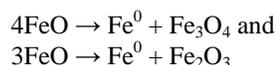


THE ROLE OF REACTION OF DISPROPORTIONATION IN THE REDOX BEHAVIOR OF IRON DURING IMPACTS.

M. V. Gerasimov¹, O. I. Yakovlev^{1,2}, Yu. P. Dikov^{1,3}. ¹Space Research Institute, RAS, Moscow, 117997, Profsoyuznaya, 84/32, mgerasim@mx.iki.rssi.ru, ²Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Moscow, 117975, Kosygin st., 19, yakovlev@geokhi.ru, ³Institute of Ore Deposits, Petrography, Mineralogy and Geochemistry, RAS, Moscow, 109017, Staromonetny per., 35, dikov@igem.ru.

Introduction: The time and conditions of formation of metallic iron phase is an intriguing problem in the evolution of terrestrial planets. There is a certain link between formation of metallic iron phases and high-temperature impact processing of silicates. Such link is present in natural impactites (e.g. in meteorites and lunar samples [e.g. 1,2]) as well as in impact and high-temperature experiments [e.g. 3,4]. The mechanism of redox behavior of iron during impacts comes to be important for evaluation of early evolution of planetary materials.

Three main processes are responsible for the reduction of iron: 1) thermally driven dissociation of oxides at high temperature; 2) chemical reactions of iron oxide with reducing agents (e.g. carbon, hydrogen, sulfur, etc.); and 3) reaction of disproportionation. Reaction of disproportionation can be presented by two types:



which does not have principal difference. Formation of iron metallic phase here is accompanied by formation of iron in highly oxidized form of Fe^{3+} . Reaction of disproportionation in a closed system (without loss of oxygen and no interaction with other elements) leads to formation of reduced and highly oxidized iron in proportion $\text{Fe}^{3+}/\text{Fe}^0 = 2$.

Reaction of disproportionation is considered to play sufficient role for mantle – core separation and it was investigated at relevant temperatures and static pressures [e.g. 5,6]. The possibility of such reaction at conditions of hypervelocity impact process was not investigated. The aim of the present work was to investigate redox paths of iron in simulated impact vaporization process.

Experimental technique: The experiments were performed using the pulse-laser setup and methodic described in [7]. The experiments were performed in He at 1 atm. pressure and room temperature. A Ni-foil was mounted in the path of the vapor expansion at the distance ~7cm from the sample to collect condensed vapor products.

Films of fluffy condensed material were etched layer by layer by argon ions (with the exposition equivalent to removal of 20-40 nm layer of a solid pyrex glass) and exposed surface every time was analyzed using X-ray photo electron spectroscopy technique to get both elemental composition and charging state of elements. Layer by layer analysis provides

chemical analyses of a cross section of the condensed films.

Experiments were performed using various mafic and ultramafic samples. Here we present results of two typical experiments. Starting sample in one case was augite with composition (mol %): Si - 18.0; Al - 4.3; Fe^{2+} - 2.1; Fe^{3+} - 0.4; Mg - 7.1; Ca - 6.1; Na - 2.0; O - 59.7. Another experiment was performed using the sample which was a pressed mixture of powders of peridotite with MnO_2 oxide. The main elements composition of the second sample was (mol %): Si - 10.1; Al - 0.7; Fe^{2+} - 3.8; Fe^{3+} - 2.0; Mg - 14.2; Ca - 1.1; Mn^{4+} - 6.1; Mn^{3+} - 2.6; O - 59.4.

Results: The bulk thickness of condensed film in experiment with augite was 220 nm of solid pyrex glass equivalence and the same for experiment with peridotite+ MnO_2 oxide sample was 480 nm. The concentration profile of iron in different charging states through the thickness of the condensed film from the experiment with augite is shown in Fig. 1.

