REDOX REACTIONS DURING THERMAL AND DECOMPRESSION EVAPORATION OF IRON-BEARING SILICATE MELTS

(THE PROBLEM OF IRON VALENCE STATE IN TEKTITES AND IMPACTITES)

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Introduction

The study of chemical compositions of tektites and same types of impactitic glasses is evidence of redox reactions availability during their formation with change of valency state of iron and other elements. Tektites are characterized by extremely low Fe³⁺/Fe²⁺ ratios in comparison with acid volcanic and other Earth's crust rocks that could be source-target rocks for tektites at impact events. Possible reasons of iron oxidation state change in impact processes are debated [1]. The aim of this contribution is further development of early proposed suggestion that reduction reactions with the assistance of ions of iron and other elements in consequence of oxygen regime change at melting and evaporation of the terrestrial matter during powerful impact events are the main reason of tektites and some types of impactites reduced state [1-3]. These reactions in impact melts must inevitably take place in the process of adiabatic decompression of the matter at very high temperatures after its impact compression independently from system openness degree.

Oxidation and reduction of iron ions during evaporation oxide melts

Thermodynamic analysis of relatively simple systems Fe-O and SiO_2 -FeO-Fe $_2O_3$ allows to conclude that evaporation of oxide melts containing ferrous and ferric iron ions with temperature increase or pressure decrease must be accompanied by redox reactions both under open and closed conditions. The reason of this phenomenon is an incongruent character of melt evaporation. Depending on initial oxidation degree of iron either oxidation or reduction of iron is possible that results in the attainment of some limit Fe^{3+}/Fe^{2+} ratio in residual melt. Fig. 1 demonstrates these possibilities during isothermal decompression of melts in Fe-O system. In consequence of evaporation with pressure decrease from P_1 to P_2 the initial relative oxidized composition $\bf a$ is reducing and initial more reduced composition $\bf b$ is oxidizing. Both melts tend to Lm composition that evaporates congruent under these conditions.

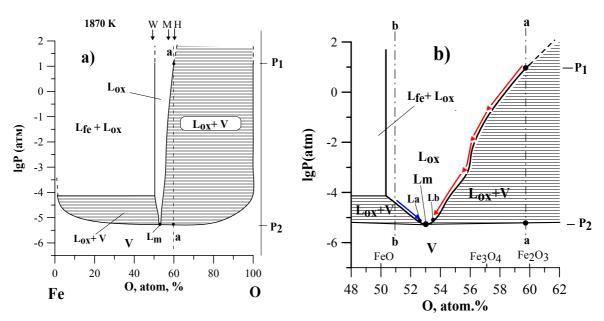


Fig.1. a) - Isothermal section of the Fe - O system at 1870 K, constructed using data from [4]; b) - The fragment of this section on a large scale. L_{fe} - metallic iron melt, L_{ox} - oxides iron melt, L_{m} - oxides iron melt with congruent evaporation with pressure decreasing. Shaded phase fields – equilibration of melts and vapor. Arrows shows the change of parts of residual liquids in the decompression process of initial compositions $\bf a$ and $\bf b$.

 SiO_2 -FeO-Fe $_2O_3$ system melts evaporation induced by temperature increase or pressure decrease leads to iron redox state change in residual melt (similar to that in the Fe – O system). Decompression evaporation of initial relatively oxidized melts, containing more Fe_2O_3 than W_m (located from the right of SiO_2 - W_m line on fig.2) is accompanied by the formation of vapor phase with O/(Fe+Si) ratio higher than that in melt. As a result Fe_2O_3/FeO ratio in melt should increase, i.e. the melt will be more reduced. On the other hand the decompression evaporation of reduced melts (located from the left of SiO_2 - W_m line on the fig.2) leads to formation of vapor with $[O/(Fe+Si)]_{vapor} < [O/(Fe+Si)]_{melt}$ and so to oxidation of ferric iron in melt. Fe^{3+}/Fe^{2+} ratio in the melt during decompression reduction (or oxidation) will tend to the same limit value, that corresponds to conditions when $[O/(Fe+Si)]_{vapor} = [O/(Fe+Si)]_{melt}$. Apparently this Fe^{3+}/Fe^{2+} limit value for SiO_2 -FeO- Fe_2O_3 melts and melts of more complicated natural composition will not coincide with the limit value for oxide melts of the Fe-O system through the influence of other components in melt.

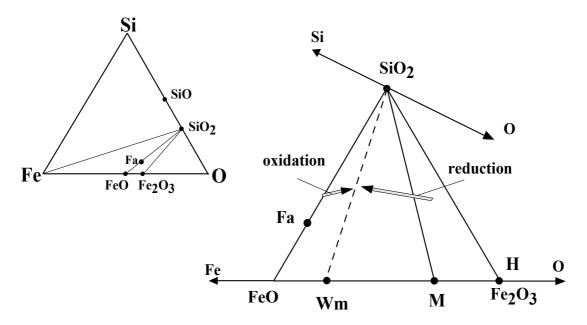


Fig.2. Evaporaton effect on redox state of melts in the SiO_2 -FeO-Fe $_2O_3$ system. Fa – faylite, W_m – wüstite composition with congruent evaporation at given temperature, M – magnetite, H – hematite. Arrows show trends of melt compositions change and their redox state during evaporation. Dashed line – assumed location of melt compositions with congruent evaporation.

Conclusion

Redox reactions inevitably have to occur in oxide melts of Fe-O and SiO_2 -FeO-Fe₂O₃ systems, containing various ions of iron, in consequence of incongruent evaporation of melts during pressure decrease under high temperature conditions. This property of Fe-bearing systems is important for understanding the redox state of melts forming in impact processes as a result of melting and evaporation of crust matter [5]. Adibatical decompression of high temperature impactitic melts should be accompanied by their reduction (Fe³⁺/Fe²⁺ decrease) in comparison with initial matter of the target. The main condition for reducing reactions to proceed is full melting of matter, involved in the impact process, and the attainment of very high temperatures (>1700-2000°C) that are characteristic for impact bombs and tektites formation at the unloading stage. The higher is the temperature the stronger is the effect of decompression reduction. Anomalous low Fe³⁺/Fe²⁺ ratios in tektites are apparently the result of decompression reduction of the most high temperature impact melts.

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