

**REFRACTORY METAL NUGGETS IN CARBONACEOUS CHONDRITES ARE EARLY SOLAR NEBULA CONDENSATES.** D. Schwander<sup>1,2</sup>, T. Berg<sup>1,2</sup>, G. Schönhense<sup>2</sup>, U. Ott<sup>1</sup> and H. Palme<sup>3</sup>, <sup>1</sup>Max-Planck-Institut für Chemie, Joh.-Joachim-Becher-Weg 27, D-55128 Mainz, Germany. E-mail: d.schwander@mpic.de. <sup>2</sup>Institut für Physik, Johannes Gutenberg-Universität, Staudingerweg 7, D-55128 Mainz, Germany. E-Mail: bergt@uni-mainz.de. <sup>3</sup>Forschungsinstitut und Naturmuseum Senckenberg, Senckenberganlage 25, D-60325 Frankfurt am Main, Germany.

**Introduction:** Ca, Al-rich inclusions (CAI) from chondritic meteorites contain inclusions with minerals predicted to be condensates from a cooling gas of solar composition, such as spinel, melilite, hibonite and perovskite [e.g. 1]. However it has become evident that CAI often have a complex alteration history at lower temperatures involving reactions with the ambient gas leading to modifications of the primary mineralogy. In addition, most CAI were once molten [2], thus erasing a possible primary nebular record. As a consequence so far no mineral grain contained in a CAI could unambiguously be identified as a nebular condensate.

Among the early condensing elements are the refractory siderophile elements Re, Os, Ru, Ir, Mo, W, Pt and Rh. Most CAI are enriched in these metals (e.g [1,3]). Palme and Wlotzka [4] found a 30 $\mu$ m aggregate of refractory metals in the Allende meteorite which they interpreted as a metal condensate modified by exsolution, sulfuration and oxidation at lower temperatures. On the basis of condensation calculations these authors assumed that the refractory metals originally condensed in a single common alloy. Similar aggregates were found by [5] and were later termed “Fremdlinge” by [6] because they were thought to have formed at a different location than the host CAI. It is clear by now that “Fremdlinge” are “domestic”, low temperature alteration products of high temperature metal condensates [7]. Melting of the inclusion may have concentrated the refractory metals in the host inclusion. Therefore the term opaque assemblage (OA) was used to describe these objects.

It was shown by [8] that OA cannot be the only reservoir of refractory metals in CAI, based on the refractory metal contents of bulk mineral grains from Allende CAI. Some authors [e.g. 9] have indeed identified a few nanometer sized refractory metal nuggets (RMN) exclusively consisting of these refractory elements in different CAIs. In this contribution we provide new evidence for a condensation origin of tiny sub  $\mu$ m RMN isolated from the Murchison meteorite and now identified in a CAI from Allende.

#### RMN in acid resistant residues

A large number ~500 of these RMN was identified by Berg et al. [10] in a silicon-carbide rich acid resistant residue of the CM chondrite Murchison after extensive chemical treatment. Detailed analysis of 88 RMN showed that they have variable compositions, which match those predicted for nebular condensates having equilibrated with a solar composition gas over the temperature range of 1400 K to 1600 K (at 10<sup>-4</sup> bar). However, because of the acid dissolution of the meteoritic bulk material no information about the original host minerals of these particles is available.

Extending the work of [10] a second SiC rich acid resistant residue of ~15 g of Murchison was prepared using procedures described by [11] that originally were developed for isolation and enrichment of presolar grains. Additionally we enriched the RMN by density separation using diiodomethane (3.31 g/cm<sup>3</sup>). Several hundred RMN were identified in the residue by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The chemical compositions of 123 extracted nuggets 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.

Condensation calculations were performed using the procedure described by [4] and measured compositions were compared to the theoretical results [10]. The 123 RMN identified in the second acid resistant residue have a similar size range as the RNM of the first residue varying between ~20 nm and a maximum of ~1300 nm. The compositions are also similar. The new set of data therefore covers a similar range of condensation temperatures as the results of [10]. An example is shown in Fig 1 where the temperature-dependent mass fraction of Os in the RMN is plotted vs. the theoretical composition deduced from condensation calculations for the two sets of RMN.

#### In situ detection of RMN

We have begun a search for in situ occurrences of RMN in a polished thin section of the CV chondrite Allende and a separate section of an assumed type B Allende CAI. The *in-situ* search was performed using a FEI NanoSEM 630 field emission SEM in backscattered detection mode. So far we have not found any

RMN in the matrix or in chondrules of Allende. In the CAI section we discovered numerous sub-micrometer RMN nuggets. Most of the RMN are associated with spinels enclosed in large melilite grains. Occasionally RMN are hosted inside spinel or melilite (Fig. 2). Preliminary results indicate that the RMN found in the CAI compositionally fit calculated condensation curves. Contrary to the Murchison grains the Allende CAI RMN seem to represent two distinct populations centered around condensation temperatures of  $\sim 1440$  K and  $\sim 1580$  K (at  $10^{-4}$  bar), as shown in Fig. 1.

