7. Pressure Effect on Mn, Co and Ni Partitioning between Iron Hydride and Mantle Minerals

By Toshihiro SUZUKI,^{*)} Masaki AKAOGI,^{*)} and Takehiko YAGI^{**)}

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Abstract: Partitioning behaviors of Mn, Co and Ni between iron hydride and mantle minerals (olivine, pyroxene and magnesiowüstite) under high pressure were experimentally investigated at 1400°C and 3~11 GPa. The present experimental results showed that the siderophile nature of Co and Ni, and the lithophile nature of Mn decrease under high pressures: all the observed metal/mineral partition coefficients, $K' = (X_i/X_{Fe})^{metal}/(X_i/X_{Fe})^{mineral}$, $i = \text{Mn, Co and Ni}$, approach 1 with increase in pressure. K' also depends on the composition of the mineral phase: K' decreases with an increase in MgO mol fraction. From these experimental results, it is expected that the observed upper mantle elemental abundance may be explained by the equilibrium between metal and silicates under extremely high pressure.

Key words: High pressure; elemental partition; earth's core.

It has been pointed out that transition metal abundance in the Earth's upper mantle is too large if the core and the mantle separated under equilibrium condition at the early history of the Earth. In order to explain this observed elemental abundance in the upper mantle, many hypotheses have been put forward on core formation and accompanying distribution of these elements in the Earth. Brett¹⁾ pointed out that transition elements in the upper mantle can be simply explained by the equilibrium between metallic iron and silicates under extremely high pressure. However, lack of data of metal/silicate partition coefficients under high pressures has prevented testing this hypotheses. Recently, several studies reported partition coefficients under high pressures.^{e.g. 2)} The obtained information, however, is still insufficient for the quantitative evaluation of the transition elemental abundance in the upper mantle, and for the detailed discussion of the core formation processes.

We have reported partition behavior of iron-hydride/olivine at 5 GPa and 1000°C in a previous paper.³⁾ At that stage, however, pressure effect on the partition coefficients could not be clarified, because the obtained data were restricted to 5 GPa and they included both effects of pressure and dissolution of hydrogen. The purpose of this study is to extend the pressure range of the partition experiments and clarify the effect of pressure on the metal/silicate partition coefficients.

A wedge-type cubic-anvil high pressure apparatus was used for experiments below 6 GPa. The experiments with pressure conditions above 6 GPa were performed by a split-cylinder type 6–8 multi-anvil high pressure apparatus. Pressure values were calibrated at room temperature against load (oil pressure), based on the pressure fixed points: Bi I–II, Ba I–II, Bi III–V, and semiconductor-metal transition of ZnS. For the 6–8 multi-anvil apparatus, pressure calibration at 1000°C was attained by using the

^{*)} Department of Chemistry, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171, Japan.

^{**)} Institute for Solid State Physics, The University of Tokyo, Minato-ku, Tokyo 106, Japan.

quartz-coesite transition,⁴⁾ olivine-spinel transition of Fe_2SiO_4 ,⁵⁾ rutile- αPbO_2 transition of TiO_2 ⁶⁾ and coesite-stishovite transition.⁷⁾ A pyrophyllite cube and a semi-sintered MgO octahedron were used as the pressure transmitting medium for the cubic-anvil and 6–8 anvil, respectively. The specimen was enclosed in a Fe capsule when the 6–8 anvil was employed. Since melting of iron hydride was observed at 5 GPa and 1200°C,⁸⁾ the specimen was enclosed in a Pt capsule for the experiments using the cubic-anvil apparatus. A graphite tube was employed as heating element in the cubic-anvil, while a tubular tungsten-foil heater was used for the 6–8 anvil. Temperature was measured with a Pt/Pt-13%Rh thermocouple in contact with the outside of the tungsten heater or the Pt capsule.

The starting materials were intimate mixtures of metal, silicate minerals and H_2O -bearing oxides. The mixing ratios of the starting materials were chosen to form olivine plus pyroxene or olivine plus magnesiowüstite after reaction at high pressure and high temperature. The mixing ratios and compositions of starting materials are listed in Table I. Talc used in the starting materials was a high purity natural sample. MgO , $\text{Mg}(\text{OH})_2$ and silicic acid were powder reagents of guaranteed quality. Powdered Fe-Ni and Fe-Co alloys were prepared by reducing their oxide mixtures, as described in the previous paper.³⁾ Mixtures of powdered pure Fe and Mn were used in the Fe-Mn system.

