REDUCTION OF SILICATES AT HIGH TEMPERATURE: FULGURITES AND THERMODYNAMIC MODELING.

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Introduction: The high temperature 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]. In this work, we present a new fulgurite that contains many reduced phases, and we model condensation of the Al-Fe-Si-O system.

Petrographic Studies: Petrographic studies have begun on a new fulgurite from Farmington, Connecticut. It was formed by the combined energies of a lightning strike and a downed aluminum high voltage power line (27 kV). The power line remained active for several hours after the lightning strike.

The strike occurred on the edge of a paved road and traveled laterally into the sand and gravel berm parallel to the roadway. The downed power line heated an area several feet away from the strike; however, a melted area connects the two power sources. The source material included sand and crushed basalt roadbed fill with asphalt providing abundant carbon on the surface. Melted aluminum from the power line also contributed to the final composition. The fulgurite branches 6 meters laterally at maximum depth of 0.5 meters.

The fulgurite contains at least five distinct areas characterized by different degrees of heating and reduction. Under the power line and nearest to the surface is an area of dark green glass with large vesicles. Further underneath the surface and connecting to the strike area is degassed dark green glass with centimeter-sized Fe metal inclusions. Directly at the surface of the lightning strike is a small area of gray glass containing Fe-Si-Al-Ti metallic droplets. Below the surface and extending laterally away from the strike is frothy, light green glass with smaller metallic droplets. Farthest away from the strike and the power line is an area of tubular, linear fulgurite structure. Partially melted rocks cemented by glass coat the outsides of all the samples.

Microprobe studies have begun 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. Preliminary analyses indicate a large array of reduced metals, including metallic Si, Fe, Fe_2Si, $FeTi(Al,Si)_2$, $Fe(Al,Si)_3$, $Fe(Al,Si)_5$, and Fe_5AlSi_{10}. (Figure 1) Many of the metallic species appear to be iron silicides similar to those found previously in fulgurites, but here aluminum is replacing the silicon. As well as the metals shown in Figure 1, this fulgurite piece also consists of large amounts of heterogeneous silicate glass with relict SiO_2 crystals and Al_2O_3 which appears to be growing from the melt.

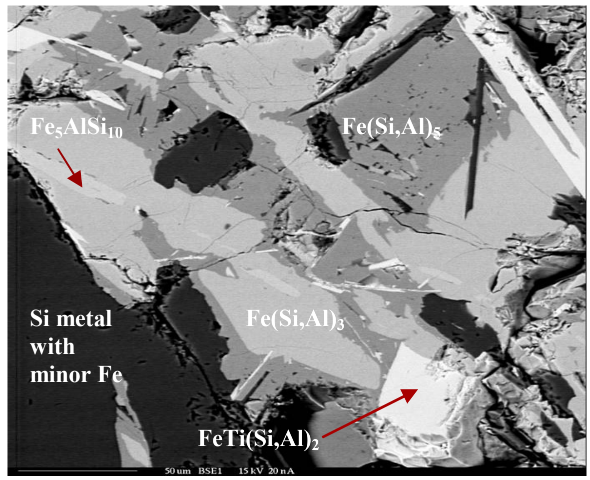

Figure 1: Backscattered electron image of a metallic area in the Farmington, Connecticut fulgurite. Image is 250 μm wide.

Thermodynamic Modeling: Thermodynamic calculations were performed using the equilibrium module in the HSC Chemistry package [5] to model the formation of fulgurite glass and investigate possible reduction mechanisms.

The predominant elements in the CT fulgurite are Si, Al, Fe, and O. For the initial modeling, only these elements and their compounds are considered. Figure 2 represents the cooling of a fulgurite glass composition (87.6 moles of SiO_2, 7.4 moles of Al_2O_3, 5 moles of FeO) with added aluminum metal (10 moles). Carbon is not considered here; however, its effect would be to further reduce the system.

The final equilibrium composition consists of 70 moles of SiO_2, 12.5 moles of Al_2SiO_5, and 5 moles of FeSi. FeO is stable from 2100 - 3400 K, and Al_2O_3 is stable from 3000 to 3650 K.

Discussion: The thermodynamic modeling approximates the degree of reduction seen in the fulgurite; however, it does not yet match the particular mineral species. Al_2SiO_5 has not yet been identified in the samples, though it is expected. Al_2O_3 is present, but it coexists with the Fe-Si-Al metals. This suggests that the sample is more reduced than the model predicts. Also, thermodynamic data is not present for all of the metallic phases.

