

SIDEROPHILE PROPERTIES OF ELEMENTS AS THE RESULT OF IMPACT THERMAL-REDUCING PROCESS

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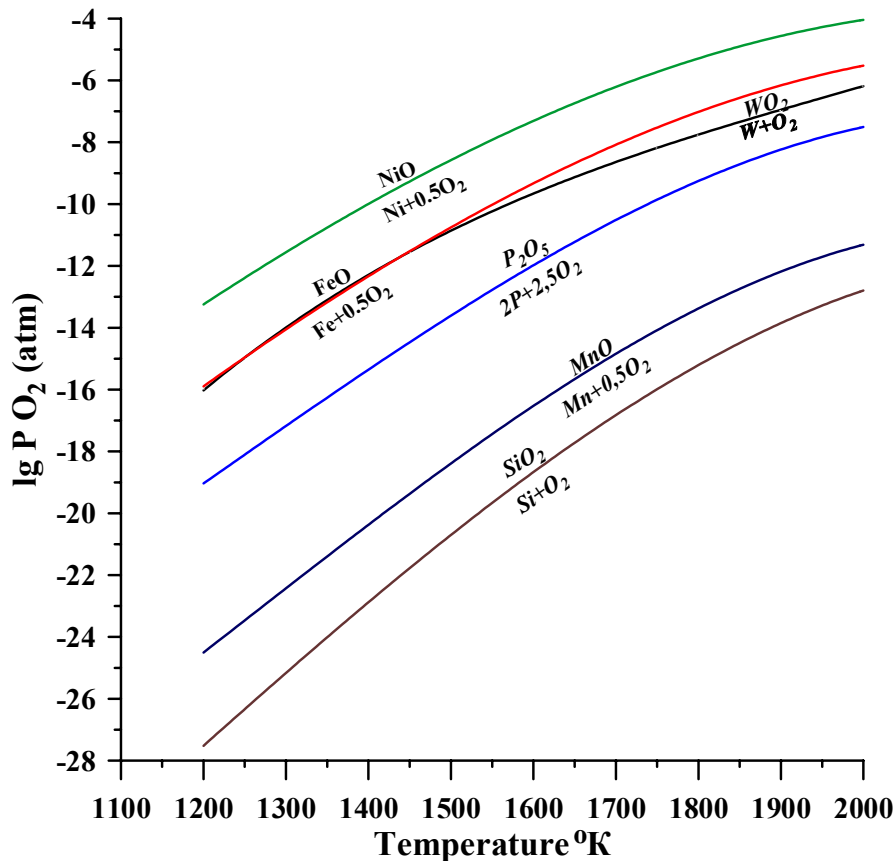
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It is known that some elements (Fe, Ni, Co, P, W, Mo and others) in dependence on conditions have siderophile or lithophile properties. The knowledge of these properties is very important for our understanding their geochemical behavior at the accretionary planetary stage when differentiation of iron and silicate phases occurred. For example, we know the typical siderophile elements as Ni, W, and P have deficit in Earth mantle that is interpreted as the result of their solution in iron phase during planetary core formation. However the reason of the change of initially lithophile properties of the elements to siderophile (or reducing) ones at the early planetary stage is not clear so far. The dominant point of view is that at early stage high temperature and reducing conditions occurred but how the impact accretionary process, which was at that time the main geological process, caused these conditions is not practically studied.

Ringwood A.E. [1] suggested that for reducing Fe and other siderophile elements it was necessary at that time "internal" reducing agent which was carbon. We believe the main reason was high temperature factor, which might determine the valent form of element. In fig. 1 it is shown the positions of red-ox reactions for some siderophile elements and for Mn and Si, which have high affinity to oxygen. The diagram shows that metallic forms of the elements may be generated at the increasing temperature at wide range of oxygen fugacity. These temperatures may be easily reached in impact process.

Fig.1.



