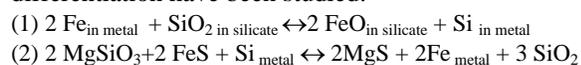


PARTITIONING OF TRACE ELEMENTS BETWEEN SILICATE, SULFIDE AND METAL AT HIGH PRESSURE AND HIGH TEMPERATURE: INVESTIGATION OF DOPANT INFLUENCE ON PARTITION BEHAVIOR. V. Malavergne^{1 and 2}, M. Tarrida²; J. Siebert³, R. Combes²; H. Bureau⁴, and S. Berthet^{1 and 2}, Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, USA, ² Lab. Géomatériaux, Université de Marne La Vallée, 77456 Marne la Vallée, France, ³ Lawrence Livermore National Laboratory-University of California, 7000 East Ave., Livermore, USA ⁴LPS – CEA-CNRS, CE Saclay, 91191 Gif s/Yvette, France.

Introduction. Determining the compositions of the Earth's core and the Martian core are essential for understanding the internal structure, evolution, and present dynamics of the Earth and Mars. Studying how and to what degree elements are partitioned into either metal or silicate is essential for understanding the processes in which these planets differentiated and what the compositions of the cores might be. Piston-cylinder (PC) and multi-anvil (MA) experiments at high pressure (HP) and high temperature (HT) have been performed in order to bring better constraints on this general topic.

Two important reactions for the planetary differentiation have been studied:



Equation (1) has now been extensively studied in literature (e.g. [1]), and is a way to explain how a light element (Si) could be incorporated into a planetary core. One purpose of this study is to constrain the behavior of the first series transition metals (Cr, Mn, Fe, Co, Ni) and W during the process (2). The second goal is to check the domain of validity of the Henry law where the initial level of dilution might interfere with the partition coefficients. Indeed, the majority of the previous studies made about the partitioning of these elements between metal and silicate phases were obtained from an initial concentration in the metallic phases ranged mostly between 10 and 1 wt%, which are well above the natural concentration levels. Moreover, recent studies (e.g. [2] and [3]) have shown the importance to reinvestigate more precisely the behavior of these partition coefficients at different P-T, with the presence of different non-metals in the alloys and with comparable silicate compositions. For example, [3] found that the effects of S and C on elemental partitioning behavior can be quite different; thus, the presence of light elements in a metal can result in different fractionation patterns. The partition coefficients of (Cr, Mn, Fe, Co, Ni) and W between liquid metal, sulfides and silicates is investigated between 1.5 GPa - 25 GPa up to 2200°C, at different oxygen fugacity and with different light elements present in the metallic phases.

Experimental and analytical procedures. The PC experiments were carried out using the Lunar and Planetary Institute QuickPress at the NASA Johnson

Space Center (Houston, Texas, USA). All the details of this PC procedure is given by [4]. MA experiments were carried out in the presses of the Bayerisches Geoinstitut, Bayreuth (Germany) and at the Laboratoire Magmas et Volcans in Clermont-Ferrand (France) under the french INSU facility. Details of these experimental procedures are given by [1] and [5]. The run durations of these experiments vary from 4mn to 35mn, which is enough to reach equilibrium in the samples (e.g. [1]). The partitioning of (Cr, Mn, Fe, Co, Ni) and W between liquid metal and silicates have been investigated at different oxygen fugacity, with different starting silicate and metal compositions. In order to be relevant to the light elements of the Martian or Earth's cores, we have performed experiments with Fe-S, Fe-Si but also with Fe-S-Si metallic phases, as S is a possible candidate for these planetary cores [6, 7], and Si a good candidate for the Earth's core [8]. Samples were analyzed with a Scanning Electron Microscope (SEM) equipped with an energy-dispersive X-ray analyzer (EDX). A CAMECA SX electron probe microanalyzer (EPMA), equipped with wavelength dispersive X-ray spectrometer (WDX) was also used to analyze the samples. For 3 samples, with an initial dopant level around 10-100ppm (depending on the element), the concentrations of trace elements in metal and in silicates have also been measured by μ PIXE operating at 2 MeV and 400pA with a focused $4 \times 4 \mu\text{m}^2$ beam. We obtained a good agreement between these two independent analytical methods. The oxygen fugacity $f\text{O}_2$ in most experiments has been calculated by using two independent buffers : iron/wüstite (IW) and SiO_2/Si according to [1].

