THERMAL REDUCTION OF SLIGHTLY SIDEROPHILE ELEMENTS AT ACCRETIONARY STAGE OF EARTH AND MOON: EXPERIMENTAL RESULTS

Yakovlev O.I. (GEOKHI RAS), **Dikov Yu.P.** (IGEM RAS), **Gerasimov M.V.** (IKI RAS)
yakovlev@geokhi.ru, dikov@igem.ru, mgerasim@mx.iki.rssi.ru

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Earth's mantle and Moon are depleted in siderophile elements as well as V, Cr and Mn. The later are in oxide state in Earth and Moon conditions, and they may be ascribed to lithophile elements. However, V, Cr and Mn had obviously siderophile properties at the impact-accretionary stage of the Earth – Moon system. So, it permits to refer them as slightly siderophile element group. According to geochemical data some shortage of these elements occurs in the Earth and Moon mantle relatively to chondrite type CI, which is thought to be the initial matter at the beginning formation of Earth – Moon system [1]. In the table the modern estimates with attendant uncertainties of depletions of V, Cr, Mn in the Earth and Moon due to core formation are shown. To ascertain these values it was divided the slightly siderophile-element to Fe ratio in the model primitive mantles of the Earth and Moon by the siderophile-element to Fe in CI (i.e., assumed bulk Earth) [2].

The geochemical problem of V, Cr, Mn is to decipher the specific conditions at the accretionary stage, which predetermined their metallic (reduction) state. It is assumed that the V, Cr, Mn depletions (as well as the whole of siderophiles) was connected with core formation at the conditions of sharply reduction environments. In our previous papers [3,4] we advanced on the experimental data the concept of the thermoreduction mechanism of Fe and other siderophiles metallization. The mechanism operated in the process of impact accretion in the high-temperature impact melts and vapor phase. Here we present new experimental V, Cr, Mn results which prove that the even slightly siderophile elements may turn to metallic form in the condition of the high-temperature impact process that most probably is main reason of their deficit in the Earth mantle and Moon.

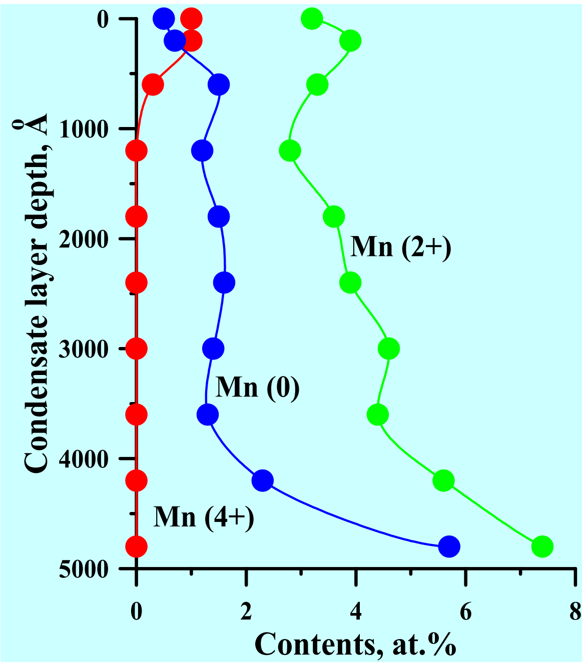

Fig. 1.

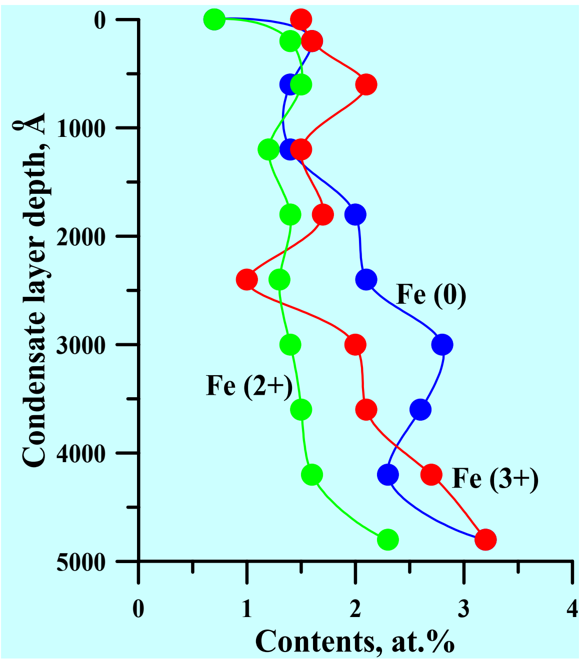

Fig. 2.