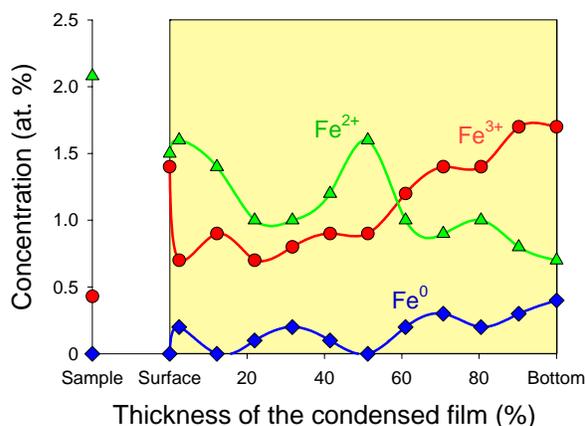


Fig. 1. The concentration profile of iron charging states through the thickness of the condensed film from the experiment with augite. Symbols on the ordinate show respective concentration in the starting sample.

Fig. 1 shows that the condensate contains metallic iron and its origin is accompanied by sufficient increase of iron in Fe^{3+} state. Both Fe^0 and Fe^{3+} concentrations have correlative increase to the bottom of the condensed film with sufficient anti-correlative decrease of iron in Fe^{2+} state.

Fig. 2 shows correlative increase of both $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}^0/\text{Fe}^{2+}$ ratios through the thickness of the condensed film from the experiment with augite. The in-

crease of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is 4 times higher than that of $\text{Fe}^0/\text{Fe}^{2+}$.

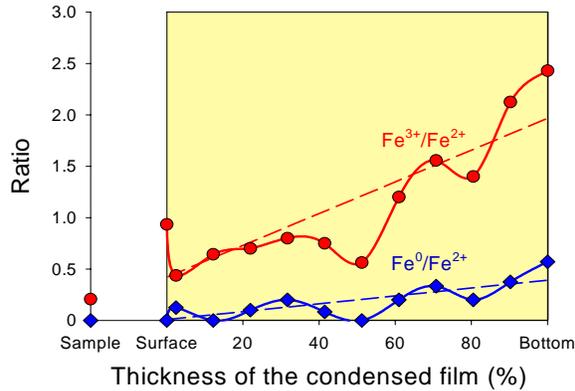


Fig. 2. Profiles of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}^0/\text{Fe}^{2+}$ ratios through the thickness of the condensed film from the experiment with augite. Dashed lines show linear regressions.

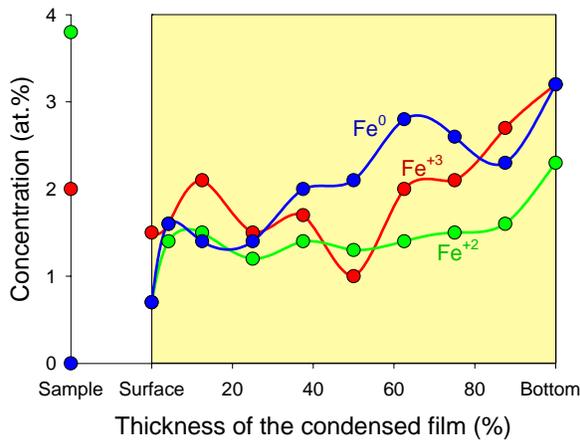


Fig. 3. The concentration profile of iron charging states through the thickness of the condensed film from the experiment with peridotite+ MnO_2 oxide sample.

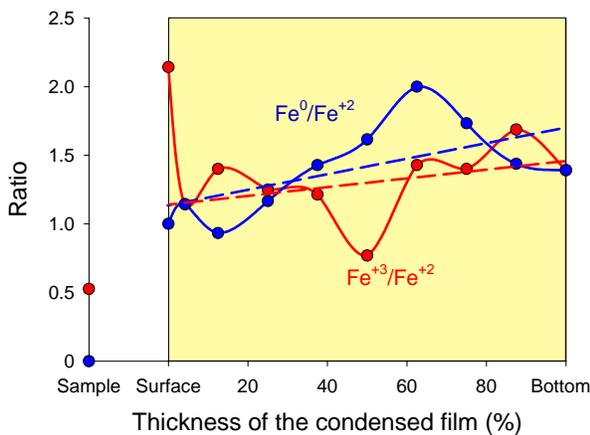


Fig. 4. Profiles of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}^0/\text{Fe}^{2+}$ ratios through the thickness of the condensed film from the experiment with peridotite+ MnO_2 oxide sample.

