FORMATION OF METAL PHASES IN CR CHONDRITES: IMPLICATIONS FROM HIGHLY SIDEROPHILE ELEMENTS. N. Nakanishi[1], T. Yokoyama[1], S. Okabayashi[1], and H. Iwamori[1, 2]. [1]Dept. of Earth & Planetary Sciences, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan (nakanishi.n.aa@m.titech.ac.jp). [2]Institute for Research on Earth Evolution, Agency for Marine-Earth Science and Technology, Yokosuka, Kanagawa 237-0061, Japan.

Introduction: Metal plays a key role in physico-chemical processes that fractionate siderophile elements from lithophile elements in the early solar system, generating variable chemical reservoirs before the onset of planetesimal formation. Highly siderophile elements (HSEs: Re, Os, Ir, Ru, Pt and Pd) have great affinity for Fe-Ni metals relative to silicates. Individual HSEs have distribution coefficients between solid metal and liquid metal ($D^{s/l}$) that are different from one another.

CR chondrites contain 40–60 vol.% of chondrules with 5–8 vol.% of metal grains and have unique characteristics for the coexistence of metal phases with chondrules [1, 2]. 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. [2] proposed that the interior and margin grains from CR chondrites have formed via melting of precursor materials during chondrule formation. In contrast, Connolly et al. [3] argued that some margin and isolated metals have formed by the recondensation of surrounding vapor, while the other metals have formed by the reduction of FeO within chondrule melts. Consequently, formation processes for the three types of metals in CR chondrites have not been unequivocally determined.

Here we report the abundances of HSEs and major elements in the metal phases from CR chondrites using femtosecond LA-ICP-MS (fs-LA-ICP-MS) and electron probe micro analysis (EPMA). These geochemical data provide useful information for understanding the formation process of the interior, margin, and isolated grains in the CR chondrites, which would shed light on the physicochemical conditions for the high temperature processes associated with chondrule formation.

Experimental: We prepared thick sections of three CR chondrites, NWA 801, NWA 7184, and Dhofar 1432. The surface of the sections was polished with 1 µm diamond paste. The petrography and the mineral compositions of the sections were determined with SEM-EDS (Hitachi 3400; Bruker Xflash 5010). The abundances of major (Fe and Ni) + minor (P, S, and Cr) elements, as well as those of the HSEs and Co for the multi-spots of these grains were measured with EPMA (JEOL-JXA-8530F) and fs-LA-ICP-MS (IFRIT, Cyber Laser + X-series II, Thermo Fisher), respectively. We analyzed 16 spots from 9 interior grains, 32 spots from 8 margin grains, and 66 spots from 12 isolated grains.

Results and Discussion: Fig. 1 shows the variation of Re/Ir and Ru/Ir ratios in the metal grains as a function of the Ir abundance. The Re/Ir and Ru/Ir ratios in metal grains decreased rapidly with the increase in Ir abundance. One of the commonly accepted models for the formation of chondritic metal grains is condensation from gaseous reservoirs [4, 5]. As shown in Fig. 1, however, most of the data points for metal grains do not follow the trajectories of equilibrium condensation calculated by adopting the equation and parameterization (e.g., partition coefficients) described in [6]. Therefore, the variation of HSE abundance ratios and Ir abundances in the CR metals cannot be explained by the equilibrium condensation process, as opposed to the argument raised by [3].

Alternatively, we consider the possibility of fractional crystallization process. Figure 2 shows the Re/Ir and Ru/Ir ratios in the margin and interior metals as a function of the Ir abundance. Also shown are the trajectories of fractional crystallization modelling calculated by varying the Ir abundance of the initial liquid metal from 0.8 to 6.8 µg/g, while holding the Re/Ir and Ru/Ir ratios (= CI values) and the S and P contents (0.8 and 0.19 wt.%, respectively) constant. In the modelling, the $D^{s/l}$ values of Re and Ru were determined by the method of [7] in which the following equation was used;

$$D^{s/l}(\text{Re, Ru}) = k(\text{Re, Ru})\{D^{s/l}(\text{Ir}) - 1\} + 1 \quad (1)$$

where k(Re, Ru) are the slopes of correlations in the logarithmic plots of Re–Ir and Ru–Ir abundances. Here, the k values were determined from the correlations of representative margin metal grains that defined highly correlated linear trends in the logarithmic plots. As shown in Fig. 2, the variations of Re/Ir and Ru/Ir ratios in each margin and isolated metal grain are successfully explained when the initial liquid metal had variable Ir abundances, indicating that the individual interior and margin metal grains have formed from multiple liquid metals that had distinct Ir abundances. The variable Ir abundances in the initial liquid metal was caused either by the evaporation and/or condensation of metal precursors during chondrule formation, or by that the precursor dusts contained HSE-rich nuggets heterogeneously.