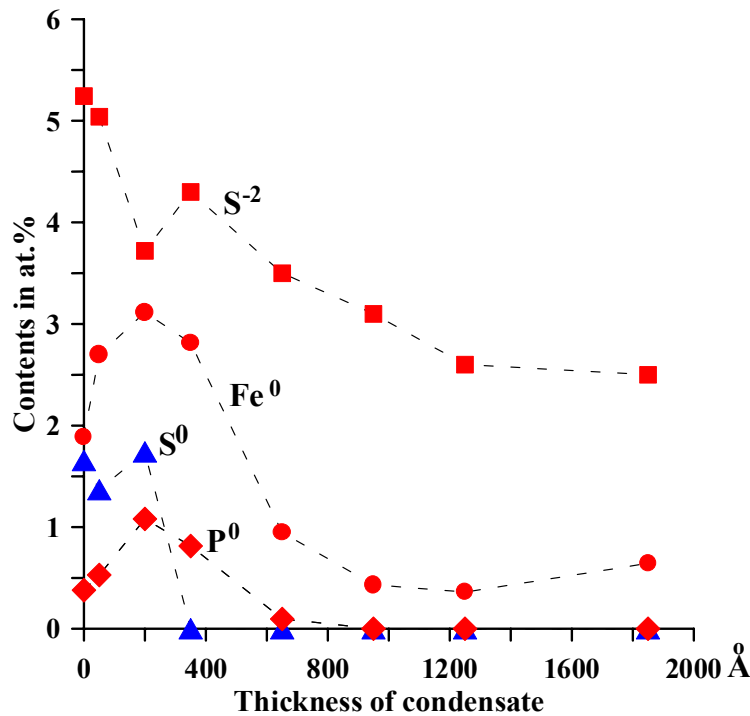
For study the temperature role in reducing of siderophile elements we carried out experiments in a pulse-laser setup in the regime of a free generation of laser radiation [1]. The Nd glass laser had the following parameters: a wavelength of $\lambda=1,06 \mu\text{m}$, pulse energy of 600 J, a power density of radiation of $\sim 10^6\text{-}10^7 \text{ W/cm}^2$, and a pulse time of $\sim 10^{-3}\text{s}$. Typical temperature under such condition is 3000-4000 K. The experiments were performed in He at 1 atm. The laser beam focused to a diameter of $\sim 2 \text{ mm}$, melted and vaporized a few tens of milligrams of the sample. A metal screen was installed in the path of the vapor and melt droplets at the distance $\sim 7\text{cm}$ from the sample. The glass spherules were found on the condensate film. They were resulted because high vapor pressure in the vaporization zone produced a vapor flow out of the cavity, carrying out some of the melt as tiny spherical particles ($1\text{-}5 \mu\text{m}$ in diameter). These parameters of the experiments roughly correspond to typical conditions of melting and vaporization at the impact velocity of about $\geq 10 \text{ km/s}$ [2].

We have studied samples with some siderophile elements (Ni, W, P, and Fe), which were initially in oxidizing forms. These were apatite, garnierite, wolframite and model sample, which were mixture of basalt, Murchison chondrite with volatile matters. The mixture was (wt.%): H 2.80, S 4.33, C 11.37, Cl 1.48, N 4.45, P 0.30, B 0.04, F 0.28, O 41.28, Si 8.83, Ti 1.32, Al 2.10, Fe 9.28, Mn 0.09, Mg 3.43, Ca 1.65, Na 3.15, K 0.32, Cr 0.08, Zn 0.52, Cd 0.53, Pb 0.53, Pt 0.54, Ga 0.34, Co 0.09, others 0.88. Phosphorus was added in $\text{NH}_4\text{H}_2\text{PO}_4$ form, sulfur - in S^0 and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ forms. These samples might be model impact melting and evaporation of cometary matter with basalt target.

Chemical analyses of condensate films are performed using X-ray photoelectron spectroscopy (XPS) method. The method allows analyzing chemical composition and charging state in the cross-section of condensed films.

The experimental results showed unambiguously that under thermo-reducing process oxidize elements became partly in metallic forms. For example, during melting and evaporation of the model mixture occurred reducing of Fe, S, and P (fig. 2). Possible interpretation of these results is the reaction with “internal” reducing agent – carbon. To exclude the influence of the agent we carried out experiment with apatite. In fig. 3 it is showed that phosphorus was partly reduced due to only thermo-reducing effect.

Fig. 2.