Fig. 3 and 4 shows the same results as Fig. 1 and 2 but for the experiment with peridotite+ MnO_2 oxide

sample. Both Fe^0 and Fe^{3+} concentrations have semi-correlative increase to the bottom of the condensed film but without reasonable anti-correlation with Fe^{2+} . Concentration of Fe^{2+} decreases compared to starting value while that for Fe^0 and Fe^{3+} increases. $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}^0/\text{Fe}^{2+}$ ratios through the thickness of the condensed film have about the same regressions with slight excess for $\text{Fe}^0/\text{Fe}^{2+}$.

Discussion: The correlative formation of Fe^{3+} together with Fe^0 with expense of Fe^{2+} is a strong evidence of reaction of disproportionation of oxygen at simulated impact vaporization conditions. Such reaction is a result of the hot and dense expanding plume. Dense cloud makes every elemental volume to behave as a closed system. Released by dissociation of FeO oxygen atoms do not leave the volume but oxidize neighbor atoms providing the formation of both Fe^0 and Fe^{3+} . Bottom layers of the condensate are corresponding to the hottest and dense parts of the plume which provide better conditions for reaction of disproportionation. The system in both experiments was not perfectly “closed” one resulting in not stoichiometric ratios of $\text{Fe}^0/\text{Fe}^{3+}$.

It is very difficult to identify the products of disproportionation in natural impactites due to high complexity of the system. The coexistence of native iron, wustite, and magnetite was identified in impactites of Janisjarvi and Gardnos craters [8]. Metal-troilite-magnetite assemblage was discovered in shock veins of Sixiangkou meteorite [9]. Analysis of the volatiles rich surface layer of Luna 16 soil sample [10], which is considered to be a result of a comet or meteorite impact, shows that it contain iron in Fe^0 , Fe^{2+} and Fe^{3+} states in proportion 1.0:1.4:0.8 respectively. The high concentrations of both Fe^0 and Fe^{3+} compared to Fe^{2+} state speaks in favor of their inherited nature rather than oxidation at terrestrial conditions. The process of oxygen disproportionation during an impact event can be here a real mechanism of formation of such strange assemblage as native iron, wustite, and magnetite.

Acknowledgment: This work was supported by RFBR grant 05-05-64198.

References:

- [1] Mehta S, Goldstain J.I. (1980) *Proc. LPSC 11th*, 1713-1725.
- [2] Wasson J., Kallemeyn G.W. (1990) *EPSL*, 101, No 2/4, 148-161.
- [3] King E.A. (1982) *Proc. LPSC XIII, P. 1, JGR*, 87, *Sup.*, A429-A434.
- [4] Yakovlev O.I. et al., (2006) *Geochem. Intern.*, 44, No 9, 847-854.
- [5] Shen P. et al., (1983) *Geochim. et Cosm. Acta*, 47, 773-778.
- [6] Frost D.J. et al, (2004) *Nature*, 428, No 6981, 409-412.
- [7] Gerasimov M.V. et al., (1999) In: *Laboratory Astrophysics and Space Research*, 279-329, KAP.
- [8] Vishnevsky S.A., Raitala J. (2003) *Meteor. & Plan. Sci. Suppl.*, 38, A43.
- [9] Chen M., et al., (2002) *Geochim. et Cosm. Acta*, 66, No 17, 3143-3149.
- [10] Dikov Yu.P. et al., (1998) *EPSL*, 155, 197-204.