The specimens were held at 1400°C for 2~5 hours at each pressure, and were then quenched isobarically. The recovered specimens were polished to observe their texture and to analyze chemical compositions. Chemical analysis was carried out with an automatic 4-channel EPMA at the Ocean Research Institute, the University of Tokyo.

The recovered specimens in these experiments were composed of metallic phase, olivine, pyroxene and magnesiowüstite. By the metal-water reaction under high pressures and high temperatures, metal oxide components are supplied to the minerals, and hydrogen is supplied to the metallic phase. Although the identification of hydrogen in the metallic phase was not performed, metal-hydride must have existed at the present experimental conditions, as discussed in our previous paper.⁸⁾ Composition of thus produced metal-hydride is estimated to be $(\text{Fe},\text{M})\text{H}_x$, $x=0.8\sim 1.0$ ($\text{M}=\text{Co}$, Ni and Mn),

Table I. Mixing ratios and compositions of starting materials

Run no.	Mixing ratio	mol ratio				$\text{H}_2\text{O}(\text{wt}\%)$
		Metal	SiO_2	MgO	H_2O	
N1	10FN2+Talc+ $\text{Mg}(\text{OH})_2$ +SA	10	5	4	2.6	4.4
N2	10FN2+Talc+6MgO+3Mg(OH) ₂	10	4	12	4.0	5.3
N3	12FN2+Talc+6MgO+3Mg(OH) ₂	12	4	12	4.0	5.5
N4	10FN2+Talc+2MgO+3Mg(OH) ₂	10	4	8	4.0	6.0
N5	15FN2+3Talc+4MgO+2Mg(OH) ₂	15	12	15	5.0	3.5
C1	8FC+Talc+ $\text{Mg}(\text{OH})_2$ +SA	8	5	4	2.6	4.9
C2	10FC+Talc+6MgO+3Mg(OH) ₂	10	4	12	4.0	5.3
C3	10FC+Talc+2MgO+3Mg(OH) ₂	10	4	8	4.0	6.0
M1	19Fe+Mn+4Talc+3Mg(OH) ₂ +2MgO	20	16	17	7.0	4.4
M2	9Fe+Mn+Talc+6MgO+3Mg(OH) ₂	10	4	12	4.0	4.3
M3	9Fe+Mn+Talc+2MgO+4Mg(OH) ₂	10	4	9	4.0	5.8

Abbreviations: FN2, $\text{Fe}_{80}\text{Ni}_{20}$ alloy; FC, $\text{Fe}_{80}\text{Co}_{20}$ alloy; SA, silicic acid ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$, $x=0.636$); Talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$.

from theoretical calculations on the solubility of hydrogen in transition metals at high pressures.⁹⁾

The chemical compositions of coexisting phases in the central part of each run product were determined. Since the composition varied slightly from grain to grain, we estimated the partition coefficients by determining the compositions of many different pairs of metal and mineral grains which were in contact with each other, because it was expected that these grains were nearly in equilibrium.

The partitions of Mn, Co and Ni between metallic Fe and minerals should be recognized as exchange reactions. For example, the exchange reaction of Fe and Ni between metal and olivine can be written as

and the apparent partition coefficient, K' , is expressed as

$$K'_{\text{Fe-Ni}}(\text{met/ol}) = (\text{X}_{\text{Ni}}/\text{X}_{\text{Fe}})^{\text{met}}/(\text{X}_{\text{Ni}}/\text{X}_{\text{Fe}})^{\text{ol}}$$

where X represents the molar fraction of Fe or Ni in metal or olivine. When the reaction is written in this way, it appears to be independent of oxygen fugacity. However, it does not mean that the K' is independent of oxygen fugacity. If the oxygen fugacity is increased in the system, Fe^{2+} content of olivine is increased, and K' is changed by the compositional effect, which results from the nonideality in the activity-composition relations in olivine and metallic phase.