This effect it is possible to see at the high-temperature evaporation of garnierite - $(\text{Ni,Mg})_4[\text{Si}_4\text{O}_{10}](\text{OH})_4 \cdot 4\text{H}_2\text{O}$. The results show that the most typical form is Ni^0 (fig. 4).

Fig. 3

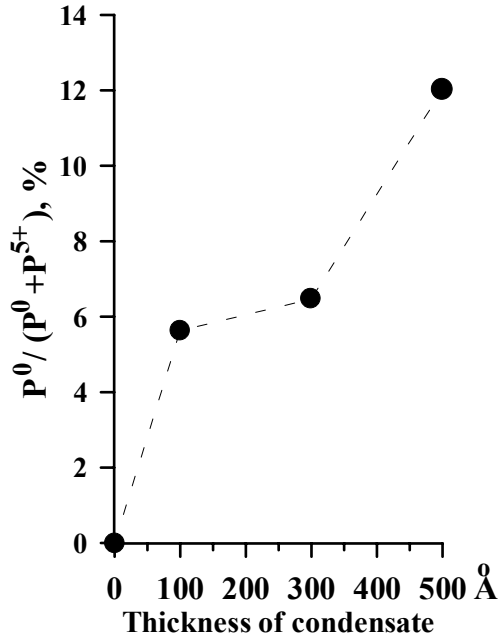
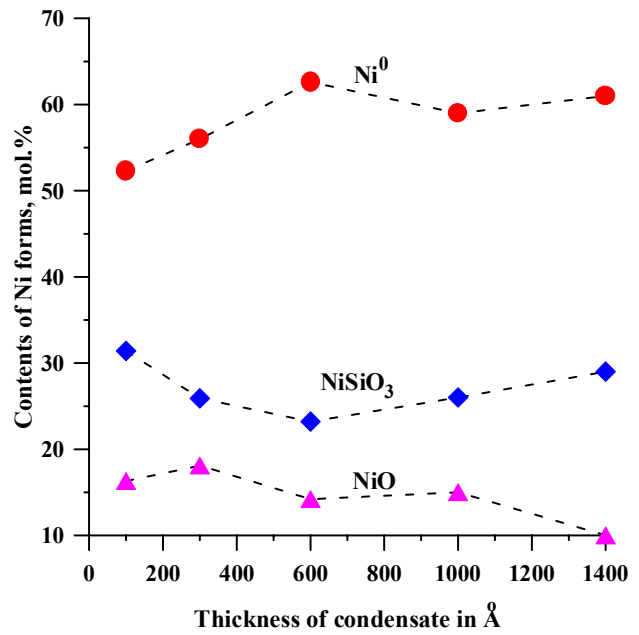


Fig. 4



The same results we see on wolframite ((Fe,Mn)WO₄) evaporation (fig. 5, 6, 7). In fig. 5 it is shown the contents the metallic form of Fe⁰, W⁰, Mn⁰ in the condensate layers. In fig. 6 it is shown the contents of W valent forms separately. These data clearly demonstrate the possibility of thermo-reducing effect for W.

Fig. 5.