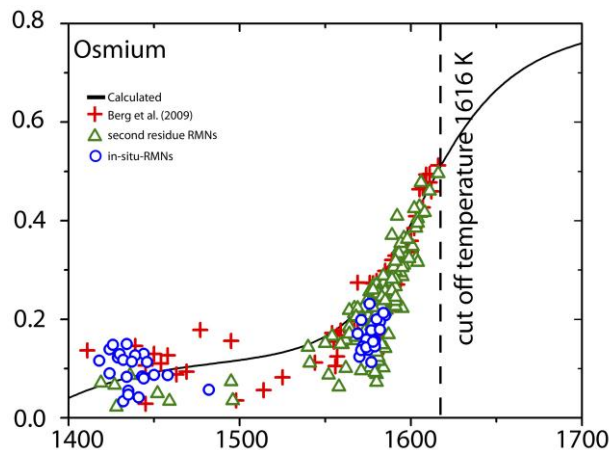


Fig. 1: Comparison of equilibrium calculations with measured mass fraction of Os of all RMN measured in this work (123 in second residue and 48 found *in-situ*) and by [10]. Striking agreement of theoretical predictions and measurements is observed between 1450 K and 1616 K ( $P=10^{-4}$  bar).

**Discussion:** All Murchison grains from this and earlier work [10] fit single-phase condensation calculations in the temperature range from  $\sim 1400$  K to 1616 K. The new data for RMN from an Allende CAI with similar compositions as the Murchison RMN, demonstrate that the RMN extracted from Murchison acid residues are not affected by the acid dissolution procedures. The data suggest a common origin of both populations. The presence of the theoretically expected amounts of the easily oxidizable elements Mo and W in the alloy, makes alteration of the RM nuggets during dissolution and also in the meteoritic environment very unlikely and suggests that the analyzed RMN are pristine solar nebula condensates as proposed by [10]. Strong support for the condensation origin in a single alloy comes from TEM studies of 15 RMN from the first population of Murchison grains [12]. It was found that all 15 grains are compositionally homogeneous monophase hpc single crystals, without evidence for exsolution [12], confirming that the refractory metals condense in a single alloy and not in separate hcp, fcc and bcc structured alloys as suggested by [13].

The presence of these particles in the early condensing CAI minerals melilite and spinel suggest that RMN must have formed very early perhaps using silicates or oxides as condensation sites. Further condensation of silicates or oxides would completely enclose RMN from equilibrium with the solar gas.

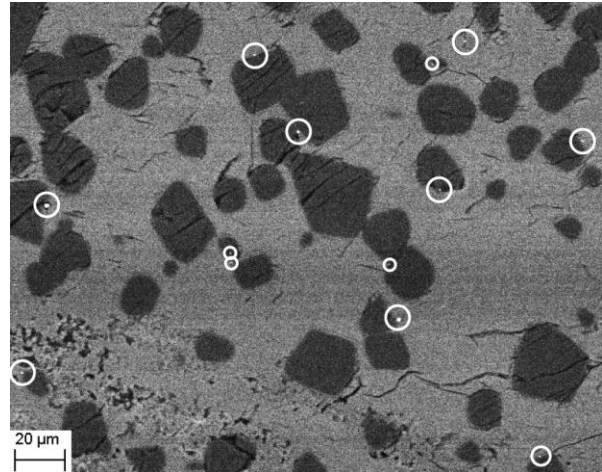


Fig. 2: BSE-Image of an area of a large CAI from Allende. RMN are marked in white circles; spinel=dark grey; melilite= light grey.

**References:** [1] Grossman, L. (1980) *Annu. Rev. Earth Planet. Sci.*, 8,559. [2] MacPherson G.J., in *Meteorites, Comets, and Planets*, Davis A.M., Ed., Vol. 1 *Treatise on Geochemistry*, Holland H.D. and Turekian K.K., Eds. (Elsevier-Pergamon, Oxford), 201-246.. [3] Wänke, H. et al. (1974) *Earth Planet. Sci. Lett* 23, 1;. [4] Palme, H. and Wlotzka, F. (1976) *Earth Planet. Sci. Lett.*, 33, 45. [5] Wark, D. A., & Lovering, J. F. 1976, *Lunar Planet. Sci. Conf.*, VII, 912. [6] El Goresy et al. (1978) *Proc. 9th Lunar Planet. Sci. Conf.* 1279. [7] Blum et al. (1988) *Nature* 331, 405; [8] Palme et al. (1994) *Geochim. Cosmochim. Acta* 58, 495. [9] Wark, D. (1976) *Astrophysics and Space Science*, 65, 275. [10] Berg T. et al. (2009) *ApJ*, 702, L172. [11] Amari, S. et al. (1994) *Geochim. Cosmochim. Acta*, 58, 459. [12] Harries D. et al. (2011) 42nd Lunar and Planetary Science Conference; Abstract#1837. [13] Sylvester P. J. et al. (1990) *Geochim. Cosmochim. Acta* 54, 3491.