The experimental conditions and observed K' values are summarized in Table II. The observed $K'_{\text{Fe-Ni}}(\text{met/ol})$ and $K'_{\text{Fe-Ni}}(\text{met/MW})$ are illustrated in Fig. 1, as examples of pressure-composition relation of K' . In this figure, plotted points represent the average of the observed K' values of 10–50 analysis points in each run product, and error bars show $\pm$ one standard deviation. It is found in this figure that K' decrease with increase of pressure, and increase of Mg mol fraction. At each pressure, the relationship between $\ln K'$ and mineral composition can be approximately expressed by a straight line. These partition coefficient lines would have the same gradient at all pressures, because pressure effect on the nonideality of the relevant phases could be neglected. Therefore, the partition coefficient lines were acquired by least squares fit of the straight lines to the data points, by assuming that the gradients were the same in all the pressures. For the other systems, pressure effect on K' is also obtained, in a similar manner to that in the $K'_{\text{Fe-Ni}}(\text{met/ol})$ and $K'_{\text{Fe-Ni}}(\text{met/MW})$.

Since $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio of the Earth's upper mantle is estimated to be approximately 0.88, $K'(\text{met/ol})$ values at this composition were estimated from the present experimental results by least squares fitting of the observed K' values at each pressure, and then plotted in Fig. 2. $K'(\text{met/ol})$ values at atmospheric pressure are based on the thermodynamic data.¹⁰⁾ The estimated $K'(\text{met/MW})$ values with Mg mol fraction of 0.55 are also plotted in Fig. 2, because magnesiowüstite with this composition is expected to be in equilibrium with the mantle olivine.

These results indicate that K' values of Ni and Co decrease with increase of pressure. Ohtani *et al.*²⁾ reported the partition behavior of siderophile elements between metallic iron and Mg-perovskite or magnesiowüstite at 25–27 GPa and 1700–1900°C. Their results at 27 GPa and 1700°C are also plotted in Fig. 2. Since it is expected that K' values approach to 1 with an increase in temperature,¹¹⁾ a small correction should be required to compare with the present results. We also have to consider the difference of composition of magnesiowüstite because the Mg mol fraction of magnesiowüstite in their experiments was reported to be about 0.3. In spite of these differences, it is easily recognized that the results of Ohtani *et al.*²⁾ are consistent with the present results. Fig. 2 also shows that the $K'_{\text{Fe-Mn}}$ value increases with increase in pressure, when we consider both of the present data and those by Ohtani *et al.*²⁾ The decrease of K' in Co and Ni, and the increase in Mn,

Table II. Experimental conditions and results. All experiments were performed at 1400°C. Errors are one standard deviation of 10~50 observed points in each run product

