INVESTIGATING REDOX CHANGE DURING IMPACTS. S. E. Roberts[1], A. A. Sheffer[2], M. C. McCanta[1], M. D. Dyar[3,4] and E. C. Sklute[3,4], [1]Dept. of Earth and Planetary Sciences, Univ. of Tennessee, Knoxville TN 37996 (srober76@vols.utk.edu), [2]Space Studies Board, Washington D.C., 20001, [3]Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075 [4]Planetary Science Institute, 1700 East Fort Lowell, Suite 106, Tucson, AZ 85719.

Introduction: Melts preserve evidence of the oxygen fugacity (*f*O_2) conditions during their formation as recorded in the oxidation state of multivalent elements [e.g. 1,2]. Redox states can reveal primary *f*O_2 conditions and are commonly used to infer conditions in magma source regions and planetary interiors [e.g. 1]. However, post-formation processes such as mineral fractionation and metasomatism [e.g., 3,4,5] may alter redox states. We focus here on shock metamorphism, which may result in significant geochemical changes [6,7]. These potential changes complicate interpretation of the geochemical history of a planet.

Shock-metamorphosed materials are relatively uncommon on Earth and many have been altered through additional geologic processing. Lightning strikes can be good analogues for impact processes as they result in similar physical conditions [8]. Because lightning strikes are non-discriminatory in their target materials and can produce melts (i.e., fulgurites) [9,10], they permit the potential effects of shock as a function of target composition to be evaluated.

Previous studies have investigated bulk changes in oxidation state in fulgurites [11,12,13,14,15]. Reduction of oxides seen in fulgurites may be explained by thermodynamic breakdown at superheated temperatures, and/or by shock wave propagation from the lightning strike [12]. Recent discoveries of shocked minerals in fulgurites support the latter theory and also support fulgurites as good analogs for impact events [8,15,16].

To investigate the changes that occurs in oxidation state during impact, $Fe^{3+}/\Sigma Fe$ was measured using Mössbauer spectroscopy and x-ray absorption spectroscopy (XAS) in fulgurites and Trinitite and corresponding pristine unshocked country rocks [19].

Methods: Nine fulgurites and a sample of trinitite were selected for this study (Table 1). Images and chemical analyses were collected from thick sections to provide a baseline understanding of rock type. Back Scattered Electron (BSE) images were collected on a Phenom Pro XL scanning electron microscope (SEM) at the Univ. of Tennessee. Major and minor element analyses were collected by electron probe microanalysis (EPMA) using a Cameca SX-100 at UTK. Bulk samples representing pristine (to the extent possible) material and fulgurite glasses were handpicked for Mössbauer analyses, which were acquired at 295K using a source of 100-60 mCi ^{57}Co in Rh on a WEB Research (now SEE) Co. WT302 spectrometer (Mount Holyoke College).

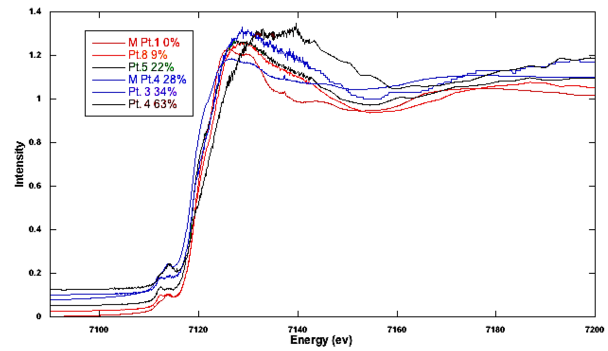

Figure 1. XAS data for individual analyses of Starke fulgurite.

To investigate the localized effects of redox state, XAS spectra of two select samples (Starke and Oregon), were collected at the GeoSoilEnviroCARS beamline at the Advanced Photon Source at Argonne National Lab using a spot size of 1 x 1 µm (Figure 1). Their Fe redox states were predicted using an updated version of the model in [20].

Results: BSE and EPMA analysis show that glass composition is generally very heterogenous. Veins and pockets of brighter glass are often found delineating borders of relict minerals that were melted. Shattered and incompletely melted mineral grains are observed in and adhered to the outside of fulgurite melts.

