ANALYSIS OF HIGHLY SIDEROPHILE ELEMENTS AND OSMIUM ISOTOPE COMPOSITIONS IN METAL PHASES FROM CR CHONDRITES.

N. Nakanishi[1], T. Yokoyama[1], S. Okabayashi[1], K. Shimazaki[1], T. Usui[2], and H. Iwamori[1, 3]. [1]Dept. of Earth & Planetary Sciences, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan (nakanishi.n.aa@m.titech.ac.jp). [2]Earth-Life Science Institute, Tokyo Institute of Technology, Japan. [3]Institute for Research on Earth Evolution, Agency for Marine-Earth Science and Technology, Yokosuka, Kanagawa 237-0061, Japan.

Introduction: Metal is one of the main components of chondritic meteorites and coexist with various meteorite components (i.e., CAI, chondrule, and matrix). Possible models for metal formation in the early Solar System include direct condensation in the protoplanetary disk, condensation during chondrule formation, and chemical reaction on their parent bodies [1–3]. These models are highly debated and still need to be resolved.

Highly siderophile elements (HSEs: Re, Os, Ir, Ru, Pt and Pd) have great affinity for Fe-metals relative to silicates. HSEs are refractory and exist as gas only at high temperatures. Therefore, geochemical investigation of HSEs in metal phases in a variety of meteorites can provide an important clue for understanding high temperature processes in the solar nebula. Specifically, the ^{187}Re-^{187}Os isotope system gives chronological information regarding the fractionation of HSEs.

CR chondrites contain about 40–60 vol. % of chondrules and 5–8 vol. % of metal grains and have unique characteristics for the coexistence of metal with chondrule [4, 5]. Therefore, CR chondrites are suitable for understanding the genetic linkage between metals and chondrules. Metal grains are found in three different locations of CR chondrites; chondrule interior ("interior grain"), chondrule surficial shells ("margin grain"), and the matrix ("isolated grain"). Jacquet et al. [5] proposed that the interior and margin grains from CR have formed via melting of precursor materials during chondrule formation, whereas Connolly et al. [2] argued that some margin and isolated metals have formed by the recondensation of surrounding vapor. Consequently, the origin of metal phases in CR chondrites is still debated, and the model for the formation process of a series of three types of metals has not been well established.

Here we report HSE abundances and Os isotopic compositions in metal phases from three CR chondrites determined using fs-LA-ICP-MS and TIMS coupled with a micro-milling technique. These geochemical data provide useful information for understanding the formation process of the interior, margin, and isolate grains, which would shed light on the physicochemical conditions for the high temperature processes associated with chondrule formation.

Experimental: We prepared thick sections of NWA 801, NWA 7184, and Dhofar 1432, of which the surface was polished with 1 μm diamond paste. The petrography and the mineral compositions of these sections were examined with SEM-EDX (Hitachi 3400; Bruker Xflash 5010). We selected four grains from each type of metal in NWA 801, two isolated grains in NWA 7184, and five isolated grains in Dhofar 1432, and analyzed the abundances of HSEs, major (Fe and Ni), and minor (P, S, Cr, and Co) elements for the multi-spots of these grains using fs-LA-ICPMS (IFRIT, Cyber Laser) and EPMA (JEOL-JXA-8530F), respectively. In addition, we determined Os isotope compositions for two isolated grains in NWA 801. The details for Os isotope analysis using a micro milling system and N-TIMS (TRITON plus, Thermo Fisher Scientific) are described in [6].

Results and Discussion: Fig. 1 shows the variation of Pd/Ir ratio as a function of Ir abundance for metal grains. The Pd/Ir ratios in metal grains decreased rapidly with the increase of Ir concentration. In this diagram, all types of CR metal grains present a single trend. Therefore, we consider that all CR metals have formed by a common process; either by gas condensation or by fractional crystallization.

Two black curves in Fig. 1 are calculated equilibrium condensation trajectories at a nebular pressure of 10^{-4} for chondritic composition (solid) and for metal enriched gas by a factor of 10^7 relative to the nebular condition (broken). Because more than 50% of the data points for the metal samples measured in this study deviate from the calculated trajectories, we conclude that equilibrium condensation from a gaseous reservoir does not account for the generation of metal phases in the CR chondrites examined.

Next, we discuss the possibility of fractional crystallization as for the origin of CR metals. For this purpose, we calculated the solid-metal/liquid-metal partition coefficients (D) and the initial HSE compositions for the metal samples. Fig. 2 shows the logarithmic plots of Ir vs. Os, Ru, Pt, and Pd that define highly correlated linear trends. The plots of Re are scattered because of relatively low intensity of ^{185}Re signal in the fs-LA-ICP analysis. The D values for HSEs were calculated from the following formula using the slopes of individual trends [7];

$$\text{Slope of correlation} = \frac{[D(HSE)-1]}{[D(Ir)-1]} \quad (1).$$

According to the calculated *D* values (Table 1), Os and Pd are the most compatible and incompatible elements to the solid metal among the five HSEs, respectively. The tendency of compatibility is consistent with the data for *D* values calculated from experimental partitioning data by [8].