In this sample aluminum appears to be controlling the chemistry. The same starting composition without any added aluminum metal would not result in the reduction of iron. Other reduced metallic areas (Fe and Fe-silicides) in different samples of the fulgurite do not contain Al. It is likely that the reduction in those areas is the result of carbon derived from the asphalt.

Aluminum may be very important to consider when modeling other reduced products, such as the Si-rich Fe metal in lunar regolith agglutinates.

Further modeling will be done with approximate lunar soil compositions to help evaluate this hypothesis. Continuing work on the Farmington, CT fulgurite will include analyzing samples from all of the areas characterized by different levels of reduction as well as positive identification of the metallic phases. Additional reduction mechanisms will also be modeled, such as the efficacy of the mechanical separation of solid and liquid from gas.

References: [1] Lauretta 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] Wasserman et al. (2002) *LPS XXXIII*, 1308. [5] Eriksson G. and Hack K. (1990) *Metall. Trans., 21B*, 1013-1023.

Acknowledgements: This work was supported by NASA grant NAG5-11493.

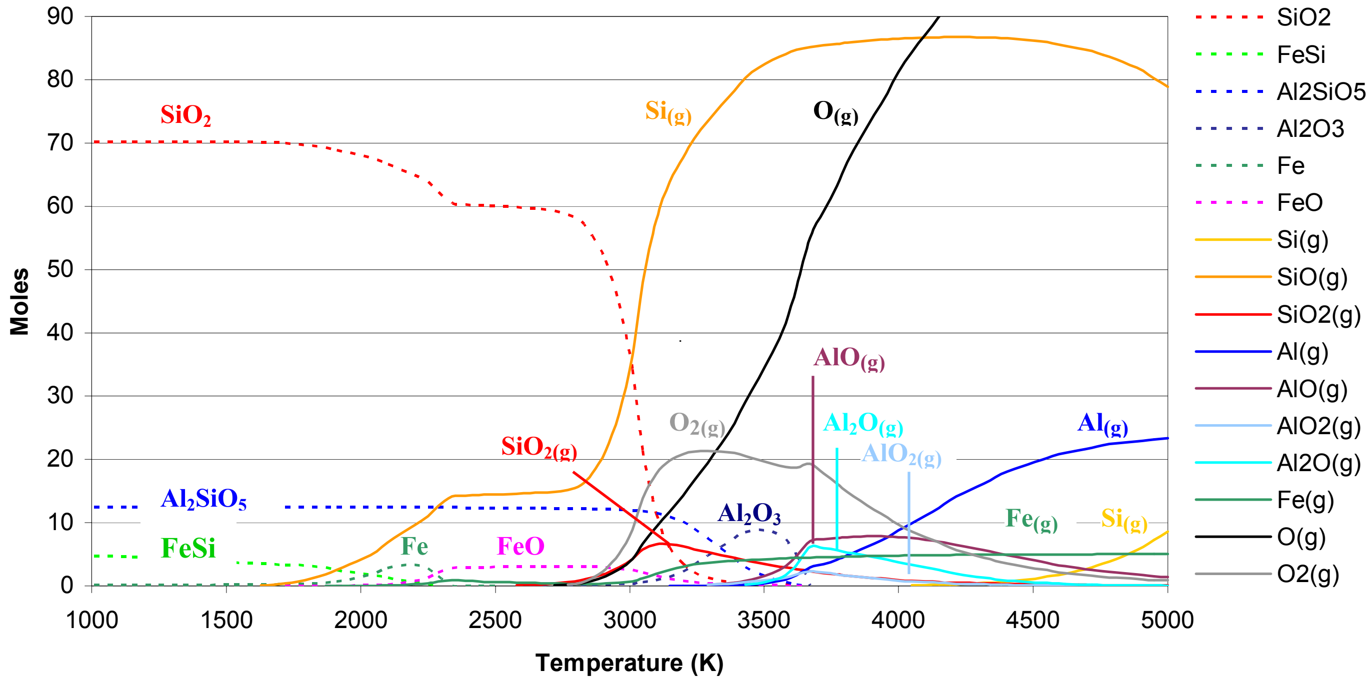

Figure 2: Thermodynamic model of a simplified fulgurite composition shown in molar concentrations of species. Initial parameters are 87.6 moles of SiO_2, 7.4 moles of Al_2O_3, 5 moles of FeO, and 10 moles Al at 1 bar pressure. Note the temperature (2250 K) where Fe and FeSi metals are initially stable upon cooling. Condensed phases are represented by dotted lines, and gases are represented by solid lines.