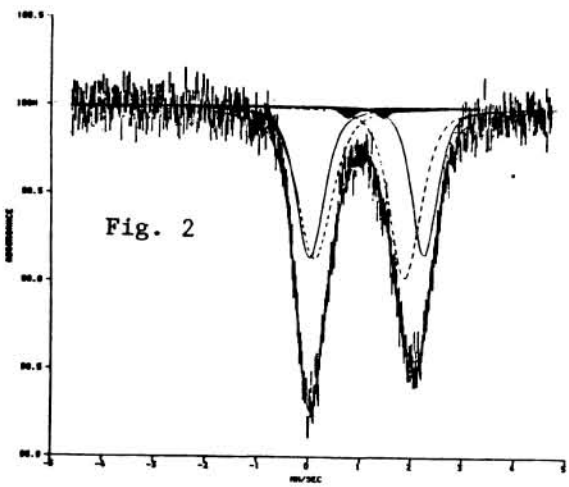

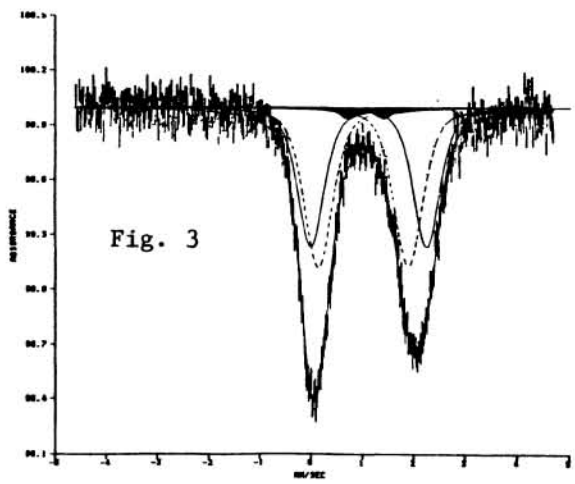

Figures 1-3 show the orange glass composition as quenched in brine/ice (#1), silicone oil (#2), and air (#3). All samples have 1-2 % of total Fe in the form of ilmenite, δ = 1.060 and Δ = 0.678 (shaded peaks). Tetrahedral Fe^{2+} peaks are shown with dashed outlines. Mossbauer parameters for the fits are as follows, relative to an Fe foil calibration:

	δ_{tet}	δ_{oct}	Δ_{tet}	Δ_{oct}
Brine-ice	0.975	1.109	1.717	2.183
Oil	0.978	1.120	1.755	2.217
Air	1.008	1.124	1.813	2.295

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(10) Research supported by NASA grant no. NSG-7604.