The red curve in Fig. 1 represents the trajectory of fractional crystallization calculated by (i) assuming 0.8 wt.% S contents (bulk S content of CR chondrites [9]), (ii) using the *D* values in Table 1, and (iii) determining the initial Pd/Ir ratio (star in Fig. 1; Table 2) that fits the observed data points. With the same approach, we determined the initial Os/Ir, Ru/Ir, and Pt/Ir ratios. As shown in Table 2, the Ir-normalized initial HSE abundances are all chondritic excluding the Pd/Ir ratio. We speculate that Pd could have been lost during chondrule formation process before metal crystallization, because Pd is relatively volatile among the HSEs. These lines of evidence support the fractional crystallization of solid-metal from liquid-metal as for the possible origin of three types of CR metal grains.

In addition to HSE abundances, we determined the $^{187}Os/^{188}Os$ ratios for two isolated grains in NWA 801. Although the grains would have experienced significant Re-Os fractionation as a result of fractional crystallization, the $^{187}Os/^{188}Os$ ratios observed were nearly chondritic (0.1261 ± 0.0001, 0.1258 ± 0.0001), which were different from those observed in iron meteorites (e.g., IIIAB irons; 0.125–0.188 [10]). The inconsistency could be caused by the difference of the analysis area for fs-LA-ICP-MS (~20 µm) and TIMS (~500 µm); the observed $^{187}Os/^{188}Os$ may represent the bulk isotopic composition of the precursor material for the isolated grains.

References: [1] Campbell and Humayun (2004) *GCA, 68,* 3409–3422. [2] Connolly et al. (2001) *GCA, 65,* 4567–4588. [3] Humayun and Campbell (2002) *EPSL, 198,* 225–243. [4] Lee et al. (1992) *GCA, 56,* 2521–2533. [5] Jacquet et al. (2013) *MAPS, 48,* 1981–1999. [6] Nakanishi N. et al. (2013) *LPSC,* abstract #2407. [7] Walker et al. (2008) *GCA, 72,* 2198–2216. [8] Chabot and Jones (2003) *MAPS, 38,* 1425–1436. [9] Dreibus et al. (1995) *Meteoritics, 30,* 439–445. [10] Cook et al. (2004) *GCA, 68,* 1413–1431. [11] Horan et al. (2003) *Chemical Geology, 196,* 5–20.

Table 1. Linear regressions of log plots of HSE vs. Ir and calculated *D* values

	Ir	Os	Ru	Pt	Pd
Slope	-	1.10	0.78	0.74	0.17
D value	1.50	1.55	1.39	1.37	1.08

Table 2. Calculated initial compositions for fractional crystallization model

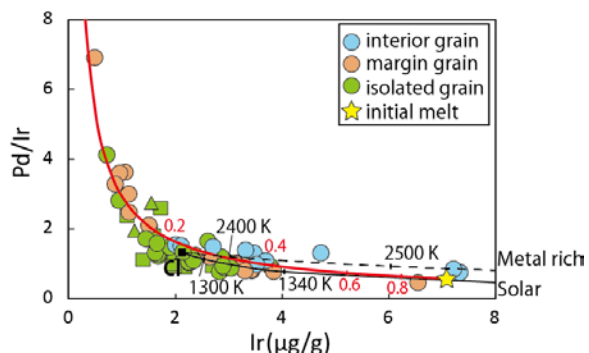|	Os/Ir	Ru/Ir	Pt/Ir	Pd/Ir
CR initial melt	1.2	1.3	1.7	0.8
CI bulk [11]	1.0	1.5	2.0	1.3

Fig. 1. Plot for Pd/Ir ratio versus Ir abundance in metal grains from NWA 801 (circles), NWA 7184 (triangles), and Dhofar 1432 (squares). Two black curves are calculated equilibrium condensation trajectories at a nebular pressure of 10^{-4} for chondritic composition (solid) and for metal enriched gas by a factor of 10^7 relative to the nebular condition (broken). The red curve shows the fractional crystallization model of 0.8 wt.% sulfur contents using calculated *D* value.
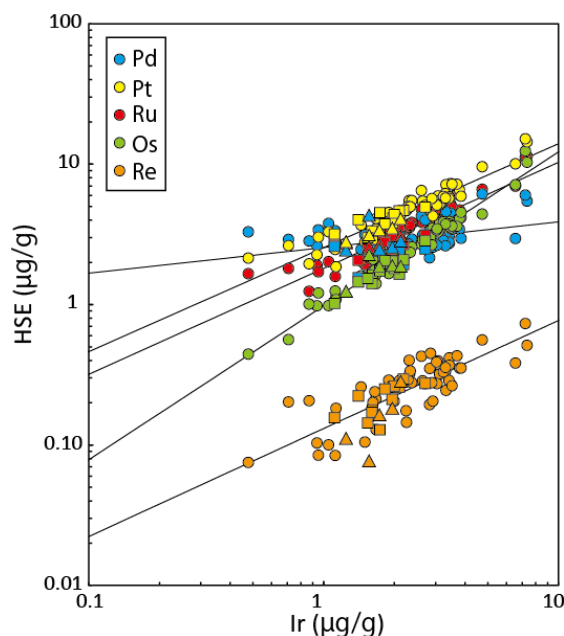

Fig. 2. Logarithmic plot of Ir versus other HSE concentrations in metal grains from NWA 801 (circles), NWA 7184 (triangles), and Dhofar 1432 (squares).