

^{57}Fe MÖSSBAUER SPECTROSCOPY OF FULGURITES: IMPLICATIONS FOR CHEMICAL REDUCTION. A. A. Sheffer¹ and M. D. Dyar², ¹Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721, abigailw@lpl.arizona.edu, ²Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075.

Introduction: The high temperature (superliquidus) processing of silicates often results in very reduced products, such as Si-bearing Fe metal in type-1 chondrules [1] and in lunar regolith agglutinates [2]. Previous work on fulgurites (the glassy products of the lightning strike fusion of sand, soil, or rock) found silicon metal and iron-silicon alloys inside the silicate glass [3, 4]. The mechanism for this extreme reduction is not yet understood. In this work, we begin a ^{57}Fe Mössbauer spectroscopy study as well as continuing a microprobe study of several fulgurites in order to better constrain the extent and process of Fe reduction.

Samples: Preliminary work has begun on three fulgurites and Trinitite – a sand fulgurite from the Pecos Plains, Texas; a basalt talus rock fulgurite from Cline Butte, Oregon; a sand and basalt gravel fulgurite from Farmington, CT; as well as Trinitite glass from the Trinity bomb test site.

Methods: The glasses were initially studied using a Cameca SX50 electron microprobe with a voltage of 15 kV and a current of 20 nA to obtain backscattered electron images and point analyses. Totals are consistently low due to cation migrations under the electron beam and small-scale compositional gradients for which the microprobe's matrix corrections cannot compensate.

Room temperature Mössbauer spectra were acquired to determine Fe^{2+} and Fe^{3+} contents. Samples were prepared by gentle crushing under acetone (to avoid oxidation), and then handpicking out pure glassy pieces. Separates containing metal blebs were also picked from the samples, and work is in progress on acquiring their Mössbauer spectra. About 300 mg of each sample were powdered and mounted. A source of 40 mCi ^{57}Co in Rh was used on a WEB Research Co. model W100 spectrometer. Run times ranged from 2-6 days. Results were calibrated against a-Fe foil of 6 μm thickness and 99% purity. Fitting methods employed quadrupole splitting distributions (QSDs) as described in Dyar [5].

Results: Microprobe analyses of the samples show a range of Fe contents. The Texas fulgurite is predictably low given its origins as a sand fulgurite. The other three samples contain higher FeO contents, reflecting the basaltic contributions from their country rocks. Other major elements are highly variable, suggesting that if there are any bulk chemistry controls on redox effects, then differences in the amount of Fe reduction might be seen for different samples.

Table 1: Microprobe analyses of Fulgurite and Trinitite glasses in weight % elements.

	Texas	Oregon	Connecticut	Trinitite
Fe	0.04	3.61	3.13	2.35
Si	45.38	30.00	35.69	31.51
Al	0.14	9.12	5.48	6.76
Ca	bd	2.71	1.76	5.81
Mg	bd	0.98	0.88	0.72
Na	bd	2.13	0.59	1.17
P	bd	0.07	bd	0.04
K	0.08	1.48	1.12	2.84
Mn	bd	0.08	0.09	0.05
Ti	bd	0.57	0.29	0.28
O	51.89	46.60	48.38	46.63
Total	97.60	97.38	97.42	98.17

bd = below detection limit

Mössbauer spectra show numerous subtle differences (Figure 1) and the expected range of parameters (Table 2). These preliminary fits of the Mössbauer spectra of the glasses suggest that the majority of the iron has been reduced to Fe^{2+} .

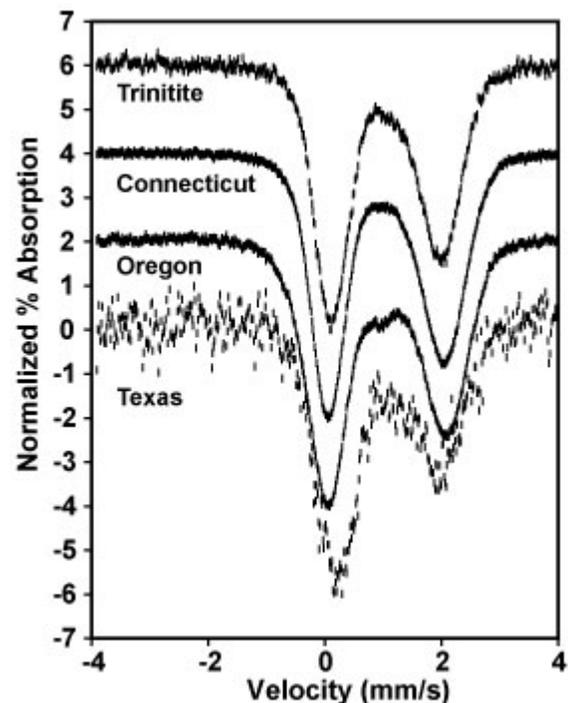


Figure 1: Mössbauer spectra of fulgurites and Trinitite glass at 300K. Data are normalized to 6% absorption and

offset for clarity. The scatter in the Texas spectrum is due to its low total Fe content.