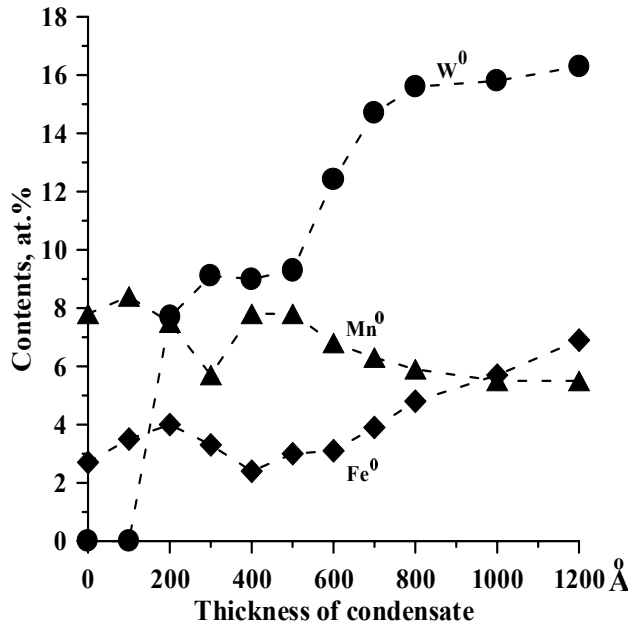
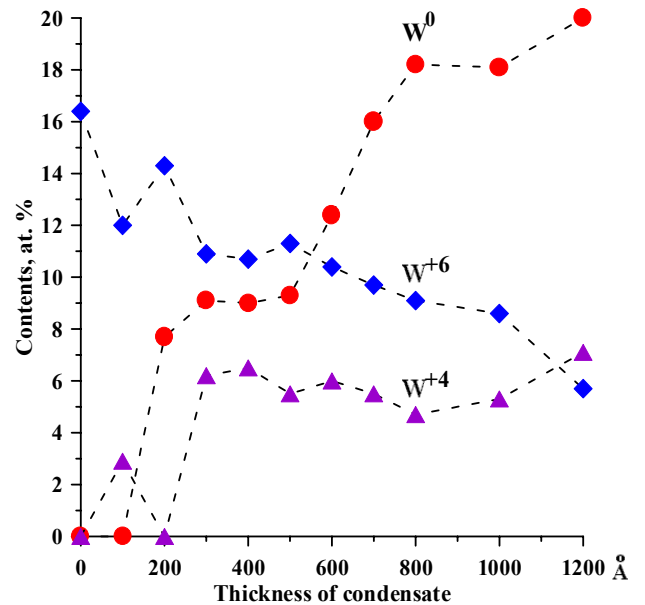
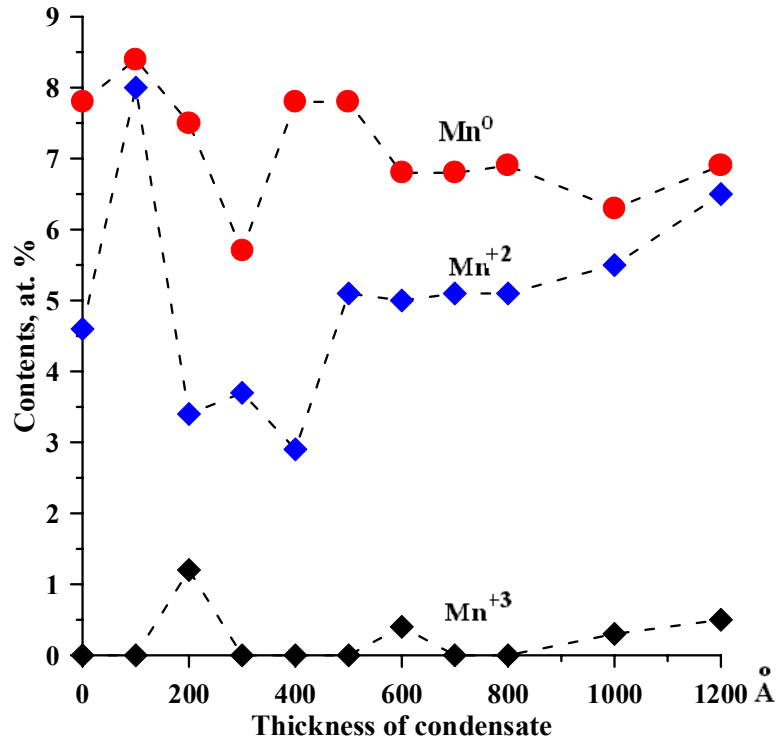


Fig. 6.



Interesting data are obtained for Mn, which has high affinity to oxygen (fig. 1) that determines its lithophile property. In Fig. 7 is shown that Mn⁰ form dominates through all condensate layers. So we may conclude that the thermo-reducing effect leads to Mn metallization too. It permits to suggest that in high temperature of impact process Mn has got siderophile properties and might be dissolved in iron phase. This property explains possibly the deficit of Mn in Earth's mantle where its content is lower in 0.7 as compared with CI chondrite [1,3].

Fig. 7.



Thus, the experimental data show that at high temperature conditions the valent state of elements may be changed by thermo-reducing effect. The results permit to suggest that during the Earth impact accretion the effect played the main role in determining of siderophile properties of elements.

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