

CHAPTER 5 : SUMMARY AND FUTURE DIRECTIONS

The oxidation state of Fe can be a sensitive indicator of planetary processes. Reduced Fe, in the Fe^{2+} or Fe^0 state, is found in many products of rapid, high temperature processing such as in tektites, fulgurites, and lunar regolith agglutinates. Previous research concerning these products has often relied upon a reducing agent such as hydrogen or carbon to remove oxygen from the Fe. Experiments using laser evaporation to simulate impact heating have indicated that a reducing agent is not necessary and that the reduction is intrinsic to the rapid heating and cooling itself (Sasaki et al., 2002; Sasaki et al., 2001; Yakovlev et al., 2003). By analyzing a suite of reduced fulgurite samples and modeling the chemical formation of moldavite tektites and lunar regolith agglutinates, this work provides firm evidence that the rapid, high temperature processing by lightning strikes and impacts is indeed intrinsically reducing.

Chapter 2 presents the results of an electron microprobe and Mössbauer spectroscopy study of ten fulgurites, a sample of trinitite, and their unmelted source materials. Nine out of eleven samples are reduced compared to their starting materials, one appears oxidized, and one has too little Fe to measure oxidation states accurately. Four of the samples have been reduced enough to form Fe metal. Only one of the nine reduced fulgurites was found to have traces of carbon from plant material that could have contributed significantly to the reduction. The report of an oxidized sample may be an error in sampling caused by accidental inclusion of Fe oxide crystals from the unmelted material into the handpicked glass sample material. The results support the theory that

the chemical reduction of Fe was caused by the breakdown of oxides during the intense energy input of the lightning strike and the rapid cooling afterwards.

Questions remain concerning the specifics of fulgurite formation, and as is common for most projects involving physical materials, more samples and analyses are always desired. These analyses are not yet enough to determine what causes one fulgurite to become more reduced than another, only that fulgurites are in general reduced. Additional samples, particularly more large Fe-rich rock fulgurites, would help to determine the direct contribution to the reduction by the electrical environment of the lightning strike itself. A larger suite of sand fulgurites is needed to determine the effect of grain size and sand composition on the morphology and reduction of the resulting fulgurites. X-ray diffraction characterization of the unnamed iron silicide found in the West Virginia fulgurite, FeTiSi_2 , could be used to confirm this as a new mineral only previously described in Essene and Fisher (1986).

Moldavite tektites, associated with the Ries crater in Germany, have been shown to be extremely reduced compared to Earth's surface sediments (Fudali et al., 1987; Rossano et al., 1999). In Chapter 3, the BNR thermodynamic code based upon Smith and Missen (1982) is used to investigate how isentropic cooling from a highly shocked state affects the chemistry of possible tektite starting materials. Beginning with simplified compositions of sands sampled from drill holes and outcrops near the Ries crater for the moldavite starting materials (Engelhardt et al., 2005), the equilibrium compositions and total entropies of a liquid + vapor + single species Fe system is calculated for a wide range of temperature and pressure. By examining the compositions

along several isentropic cooling paths, we look for the entropy, temperature, and pressure where the liquid best matches moldavite compositions. The best match to an average moldavite is a mixture of surface and subsurface sands along a 4500 J/kg-K isentropic cooling path at 3800 K and 1000 bars, consistent with an asteroid impact. This is also the best starting material and isentropic cooling path to form the Bohemian (1 bar and 3154 K) and Bohemian: Radomilice sub-strewn fields (1000 bars and 3800 K). At the same entropy of formation, the compositions of the Lusatian and Moravian sub-strewn fields agree more closely with a starting material of entirely surface sands. These results suggest that the moldavites farthest away from the Ries crater formed early from the uppermost surface layers under the impact, and the moldavites found closer to the crater formed later from the excavation and mixing of subsurface sediments into the surface layers.