Table 2: Preliminary Mössbauer data on Fulgurite and Trinitite glasses at 300 K

	Texas	Conn.	Trinitite	Oregon
Δ_0	1.86	1.98	1.91	2.07
δ_Δ	1.15	1.28	1.19	1.23
δ_0	0.97	0.90	0.89	0.97
δ_1	0.04	0.07	0.08	0.06
δ	1.06	1.05	1.04	1.10
Area	38%	82%	78%	50%
Δ_0	2.11	0.80	2.20	1.97
δ_Δ	1.89	2.00	2.00	1.94
δ_0	0.70	0.97	0.75	0.70
δ_1	0.18	-0.05	0.09	0.07
δ	1.08	0.92	0.97	0.84
Area	34%	13%	9%	37%
Δ_0	0.72	2.24	0.75	0.58
δ_Δ	1.16	2.00	1.02	1.08
δ_0	0.70	0.73	0.70	0.70
δ_1	0.14	0.04	0.14	-0.07
δ	0.80	0.83	0.80	0.66
Area	28%	5%	13%	13%
χ^2	0.68	0.72	0.57	0.68

Results are given in mm/s relative to the center point of a Fe foil calibration spectrum. γ , which is the Lorentzian full peak width and half maximum intensity, was constrained to be 0.20 mm/s, which is the natural linewidth of Fe. Δ_0 = the center of a Gaussian component of the Δ -distribution. δ_Δ = the width of the quadrupole splitting distribution. δ_0 = the value of isomer shift, δ , when the distributed hyperfine parameter has a value of zero. δ_1 = the coupling of δ to the distributed hyperfine parameter. $\delta = \delta_1 * \Delta_0 + \delta_0$. A = the relative area of doublet. h_+/h_- = the ratio of Lorentzian heights of the two lines in an elemental quadrupole doublet, was constrained for all components to be equal to zero. Details can be found in [6].

Each spectrum was fitted with three independent components representing distributions of Fe atoms in non-homogeneous environments, as is appropriate for glasses. All components were broad QSD. The largest component in all spectra is unequivocally that of Fe²⁺ (first 6 lines of data in Table 1), with parameters representing 4-6-coordinated Fe²⁺. The other components with values of $\delta > 0.90$ mm/s can be assigned to 4-coordinated Fe²⁺, but those with lower δ values (bold) probably represent some combination of Fe³⁺ and Fe²⁺ that cannot be resolved. Thus, the Fe³⁺ contents of these samples ranges from its lowest in the Connecticut sample, increasing in the Trinitite, Texas, and Oregon (highest Fe³⁺) samples. Figure 2 shows the fit to the Oregon fulgurite glass spectrum.

Discussion: Further investigations of the country rock from these localities are underway, because we expect that the porosity and mineralogy of the starting material will have an effect on the post-melting result.

High porosity/surface area may also affect the ability of air to react during melting.

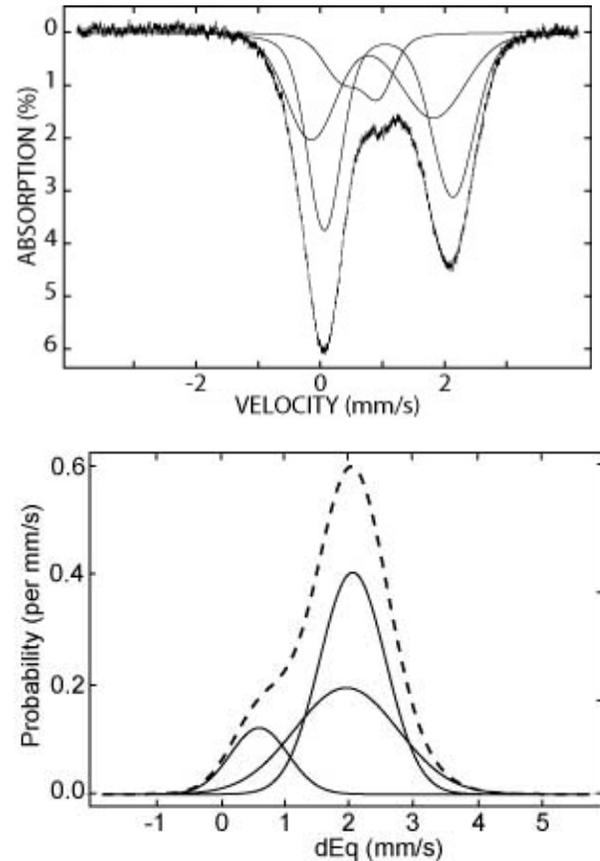


Figure 2. Room temperature Mössbauer spectrum of the Oregon fulgurite, with accompanying quadrupole splitting distribution. Note that some of the distribution is at low values of quadrupole splitting, representing some contribution from Fe³⁺.

Future work will include analyses of several more fulgurites, as well as reduced Fe-Si metal blebs from the Connecticut fulgurite. In addition, the original material will be analyzed in order to compare Fe oxidation states before and after heating. The before and after compositions and oxidation states will allow accurate thermodynamic modeling to order identify the reduction mechanism. The modeling can then be applied to more other materials such as chondrules, lunar regolith agglutinates, tektites, and impact glasses.

References: [1] Laurretta D. S. et al. (2001) *GCA*, 64:8, 1337-1353. [2] Anand M. et al. (2002) *LPS XXXIII*, 1653. [3] Essene E. J. and Fisher D. C. (1986) *Science*, 234, 189-193. [4] Sheffer A. A. et al. (2003) *LPS XXXIV*, 1467. [5] Dyar M. D. (2003) *MaPS*, 38, 1733-1752. [6] Rancourt D. G. and Ping J. Y. (1991) *NiMiPR:B*, v58, 85-97. **Acknowledgements:** This work was supported by NASA grant NAG5-11493.