CLUES TO THE FORMATION HISTORY OF REFRACTORY METAL NUGGETS. D. Schwander[1], T. Berg[1], G.Schönhense[1], H. Palme[2] and U. Ott[3,4], [1]Institut für Physik, Johannes Gutenberg-Universität, Staudingerweg 7, D-55128 Mainz, Germany (schwandd@uni-mainz.de). [2]Forschungsinstitut und Naturmuseum Senckenberg, Senckenberganlage 25, D-60325 Frankfurt am Main, Germany. [3]Max-Planck-Institut für Chemie, D-55128 Mainz, Germany [4]University of West Hungary, H-9700 Szombathely, Hungary.

Introduction: Refractory metal nuggets (RMNs) are predicted to be among the first solids to condense from a cooling solar composition gas, over a temperature range of 1400 K to 1600 K (at 10^{-4} bar) [1]. They contain the early condensing refractory siderophile elements Re, Os, Ru, Ir, Mo, W, Pt and Rh. These nuggets are found in CAIs from chondritic meteorites [e.g. 2], but similar ones have also been observed in presolar graphite grains [3]. Concerning the "solar nuggets", it has become evident that CAIs often have a complex alteration history involving reactions at lower temperatures with the ambient gas leading to modifications of the primary mineralogy. In addition, most CAIs were once molten [4], thus erasing a possible primary nebular record. How the RMNs enclosed by molten CAIs were affected by these secondary processes is not clear. From [5], who studied the oxidation behavior of similar alloys, it is clear that Mo, Re and W are not very stably bound in those alloys. Tungsten was found to be more easily oxidized than Mo, so in the process the alloy will first lose W and then, with increasing oxygen fugacity, Mo. Thus, RMNs from meteorites with a significant thermal alteration history could have been affected by oxidizing processes, which would also erase a possible primary nebular record. A pristine nature for 88 extracted and analyzed RMNs from the chondritic meteorite Murchison was assumed by [1], who calculated effective condensation temperatures for each grain based on a multi-element fit to the condensation model of [6].

Extending the work of [1] we present a statistical analysis of chemical compositions of extracted RMNs from the chondritic meteorites Murchison, Allende and Leoville. We studied a variety of RMNs from meteorites with different alteration histories and oxidation stages in order to gain insight whether the RMNs are altered or are indeed pristine. We will also discuss formation of RMNs in different scenarios e.g. condensation and precipitation during melting processes.

Extracting RMNs: Following the approach of [1] three new SiC rich acid resistant residues were prepared from ~15 g of the meteorite Murchison, ~15 g of Allende and ~4 g of Leoville, using procedures described by [7] that originally were developed for isolation and enrichment of presolar grains. Additionally we performed a density separation on the residue using diiodomethane (3.31 g/cm^3) in order to enrich the RMNs in the heavy fraction. An estimated number of several thousand RMNs were found deposited on the platelets of each sample within an area of 2 mm in diameter. Several hundred RMNs were identified and analyzed in the residue by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The chemical compositions of 212 extracted nuggets (including RMNs from all three meteorites) were obtained by standardless quantitative EDS analysis. The reliability of the EDS quantification was verified by the analysis of two standard alloys with known composition.

Results: RMNs from the three meteorites have similar sizes ranging from ~40 nm to ~ 1µm (Murchison) or ~3µm (Allende). RMNs from Leoville have smaller range between ~150 nm and 800nm. Figure 1 shows data of all measured RMNs for selected elements compared to the condensation trends according to the model of [6]. The alloys consist mainly of Os, Ir, Ru and Mo, but show a large variation in the abundance of these main elements. The populations from the three different meteorites differ slightly. While some RMNs from Allende are W depleted (Figure 1a), in Murchison and Leoville RMNs this element are virtually constant, and the W/Re ratio is remarkably close to the solar system ratio as given by [8]. For these the data plotted in Fig 1 partly agree with the predictions for the lower condensation temperature range around 1400 K, but even for these there are inconsistencies due to the Ru (Figure 1b), Ir and Pt contents [9].

Alteration of RMNs: According to [10] many CAIs - probably the main carrier of RMNs in Allende - were affected by high thermal alteration processes. Most susceptible to oxidation at high temperatures at increasing oxygen fugacity are W and Mo [5]. While several RMNs from Allende are oxidized and depleted in W and slightly depleted in Mo [9], others have a solar Re/W ratio. Given this behavior of W and Mo in the Allende RMNs and the generally solar Re/W ratios in RMNs from Murchison and Leoville, we suggest a pristine nature of these nuggets and a thermal alteration for several Allende RMNs prior incorporation into the parent body.

Formation of RMNs: RMNs contain only low vapor pressure metals. They must have formed at high temperatures, either by condensation from a gas of solar composition or by evaporation of chondritic material. The presence of appropriate amounts of W and Mo makes the second possibility unlikely (see [1]). Since all observed RMN are probably from CAI, the question arises whether the observed nuggets are direct nebular condensates or whether their present composition is affected by melting of CAI or other secondary processes.