Results. In the samples of this study, the metallic phases were always liquid during the heating, this is not always the case for the silicates which could be solid or liquid depending on the P-T of the experiment. It is possible to determine the distribution coefficient $D_{\text{metal-silicate}}^X$ (X is a trace element) which is defined as the ratio of wt% in metal / wt% in silicate and the exchange coefficient $K_{\text{D metal-silicate}}^X$, defined as : $K_{\text{D metal-silicate}}^X = D_{\text{metal-silicate}}^X / (D_{\text{metal-silicate}}^{\text{Fe}})^{y/2}$, where y is the effective valence state of X in its oxide component. In each sample, several chemical profiles or mappings have

been made with EPMA in order to test local equilibrium. The largest particles of metal observed in the samples (between 200 μ m and 50 μ m) in contact with silicates exhibit the same global composition as the tiny metal grains (between 10 μ m and 4 μ m) embedded within the silicate matrix. This is a good indication for local equilibrium at the scale of several tens of micrometers in these samples. Some quenched melt textures have been characterized in the metallic phases as already observed in previous similar studies with Fe-S and Fe-S-Si metallic phases [5] or with Fe-Si phases [9]. Our results have been summarized in Fig. 1 and Fig. 2.

Discussion. Our preliminary results (Fig. 1 and 2) are presented only for two elements: Mn, a slightly siderophile element, and Ni, a moderately siderophile element. For Mn, our data are in good agreement with previous studies. The level of dilution of Mn in the starting material (wt% or ppm) might not be a major parameter for the $D^{\text{Mn}}_{\text{metal-silicate}}$ evolution compared to the P, T, redox conditions, and the starting chemistry (Fig. 1). The valence state of Mn in the silicate phases is in good agreement with 2+ as already observed in previous studies. For Ni, the influence of the dopant concentration on its partition behavior might not be negligible, and should be well investigated in our future work. The valence state of Ni in the silicate phase should be 2+ as already observed in previous studies, this is well the case at high pressure here, but at P<10 GPa, the results (of the present work combined with previous studies) are difficult to explain with a simple 2+ state (Fig.2). This discrepancy might simply reflect the influences of the silicate and/or metal compositions which are not the same in all these plotted data. The same study will be done for all the trace elements added in our experiments and should allow us to constraint the accretion models for terrestrial planets, as Mars and the Earth, which are based on the distribution of (slightly to moderately to highly) siderophile elements.

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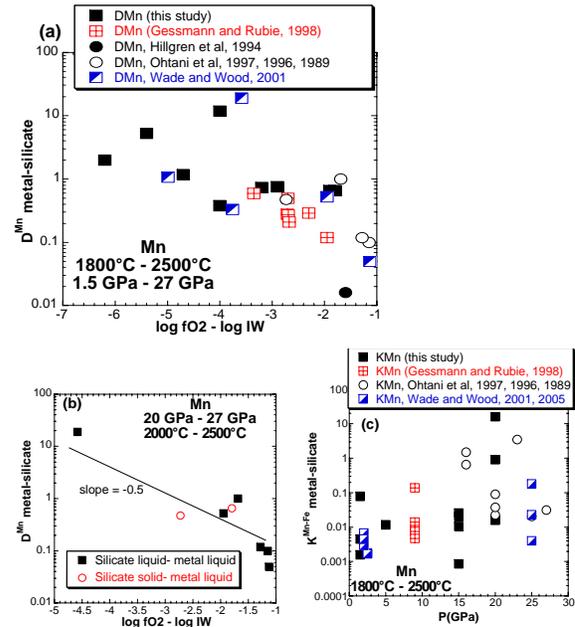


Fig. 1: Results for Mn and previous work. (a) $D^{\text{Mn}}_{\text{metal-silicate}}$ vs $f\text{O}_2$. (c) $K^{\text{Mn}}_{\text{metal-silicate}}$ vs P.

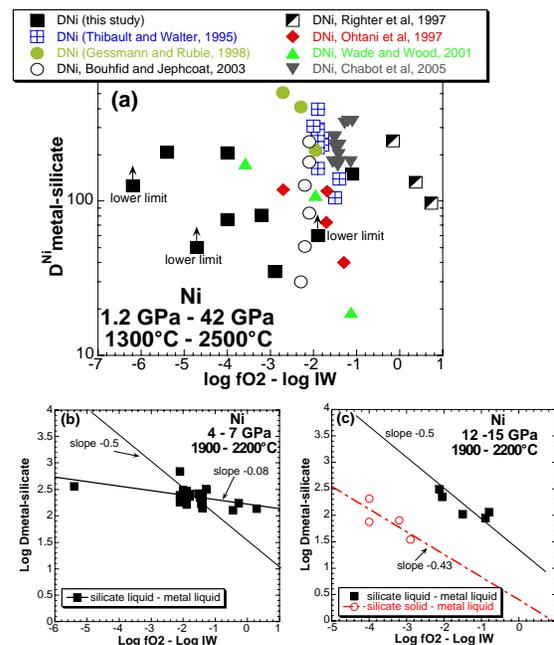


Fig. 2: Results for Ni and previous work. (a) (b) (c) $D^{\text{Ni}}_{\text{metal-silicate}}$ vs $f\text{O}_2$.