HIGH-TEMPERATURE REDUCTION OF SLIGHTLY SIDEROPHILE ELEMENTS (V, Cr, AND Mn) IN IMPACT PROCESS. Yu. P. Dikov1,2, M. V. Gerasimov2, O. I. Yakovlev3,2. 1Institute of Ore Deposits, Petrography, Mineralogy and Geochemistry, RAS, Moscow 109017, Staromoskovskiy per., 35, dikov@igem.ru, 2Space Research Institute, RAS, Moscow 117997, Profsoyuznaya st., 84/32, mgerasim@mx.iki.rssi.ru, 3Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Moscow 117975, GSP-1, Kosygin st., 19, yakovlev@geokhi.ru.

Introduction: V, Cr and Mn are considered as lithophile elements. But deficit of these elements in the Earth’s mantle due to possible segregation into the core suggest their partially siderophile behavior during accretion. These elements are classified as slightly siderophile. There is still a problem to determine specific conditions at a stage of accretion which provided metallization of these elements. We suggested [1, 2] an experimentally proven idea about an impact-induced mechanism of high-temperature reduction of iron and other siderophile elements. This mechanism provided metallization of elements during impacts in both high-temperature impact melts and vapor phase. Here we present new experimental results which show that impact-induced high temperature provides metallization of slightly siderophile elements. This effect can contribute to the deficit of slightly siderophile elements in silicate mantles of the Earth and Moon.

Experimental technique: The experiments were carried out in a pulse-laser setup in the regime of a free generation of laser radiation [3]. The Nd glass laser had the following parameters: wavelength λ=1.06 µm, energy of a pulse ~700 J, power density of radiation ∼106-107 W/cm2, and duration of a pulse ∼10-12 s. Typical temperature under such condition is 4000-5000 K. The experiments were performed in He at 1 atm. The laser beam was focused to a diameter of ∼3 mm. It melted and vaporized a few tens of milligrams of the sample. A Ni-foil screen was installed in the path of the expanding vapor at a distance ∼7 cm from the sample to collect vapor products and dispersed droplets of high-temperature melt. Glass spherules (1-5 µm in diameter) were found on the film of the condensate. Parameters of the experiments roughly corresponded to typical conditions of melting and vaporization at impact velocity of about ≥10 km/s [3].

Starting samples were the mixtures of peridotite with oxides of V2O3, Cr2O3 and MnO2. Peridotite was selected to reflect the bulk composition of mantle material and oxides were added to enrich concentration of these elements for analytical purposes. Powders of both peridotite and each of oxides were carefully mixed and pressed into tablets. The main elements composition of peridotite was (mol %): Si - 16.7; Al - 1.1; (Fe2+ + Fe3+) - 3.3; Mg - 19.4; Ca - 0.7; O - 58.8. Three starting samples had the following compositions (without Ca and Al in the balance) (in mol %): 1) Si - 12.3; Fe - 2.4; Mg - 14.3; V - 11.7; O - 59.2; 2) Si - 15.1; Fe - 3.0; Mg - 17.5; C - 5.4; O - 59.0; and 3) Si - 12.7; Fe - 2.5; Mg - 14.8; Mn - 9.0; O - 61.0. It is worth to remind that all elements in starting samples were in oxidized state. Chemical analyses of glass spherules were performed using PHI 660 Scanning AUGER Microprobe. Chemical analyses of condensates were performed using XPS technique.

Results: a) analyses of condensates. XPS analyses of condensates showed that interested elements were present in condensates in divers charging states from oxidized to reduced ones. XPS spectra distinctly reveal the presence of metallic states of vanadium (V0), chromium (Cr0), and manganese (Mn0), together with metallic state of iron (Fe0). Analyses of condensed films in their depths (after sequential removal of layers of the condensates by means of etching by Ar+ ions) showed anti-correlation of Fe0, V0, Cr0, and Mn0 concentrations with concentration of oxygen (Fig. 1 and 2 demonstrate respective data in experiment with Per + MnO2 sample). Average compositions of condensates were (mol %): 1) (Per + V2O3 sample) Si - 19.1, Fe2+ - 3.1, Fe0 - 1.9, Mg - 11.8, Ca - 1.5, V4+ - 0.7, V3+ - 3.1, V0 - 0.7, O - 58.2; 2) (Per + Cr2O3 sample) Si - 18.4, Fe2+ - 3.2, Fe0 - 1.6, Mg - 10.4, Ca - 1.8, Cr3+ - 4.5, Cr0 - 1.2, O - 59.0; 3) (Per + MnO2 sample) Si - 16.9, Fe3+ - 1.9, Fe2+ - 1.4, Fe0 - 2.0, Mg - 14.1, Ca - 1.1, Mn4+ - 0.2, Mn3+ - 0.0, Mn2+ - 4.3, Mn0 - 1.8, O - 55.9. The average reduction of iron in condensates was ~35%, the same for vanadium, chromium, and manganese were ~15%, ~20%, and ~26% respectively.

b) analyses of spherules. Glass spherules were analyzed without extraction from the condensed film using Auger technique. Among many spherules on the surface of the condensed films we could find several ∼1 µm droplets which had sufficient conductivity. These spherules were analyzed by focused beam. Analyses show a wide diversity of compositions which reflect the variety of thermal histories of individual droplets. Spherules have a distinct deficit of oxygen. Concentration of Oxygen decreased up to 10 - 20 % compared to that in starting samples. We have calculated the Reduction Index (RI), which is the subtraction from unity of the ratio of real oxygen...
concentration in a spherule to that of a totally oxidized spherule. RI indicates how much oxygen is lacking for a complete oxidation of a spherule, or lost from an initially oxidized spherule. The value of RI circa from 25 to 70 % in experiment with Per + V₂O₃ sample, and in experiment with Per + Cr₂O₃ sample that was 13 to 50 % (Fig. 3, 4). Such a high RI is consistent with the presence of sufficient portion of metallic phases in spherules. By analogy with the composition of the condensates we can suggest that metallic phases are mainly composed of iron, vanadium, chromium, and manganese. Analytical evaluation of the state of Si and Mg in some reduced spherules also indicated their reduction and the presence of up to 15 % of Si in Si⁰ state and the same for Mg⁰ was also up to 15 %.

Conclusions: Experiments show that high-temperature processing of samples resulted in sufficient reduction of iron and slightly siderophile elements (V, Cr, and Mn) into metallic states. The main reason here is thermally driven dissociation of oxides and the loss of oxygen.

In case this mechanism provided formation of metallic phases in impacts during accretion, we can suggest that metallization of siderophile elements (including V, Cr, and Mn) with subsequent dissolution in metallic iron phases could contribute to the deficit of these elements in siliceous mantles of the Earth and Moon.


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