Table 1. Samples studied and Mössbauer results

Sample	Country Rock	Grain Size (mm)	% Fe^{3+} CR*	% Fe^{3+} Fulg.*
Algeria	Granite	0.15-0.2	40	19
Black Rock	Quartz sand	~0.5	48	37
Monahans	Quartz sand	~0.2	100	58
Mount Ararat	Basalt rock	0.05-0.5	24	30
Oregon	Basalt talus	0.2-0.4	18	30
Pecos Plain	Quartz sand	0.1-1.2	100	46
Starke	Quartz sand	~0.2	57	58
Sugarland	Quartz sand	0.2-0.4	58	47
Trinity	Arkosic sand	0.1-0.3	76	27
West Virginia	Sandstone	~1.0	12	33

*CR = country rock, Fulg = fulgurite glass

Mössbauer data (Table 1) largely show the expected result of reduction from the lightning strikes. The few exceptions to this result can be explained away by poor separation of the country rock from the starting material or difficult-to-interpret spectra. Consistent with the idea that shock should be an inherently reducing process, Fe metal was identified in several but not all the samples. This variation may have multiple indistinguishable causes: distribution of Fe in the country rock, the pressure and temperature extent of the lightning strike, and the magnitude of Fe in the bulk rock overall. The overall imprecision in our bulk analyses thus led us to pursue an alternative approach by using XAS to study redox at microscales.

In-situ XAS spot analysis of the Starke, Florida fulgurite reveals significant variation in Fe^{3+} within the fulgurite glass (Figure 2). The percentage of Fe^{3+} ranges from 0-63% with an average of 17%. The darker, primary fulgurite glass shows the widest Fe^{3+} variation from 0 to 63%, with a change from 4 to 63% Fe^{3+} occurring within 200 μm. Brighter melt has less variation in Fe^{3+} with a range of 0 to 29% Fe^{3+} and an average of 20%. Location within the fulgurite (exterior versus interior) does not appear to influence Fe^{3+} concentration.

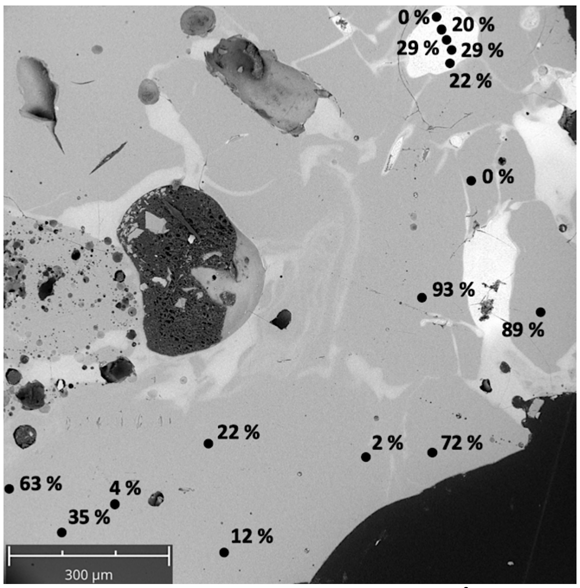

Figure 2. XAS spot locations with predicted Fe^{3+} and spectra for the Starke fulgurite.

The Cline Butte, Oregon fulgurite also reveals spatial variation in Fe^{3+} within the glass, from 1 to 11% with an average of 7%. Again, Fe^{3+} concentration does not appear to be correlated with location in the fulgurite. The streaks of brighter melt here do not appear to be more reduced or oxidized compared to the darker melt. However, the fulgurite has been reduced compared to the non-impacted country rock.

Discussion: Composition of target material and texture exert limited control on the redox changes observed in fulgurites. The basalt fulgurite Mount Ararat appears oxidized relative to the starting Fe^{3+} of the country rock, consistent with the results of [14] from a gabbro fulgurite, but this may the result of bulk analytical issues. As the XAS data shows, Fe^{3+} concentrations can vary widely and a bulk measurement can lead to suggestions of overall shock oxidation when in fact melt reduction is observed (i.e., Oregon). The West Virginia rock fulgurite is also oxidized relative to its host sandstone, despite the suggestion of [9] that a lack of Si-rich glass may limit oxidation. The other quartz-rich rock fulgurite studied here (Algeria) was formed in granite, and is reduced compared to the country rock. Again, the amount of quartz does not appear to affect redox changes, so there is no apparent relationship between reduction and quartz content. However, imaging and in-situ EPMA analyses demonstrate the heterogeneity of fulgurite melts, which often contain a mixture of relict phases that have been melted together and strongly suggest that microanalytical in-situ techniques are required to fully constrain the redox characteristics.

Implications: Some contribution to the reduction by a process similar to electrolysis cannot be ruled out by these samples. If this process were active, the degree of reduction would correlate with lightning duration and the volume of melted glass. The longer that the lightning strike channel is in contact with the surface, the more reduced and glassy the sample would become. In this case, the interior of the glassy tube should be more reduced than the exterior. Because source materials respond differently to lightning strikes, this comparison can only be made within single source material groups. The sand fulgurites are the only group with enough samples to compare glass thicknesses; however, these fulgurites have very thin tubes of glass making it impossible to separate the inside from the outside. The best sample set to evaluate the contribution from electrolysis would be several large fulgurites of the same rock type (e.g., basalts).

Summary: Shock metamorphism results in significant redox heterogeneity though it is overall reducing. Composition and density of the target material likely determine the degree of redox change, making modeling of alteration by shock metamorphism difficult.

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