The experiments were carried out in pulse-laser setup in the regime of a free generation of laser radiation. Starting samples of the experiments were prepared as pressed tablets of carefully mixed powders of peridotite with V_2O_3, Cr_2O_3, and MnO_2 oxides. The composition of pridotite was (at.%): Si 16.7; Al 1.1; (Fe^{2+} + Fe^{3+}) 3.3; Mg 19.4; Ca 0.7; O 58.8. The composition of starting samples were (at.%): 1) (mixture of peridotite + MnO_2): Si 12.7; Fe 2.5; Mg 14.8; Mn 9.0; O 61.0; 2) (mixture of peridotite + V_2O_3): Si 12.3; Fe 2.4; Mg 14.3; V 11.7; O 59.2; 3) (mixture of peridotite + Cr_2O_3): Si 15.1; Fe 3.0; Mg 17.5; Cr 5.4; O 59.0. Laser experiments had following parameters: temperature 3000-4000K; pulse time ~10^{-3} s. Melting and vaporization of samples was performed in helium at 1 atm. It was important that all elements in starting samples were in oxidized state. The laser beam was focused to a diameter of 3 mm. It melted and vaporized a few tens of milligrams of a sample. A metal screen was installed in the spreading path of the vapor at a distance 7 cm from the sample. Glass tiny spherical particles, which were frown out from the melted sample by expanding vapor, were found on the film of the vapor-condensate.

Chemical analyses of glass spherules were made using PHI 660 Scanning AUGER Microprobe. Chemical analyses of the condensate were made with XPS technique.

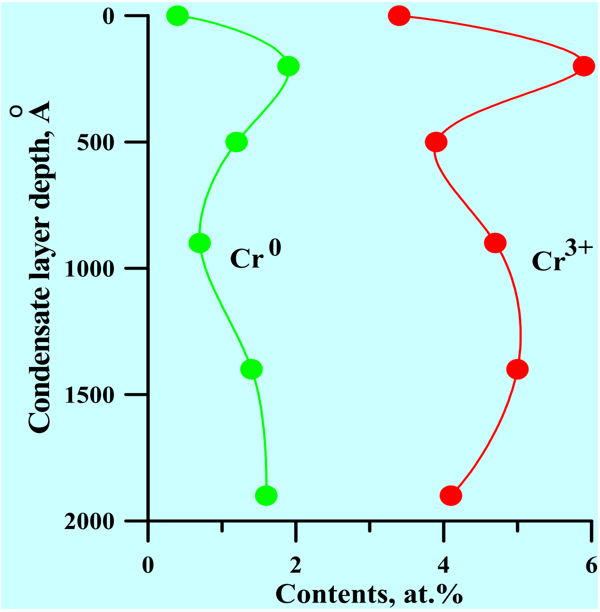

Fig. 3.

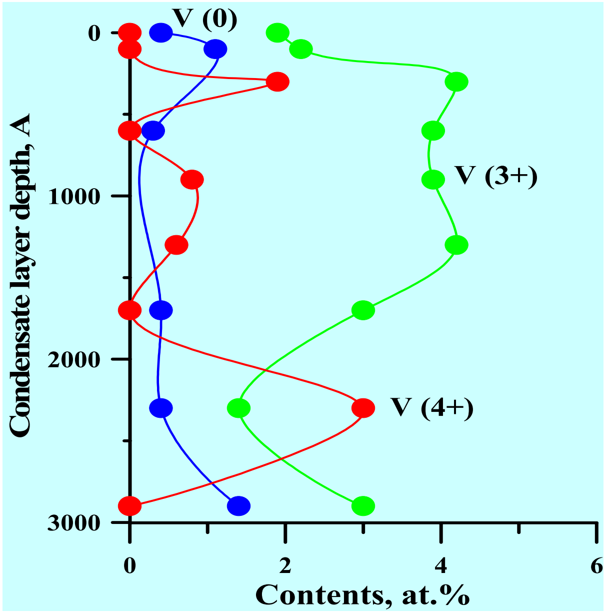

Fig. 4.

Analyses of the condensates have shown unequivocally that the reduction of Fe, Mn, V, Cr occurred partly. The average composition of the condensate in the run with V_2O_3 is (at.%): Si 19.1; Fe^{+2} 3.1; Fe^0 1.9; Mg 11.8; Ca 1.5; V^{+4} 0.7; V^{+3} 3.1; V^0 0.7; O 58.2. The average composition of the condensate in the run with Cr_2O_3 is (at.%): Si 18.4; Fe^{+2} 3.2; Fe^0 1.6; Mg 10.4; Ca 1.8; Cr^{+3} 4.5; Cr^0 1.2; O 59.0. The average composition of the condensate in the run with MnO_2 is (at.%): Si 16.9; Fe^{+3} 1.9; Fe^{+2} 1.4; Fe^0 2.0; Mg 14.1; Ca 1.1; Mn^{+4} 0.2; Mn^{+3} 0.0; Mn^{+2} 4.3; Mn^0 1.8; O 55.9. The average degree of reduction of iron in the condensates was 35%, for chromium was 20%, for vanadium - 15%, for manganese – 26%. Analytical results of the condensates are also presented in the figures (figs. 1–4). The figures are drawn identically: element concentrations in its valency form in at. % are on the horizontal axis, and the condensate thickness reduced to 100% – on vertical axis. The bottom and the surface of condensate film are also shown. Graphic results demonstrate the distributions of valency forms of Fe, V, Cr, Mn in the condensate layers.