Figure 3 shows the Re/Ir and Ru/Ir ratios in the isolated metals as a function of the Ir abundance. Also

shown are the trajectories of fractional crystallization modelling calculated by varying the Ir abundance of the initial liquid metal from 1.4 to 5.4 µg/g while holding the Re/Ir and Ru/Ir ratios (= CI values) and the S and P contents (0.8 and 0.19 wt.%, respectively) constant. The $D^{s/l}$ (Re, Ru) values were determined using the mean values of k(Re, Ru) calculated separately for some isolated grains that have at least five data points. The HSE abundances in the initial melt of isolated metal grains are thought to be less variable than those of the margin metal grains. This result agrees with the model that the isolated grains have formed by the merger of multiple liquid metal droplets that escaped from the chondrule surfaces [8, 9], thereby minimizing the extent of heterogeneity regarding HSE abundances in the initial liquid metal of isolated metal grains.

The formation process of metal grains in CR chondrites discussed above further suggests the genetic linkage between chondrules and matrix. The isolated grains found in the CR chondrite matrix is most likely formed by the separation of metal droplet from the rim of the chondrules. Therefore, isolated metal grains and matrix of CR chondrites are thought to have formed contemporaneously. This suggests that chondrules and matrix components including isolated metals of CR chondrite would have formed in the same place, which negates the stellar wind model for the formation process of CR chondrules. Our interpretation is supported by a narrow time interval between the Hf–W age of CR chondrite (3.6 Myr after the CAI formation) that corresponds to the chondrule formation age [10], and the Mn–Cr carbonate age of CR chondrite (4.3–5.3 Myr after CAI formation) that gives the upper limit for the accretion age of CR parent body [11].

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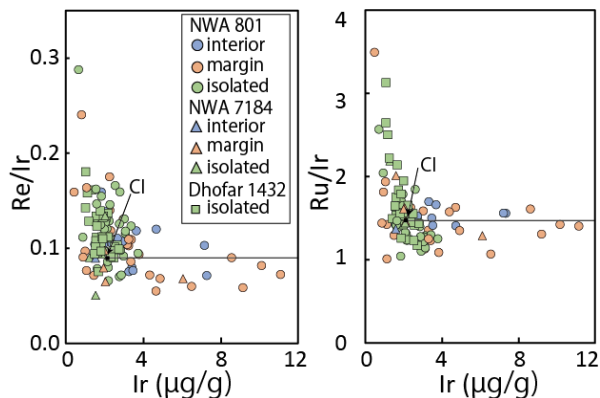

Fig. 1. Plot for Re/Ir and Ru/Ir ratios versus Ir abundance in metal grains. Bold line is the trajectory of equilibrium condensation of metal grains from a gas reservoir with the solar composition and the pressure of 10^{-4}. CI data are from [12].
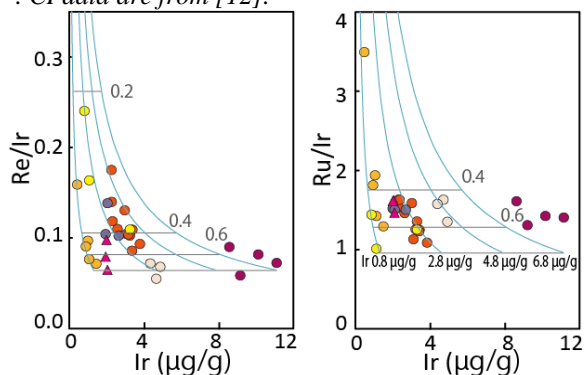

Fig. 2. Results of fractional crystallization modelling plotted on the Re/Ir and Ru/Ir versus Ir diagrams for interior and margin metals. The different symbols shows the data from different metal grains. Ir abundance in the initial liquid metal was variable, while the Re/Ir and Ru/Ir ratios in the initial melt were fixed to be the CI values. Gray numbers are degree of crystallization. Gray lines connect the same degree of crystallization.
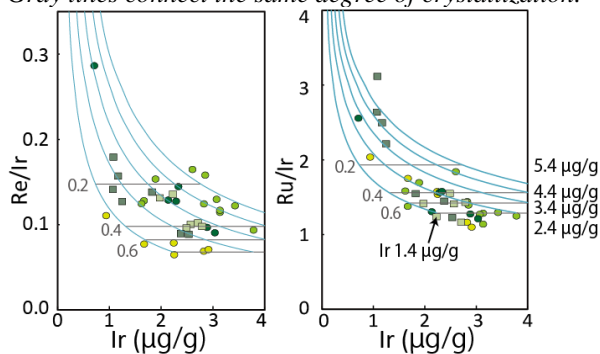

Fig. 3. Results of fractional crystallization modelling plotted on the Re/Ir and Ru/Ir versus Ir diagrams for isolated metals. The different symbols shows the data from different metal grains. Ir abundance in the initial liquid metal was variable, while the Re/Ir and Ru/Ir ratios in the initial melt were fixed to be the CI values.