Although the trends are clear, the starting material compositions used in the model do not yet exactly reproduce moldavite compositions. The model is limited by the inclusion of only six elements, and the future addition of more elements to the model should help increase the accuracy of the results. The models do clearly show that the possible isentropic cooling paths experienced by moldavites are intrinsically reducing for Fe. When the starting material contains Fe in the 3+ oxidation state as is common on the surface of the Earth, all or most of the Fe becomes reduced to the 2+ oxidation state in the tektite liquid at every modeled entropy. If the starting material begins with reduced Fe in the 2+ state, the Fe remains reduced. As the system of liquid and vapor cools and decreases in pressure, a blocking temperature and pressure are reached where the liquid

can no longer equilibrate with the vapor. The oxygen released by the reduction of Fe from Fe^{3+} to Fe^{2+} remains in the vapor phase and is separated from the quenched liquid. Adding Fe metal to the ideal mixing of the silicate liquid phase facilitates the formation of Fe metal over a wide range of conditions. Fe metal has not been identified in moldavite tektites or in any other tektite strewn field, so the assumption of Fe metal mixing may not be appropriate for tektite formation models. The experiments by Genshaft et al. (2001) indicated that Fe metal saturation in silicate melts occurred only at conditions of high Fe content and very reducing conditions. Moldavite tektite source materials may not contain enough total Fe to allow metal formation.

Chapter 4 uses the BNR code to model the formation of lunar regolith agglutinates from lunar surface sediments by micrometeorite impacts. The majority of the Fe on the lunar surface is in the 2+ state, but it is reduced to Fe metal inside agglutinate glass and in rims around soil grains. Using mare and highland soils as starting materials, the calculated liquid compositions along several isentropic cooling paths are compared to mare and highland agglutinate compositions. The assumption of Fe metal miscibility is more appropriate for lunar conditions than for the Earth's surface. Lunar soils contain a larger percentage of Fe, and the majority of the Fe begins in the 2+ oxidation state. The models results indicate that Fe metal as a separate phase is not thermodynamically stable anywhere along isentropic cooling paths for lunar soils. To investigate the metal formation, Fe liquid is assumed to be in solution with the silicate liquid phase for the agglutinate formation model.

With the assumption of metal miscibility, Fe metal liquid does form from both the mare and highland soil starting materials on all modeled isentropic cooling paths. Unfortunately, the overall compositions of mare and highland agglutinate glasses are more difficult to reproduce. The simple separation of liquid from vapor at a blocking temperature is not adequate to explain the trends of increases and decreases of elements in the glasses compared to the starting soils. When the vapor phase is allowed to partially redeposit and mix with the liquid phase, the resulting liquid better reproduces mare agglutinate glass. The results are further enhanced if a fraction of the Fe(g) in the vapor is assumed to directly deposit as Fe metal, such as in the vapor-deposited rims around soil grains, and not allowed to recombine with the liquid. The best condition for producing mare agglutinate glass is using the $<10 \mu\text{m}$ fine soil fraction along the 8000 J/kg-K cooling isentrope at 100 bars, 4370 K with 95% of the vapor redeposited and 50% of the Fe(g) condensed as Fe metal. The model is unable to reproduce all of the trends of element increases and decreases from the mare soil to agglutinate glass; the mole fraction of Mg in the results is higher than that in agglutinate glass at all modeled conditions. Highland agglutinate glasses are much more difficult to model. The Al percentage in the final glass is always too high, and this cannot be remedied by partial vapor redeposition. The Al must either be preferentially removed from the highland soils during agglutinate formation or initially prohibited from melting.

The combination of physical investigations and chemical modeling is a powerful method for elucidating the effects of the rapid, high temperature processing of silicates, especially with respect to the oxidation state of Fe. Evidence for the reduction of Fe by

impact should be found on every solar system body with a silicate rock surface. On Earth this chemical model could be used to investigate the formation of the other tektite types, and may be able to help find the source crater of the Australasian tektite strewn field by constraining the composition of the surface sediments. This model could also be applied to predicting the compositions and Fe oxidation states of impact-produced surface glasses on other bodies, and it could be used to investigate the formation of chondrules from primitive solar system materials by rapid heating. The composition-driven thermodynamic modeling of isentropic cooling can be applied to many more problems in planetary science.