

THE THEORETICAL DETERMINATION AND EXPERIMENTAL EFFECTS OF COOLING HISTORY ON SILICATE GLASSES

M. D. Dyar, Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139; D. P. Birnie, III, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139; M. T. Naney, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831; and S. E. Swanson, Geophysical Institute and Geology/Geophysics Program, University of Alaska, Fairbanks, Alaska 99701

Cooling history studies of glasses are critical to our understanding of lunar magmatic processes and to the interpretation of remote-sensed reflectance spectra of the Moon's surface. The key issues in such studies are: (1) how can we conveniently determine the cooling history of a given glass, and (2) what features of glass structure are affected by changes in cooling rates. These questions can be best addressed through use of both theoretical calculations and experimental work:

Theoretical cooling rates for any glass quenched in any medium may be calculated if the thermal properties of the sample and its quenching medium both are known. Expressions developed by Birnie and Kingery (1) were applied to typical lunar samples with $\rho = 2.5$ g/cc, $h = 0.3$ cal/g \cdot °C, and $k = 0.005$ cal/cm \cdot sec \cdot °C. To date, cooling rate (\dot{T}) calculations for samples quenched in air and water have been made; pending completion of experiments to determine heat transfer coefficients, calculations will be extended to liquid nitrogen and vacuum environments. Preliminary results are tabulated below:

half-thickness, cm:	0.05	0.1	0.2	0.3	0.5	1	5	10	100
\dot{T} (air), °C/sec:	50	25	13	8	5	2.5	0.15	0.04	0.0004
\dot{T} (water), °C/sec:	1100	550	95	42	15	4	0.15	0.04	0.0004

These results for air quenches compare favorably with measurements performed on actual lunar samples (2,3). Development of cooling rate expressions based on sample size may be an easy way to relate known glass size distributions with thermal history scenarios on the lunar surface.

Knowledge of cooling rates is important because previous work (4) has suggested that cooling history can have profound effects on iron site partitioning and redox kinetics in synthetic silicate glasses. To test these effects in natural samples, 100 mg aliquots of representative basalt, andesite, and rhyolite compositions were melted in a CO/CO₂ atmosphere at 1343 \pm 2°C, $\log f_{O_2} = -7.85 \pm 0.5$ for 24-48 hrs. Melts were quenched in an air jet, an H₂-Ar gas jet, and an NaCl brine/ice bath (-21°C). Compositions were as follows: (5)

Sample:	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Total
Rhyolite:	73.43	13.76	1.74	0.29	1.16	4.19	4.34	0.26	0.05	0.04	99.26
Andesite:	62.91	15.63	5.87	2.70	5.80	3.45	1.83	0.62	0.12	0.11	99.04
Basalt:	54.50	13.61	12.48	3.46	6.92	3.27	1.70	2.20	0.36	0.18	99.68

Mossbauer spectra were taken of each sample using standard procedures (6); spectra were fit to a sum of Lorentzian/Gaussian combined line shapes (7). Sample sizes with minimum projected cooling rates of ~8-13°C/sec were used. In contrast with previously-studied lunar green and brown glasses (which showed Fe²⁺/Fe³⁺ variations with quenching) (4,8), compositions studied

Dyar, M. D., et al.

here show no Fe^{3+} peaks. In these 100 mg samples there are no significant variations of isomer shift and quadrupole splitting parameters. However, for the basalt glass in particular (the sample closest to observed lunar compositions) there is a systematic change in the ratio of $\text{Fe}_{\text{oct}}^{2+}/\text{Fe}_{\text{tet}}^{2+}$, which increases as the quench medium changes from brine/ice to H_2 -Ar to air. Since heat transfer coefficients of the media probably increase in that order (8), there appears to be a link between preference for octahedral coordination and slow quenches. This can be explained by the known relationship between molar volume and cooling rate: rapid quenches yield high molar volumes, and slow quenches result in denser glasses (9). Therefore the glasses behave predictably when quenched into the three media: more octahedral iron is observed in slowest quenches (densest glasses).

This work on cooling rates has several implications for lunar glass research:

- (a) knowledge of size distribution (as it relates to cooling rate) may contribute to our understanding of fire-fountaining processes on the Moon;
- (b) the correspondence between Fe site occupancy and cooling rate places constraints on earth-based attempts to synthesize lunar analogues;
- (c) changes in Fe partitioning as related to cooling rate may affect interpretations of remote-sensed spectra of areas with high glass contents in the lunar soil (10).

References

- (1) Birnie, D. P. and Kingery, W. D. (1985) J. Mat. Sci. in press.
- (2) Arndt, J. and Rombach, N. (1976) Proc. Lunar Sci. Conf. 7th, p. 1123-1141.
- (3) Uhlmann, D. R., Yinnon, H., and Fang, C.-Y. (1981) Proc. Lunar Planet. Sci. Conf. 12th, p. 281-288.
- (4) Dyar, M. D. (1984) Proc. Lunar Planet. Sci. Conf. 15th, in J. Geophys. Res. 89, p. C233-C239.
- (5) Naney, M. T. and Swanson, S. E. (1985) Contrib. Mineral. Petrol., in press.
- (6) Dyar, M. D. (1984) Am. Min., 69, 1127-1144.
- (7) Stone, A. J., Parkin, K. M. and Dyar, M. D. (1984) DEC User's Society Program no. 11-720, Marlboro, MA.
- (8) Dyar, M. D. and Birnie, D. P., III (1984), J. Non-Cryst. Solids, 67, 397-412.
- (9) Kingery, W. D., Bowen, H. K., and Uhlmann, D. R. (1976) Introduction to Ceramics (Wiley: New York, 1976), p. 92.
- (10) Research sponsored by NASA grant no. NSG-7604 (to R. G. Burns) and U.S. DOE, contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.