Table.

	Earth mantle			Moon		
	Max	Aver-age	Min	Max	Average	Min
Mn	0.8	0.55	0.33	0.95	0.5	0.31
V	0.68	0.56	0.45	0.95	0.68	0.49
Cr	1.1	0.7	0.42	0.77	0.51	0.34

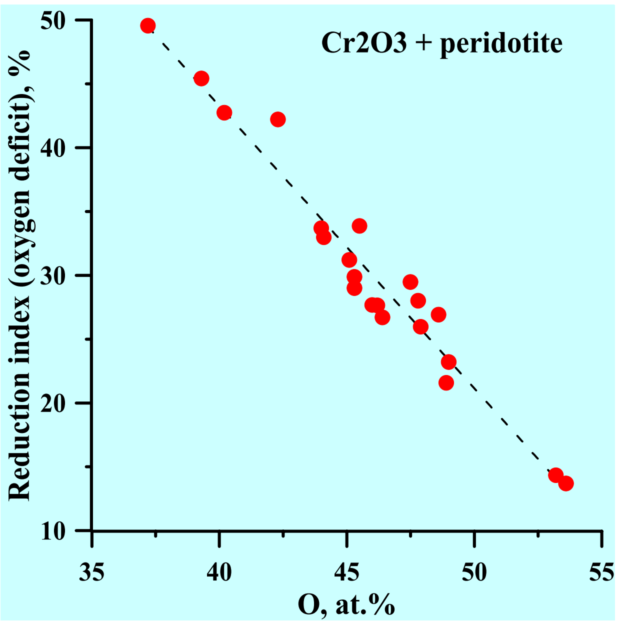

Fig. 5.

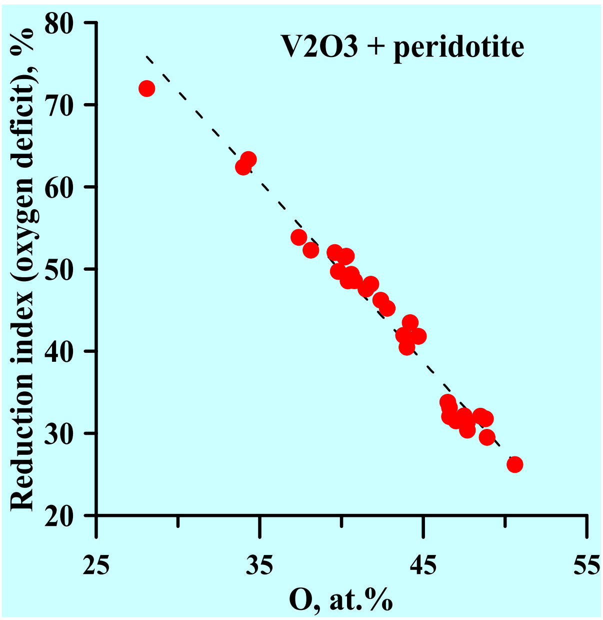

Fig. 6.

Analyses of spherules show a wide diversity of their compositions, what is indicative of individual thermal history of melted droplets. AUGER analyses show a pronounced deficit of oxygen in droplets. The quantity of oxygen was depleted compared to its starting value 10 to 20 % in average. To estimate the degree of reduction of samples we have calculated the reduction index (RI), which was the subtraction from unity of a ratio of measured concentration of oxygen in droplets to that in starting sample. RI shows the proportion of oxygen, which is lacking for the total oxidation of elements in a spherule. This index is varying between 25 and 70% for sample “peridotite+Cr_2O_3” and between 13 and 50 for sample “peridotite+V_2O_3” (fig. 5,6). Such high deficit of oxygen is the result of the presence of elements in metallic state in the melt. Taking into account analyses of condensed film, we consider that metallic component is mainly presented by iron, with some quantity of chromium and vanadium. Analytic evaluation of the state of silicon and magnesium in some spherules has shown that up to 15% of silicon and up to 15% of magnesium also can be present as Si^0 and Mg^0.

Thus, the experimental results showed definitely that the high temperature melting and vaporization of target samples leads to thermoreduction of iron as well as slightly siderophile elements as V, Cr and Mn. This process was not connected with some reduction agents, and temperature factor was main and sole reason. Based on experimental data we surmise that at the impact accretionary planetary stage the thermoreduction of Fe and other siderophiles including such oxygenphile elements as V, Cr Mn occurred. Of course, the presence at the accretionary stage the reduction agents such as C, S, H_2 one cannot exclude, but their effect could only intensify the metallization process of siderophilrs. However, the thermo reduction mechanism could mainly form the metallic phase that permits to explain the siderophile deficit in the Earth mantle and Moon.

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