- Strong arguments for the condensation origin of Murchison RMNs were provided by [1], who showed that their composition fits on average with condensation calculations. These calculations were based on ideal solid solution of metals and continuous nebular cooling. The too high Ir, Ru and Fe contents would then indicate non-ideality. During condensation the metals will form a single alloy and will be completely removed from the nebular gas by incorporation into simultaneously condensing oxides and silicates. Condensation was favored by [10] who found RMNs enclosed in "Fluffy" Type A CAIs, which are assumed to be the most pristine solar material and show no signs of melting. Moreover, a very strong argument is the finding of very similar RMNs enclosed in presolar "stardust" graphite grains, which undoubtedly must represent stellar (rather than solar) condensates [3].
- Whether the RMNs condensates were later affected by alteration in the parent body or by CAI melting is unclear. The low W/Os for Allende nuggets in Fig. 1 could indicate oxidation of Allende RMN. Allende RMNs also deviate in the Ru vs. Os plot (Fig.2) from calculated condensates and RMNs in other meteorites. CAIs may contain a variety of RMN compositions depending on the onset and end of condensation. Dissolution and reprecipitation of refractory metals in CAI melts may produce average compositions that cannot be easily fitted with simple condensation models.

At present it is difficult to decide to what extent CAI melting has affected RMN compositions. [12] found the majority of refractory metals in metal inclusions of CAI minerals, not large opaque assemblages which would argue against crystallisation of RMNs from melts. Unfortunately the thermodynamic and kinetic properties of RMN alloys during processes of condensation and crystallization from a melt are poorly known. The observed hexagonal closed packed single crystal structure of all RMN so far analysed is assumed to be the stable phase for such alloys at high temperatures [11]. It cannot, however, distinguish between an origin by condensation and one by precipitation.

References: [1] Berg T. et al (2009) *ApJ*, 525, 2:886. [2] Wark, D. A. (1983) PhD dissertation, University of Melbourne. [3] Croat K. et al. (2012) *LPS XXXIII*, Abstract #1503. [4] MacPherson G. J. (2003), in: *Meteorites, Comets, and Planets*, 1, 201. [5] Palme H. et al. (1998) *LPS XXIX*, Abstract #1611. [6] Palme H. and Wlotzka F. (1967) *Earth & Planet. Sci. Lett*., 33, 45-60. [7] Amari S. et al. (1994) *GCA*, 58, 459-470. [8] Lodders K. (1998) *ApJ*, 591, 2:1220. [9] Schwander D. et al., *in preparation.* [10] Eisenhour D. D. and Buseck P. R. (1992) *Meteoritics*, 27, 217-218. [11] Harries D. et al. (2012) *Meteoritics & Planet. Sci*,. 1-11. [12] Palme et al. (1994) *Geochem. Cosmochem. Acta*,58,495-513.

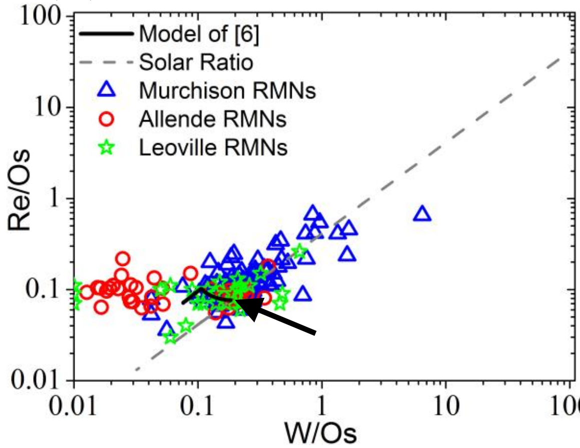

Figure 1: Elemental ratios Re/Os and W/Os of the measured RMNs from residues in comparison to the thermo-dynamic model predictions from [6] for the range from 1400 (at the black arrow) K to 1700 K.

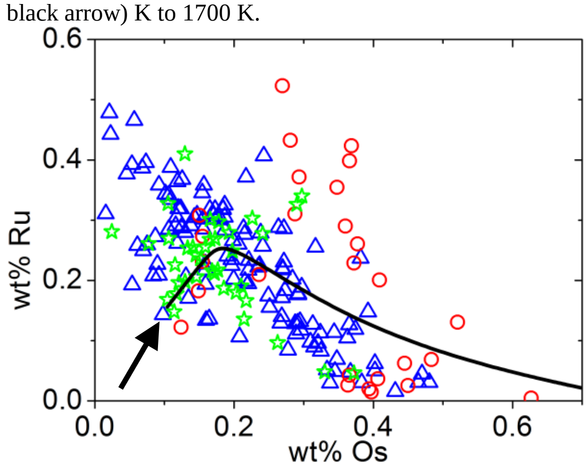

Fig. 2: Weight fraction of Ru plotted vs. weight fraction of Os for all measured RMNs in comparison with the model predictions from [6]. Signs, symbols and temperature range: See Fig. 1.