Run no.	Pressure (GPa)	Time (min)	M/(Fe+M)×100 ^a	Mg/(Mg+Fe+M)×100 ^a			K'		
			Metal	Ol	MW	Px	Met-Ol	Met-MW	Met-Px
Fe-Ni system									
N1-1	3.0	90	23±3	71±2	—	76±2	50±12	—	38±15
N1-2	5.2	300	23±3	71±2	—	76±2	36±10	—	25±15
N1-3	5.1	120	23±3	76±3	—	78±2	36±12	—	26±15
N1-4	8.2	120	23±3	69±2	—	78±2	28±12	—	22±15
N1-5	11.0	120	23±3	69±2	—	77±2	27±6	—	18±7
N1-6	11.2	120	23±3	71±2	—	78±2	21±8	—	25±8
N2-1	5.2	180	30±5	88±2	52±2	—	38±10	48±10	—
N2-2	8.2	120	25±5	88±2	53±2	—	24±6	30±6	—
N3-1	3.0	200	35±5	89±2	66±2	—	38±15	46±8	—
N3-2	5.2	300	28±5	89±2	52±2	—	30±8	46±14	—
N3-3	8.2	120	30±8	91±2	58±2	—	34±15	39±12	—
N3-4	11.2	120	25±5	88±2	61±2	—	21±7	22±5	—
N4-1	3.0	90	50±8	79±2	27±2	—	82±30	85±30	—
N4-2	5.2	300	35±5	81±2	28±2	—	55±15	88±18	—
N4-3	8.2	120	30±5	82±2	34±2	—	44±20	47±10	—
N4-4	11.2	120	25±5	79±2	32±2	—	25±5	35±6	—
N5-1	3.0	200	50±8	68±2	—	10±2	70±25	—	65±20
N5-2	5.2	200	30±5	53±2	—	10±2	54±22	—	35±15
N5-3	11.2	120	30±5	63±2	—	10±2	27±4	—	30±15
Fe-Co system									
C1-1	3.0	200	30±5	56±3	—	69±3	18±6	—	23±10
C1-2	8.2	120	25±5	63±3	—	77±3	10±3	—	10±3
C1-3	11.2	120	23±5	—	—	77±3	—	—	8±2
C2-1	3.0	200	21±5	91±2	54±3	—	10±3	13±3	—
C2-2	8.2	120	21±5	91±2	62±3	—	7±2	9±2	—
C2-3	11.2	120	21±5	88±2	59±3	—	6±2	6±1	—
C3-1	3.0	200	40±10	78±2	27±2	—	11±2	14±2	—
C3-2	8.2	120	28±5	79±2	48±3	—	5±2	9±2	—
C3-3	11.2	120	30±5	78±2	28±2	—	6±2	10±2	—
Fe-Mn system									
M1-1	3.0	200	0.2±0.1	72±2	—	77±2	0.004±0.003	—	0.004±0.002
M1-2	8.2	120	0.2±0.1	70±2	—	77±2	0.006±0.003	—	0.004±0.002
M1-3	11.2	120	0.2±0.1	68±2	—	77±2	0.008±0.004	—	0.004±0.002
M2-1	3.0	200	0.2±0.1	88±2	66±2	—	0.003±0.002	0.009±0.003	—
M2-2	8.2	120	0.2±0.1	89±2	64±2	—	0.004±0.002	0.009±0.003	—
M2-3	11.2	120	0.2±0.1	89±2	64±2	—	0.005±0.002	0.012±0.004	—
M3-1	3.0	200	0.2±0.1	82±2	38±2	—	0.005±0.003	0.013±0.005	—
M3-2	8.2	120	0.2±0.1	82±2	38±2	—	0.005±0.003	0.011±0.005	—
M3-3	11.2	120	0.2±0.1	80±2	38±2	—	0.006±0.003	0.012±0.006	—

Abbreviations: Met, Metal; Ol, Olivine; MW, Magnesio-wüstite; Px, pyroxene. ^aM=Mn, Co, Ni.

with increasing pressure, suggest that all of the K' would approach 1 under extremely high pressures. This reveals that the siderophile nature of Ni and Co, and lithophile nature of Mn are decreased at very high pressures.

The abundance pattern of transition elements in the upper mantle shows a nearly

Fig. 1. Compositional dependence of observed $K'_{\text{Fe-Ni(met/ol)}}$ (a) and $K'_{\text{Fe-Ni(met/MW)}}$ (b). Plotted points represent the average of observed K' values in each run product, and the standard deviation is expressed as error bars. K' lines are drawn by least square fitting of the observed K' with assuming that the gradient of the line is the same at all of the pressures.

Fig. 2. Pressure dependence of K' . $K'(\text{met/ol})$ with Mg mol fraction of 0.88 and $K'(\text{met/MW})$ with Mg mol fraction of 0.55 are estimated from the present experimental results, and are illustrated. The observed partition coefficients of metal/magnesiowüstite and metal/Mg-perovskite at 27 GPa and 1700°C⁽²⁾ are also plotted in this figure.

chondritic pattern. The present results, where K' values approach 1 with increase in pressure, suggest the possibility that the pressure effect on K' had played an important role on the chemical evolution of the Earth's mantle. Since the pressure value of the core-mantle boundary is estimated to be approximately 140 GPa in the present Earth, it may be possible that the partition coefficients of most of the elements are close to 1 in the Earth's deep interior. Moreover, the other effects on K' values, such as temperature or dissolution of other light elements in the metallic phase, are also expected to reduce the siderophile and lithophile nature of the elements. Hence, if we consider metal/silicate equilibrium at extremely high pressure condition, elemental abundance in the upper mantle may be explained by an "equilibrium Earth".

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