

PRESOLAR REFRACTORY METAL NUGGETS. T. K. Croat¹, T. Berg^{2,3}, M. Jadhav⁴ and T. J. Bernatowicz¹,
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Introduction: Refractory metal nuggets (RMNs) highly enriched in W, Os, Ir, Mo and Ru have been found within meteorites, both in assemblages (with Fe-Ni metal, sulphides, and oxides [1]) and as isolated grains [2]. Condensation models [e.g., 3] suggest the isolated grains may be direct condensates from the gas, either from the solar nebula or perhaps from circumstellar environments, although SIMS measurements indicate the former [2, 4]. We report phase and compositional data from RMNs found within presolar graphite (pRMNs) and apply condensation models suggesting pRMN encapsulation within graphite in the 1580-1815 K temperature range (depending on graphite density). The strong similarities between pRMNs from circumstellar environments and isolated RMNs from meteorites (mRMNs) suggest the mRMNs are also direct condensates from the gas and thus are likely some of the first solids to form in the solar system [2].

Experimental Methods: Two RMNs (henceforth MUR1 and MUR2) were found within separate graphites from the KFC1 Murchison high-density fraction (2.15-2.2 g cm⁻³, >1 μm, [5]) from which ~600 graphites were ultramicrotomed en masse [6]. Due to later TEM grid failure, isotopic data from MUR1 and MUR2 are unavailable. A third RMN (henceforth ORG1) was found within a low-density Orgueil graphite (OR1d3m-7 from the OR1d separate; 1.75-1.92 g cm⁻³, >1 μm [7]), which was ultramicrotomed into ~70 nm thick sections (16 studied in TEM). Bulk NanoSIMS measurements of the ORG1-containing graphite showed ¹³C enrichment but isotopically solar O, N and Si within errors [8]. All sections were examined in a JEOL 2000FX analytical TEM equipped with a NORAN Energy Dispersive X-ray Spectrometer (EDXS).

Results and Discussion: Internal pRMNs of size 20-50nm and their host graphites are shown in Fig. 1. All three pRMNs were found to be single phase close packed hexagonal structures (a= 2.75+/-0.03, c= 4.32+/-0.03) using electron diffraction, which is consistent with all 15 mRMNs from [9]. Table 1 lists the pRMN major element EDXS compositions, which all show 6-7 orders of magnitude enrichments in the most refractory Pt group metals (e.g., Os and W). The pRMNs follow the same compositional trends noted in isolated mRMNs from [2] (Figure 2). There, a temperature of last equilibration with the gas was determined based on best fits between the EDXS major element

compositions and calculated condensation curves [2]. Curves are calculated at 10⁻⁴ atm pressure applicable to nebular condensation, which is at the high end of the likely pressure range for carbonaceous grain growth in AGB outflows [e.g., 10]. The temperatures inferred for the MUR1 and MUR2 pRMNs (see also Table 1) exceed those of mRMNs, presumably reflecting the fact that graphite condenses at a higher T than perovskite and other phases that encapsulate most mRMNs [2]. The ORG1 pRMN composition suggests that low-density graphites condense at a lower T than high-density ones. This is also consistent with finding SiC (a

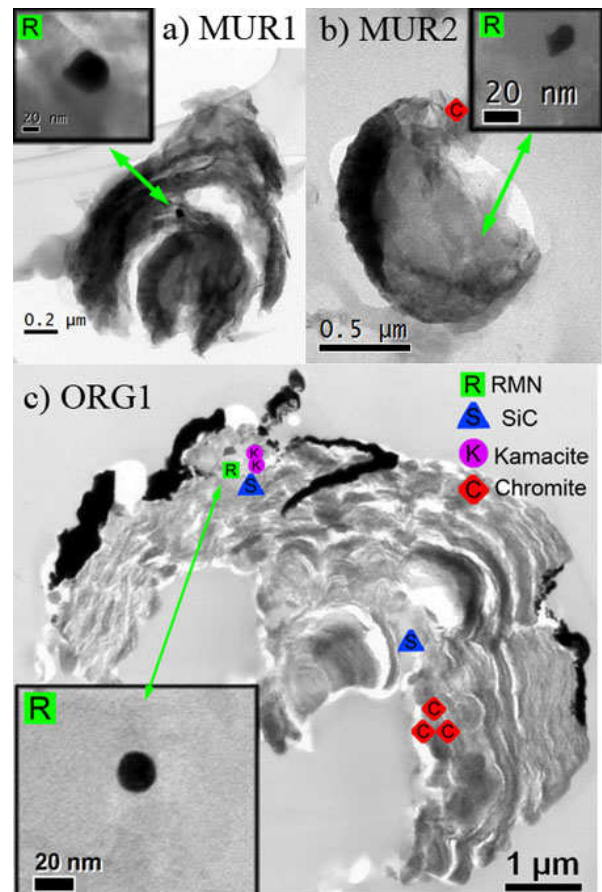


Fig. 1. a) and b) TEM images of internal RMNs (MUR1 and MUR2) found within separate high-density KFC1 graphites and c) ORG1 RMN within low-density Orgueil graphite OR1d3m-7. Positions of other internal grains are also indicated.

Table 1. pRMN compositions (wt. %) and calculated temperature of last equilibration

pRMN	Os	Ru	Mo	Fe	W	Ir ¹	T _{ea}
MUR1	83	6	3	1	7	<3.6	1815
MUR2 ²	59	28	4	2	7	<2.6	1630
ORG1	24	23	19	8	1	25	1580

1. Upper limit listed in table when Ir was not detected; 2. Cr present in MUR2 but excluded from quantization

less refractory phase [10]) within ORG1. TiCs, though common in presolar graphite, were not found in any of the three graphites. The range of graphite condensation temperatures inferred from the pRMN compositions (1580-1815K) is consistent with the formation range predicted by [10] at plausible C/O ratios, with higher T condensation at higher C/O ratios. Graphite condensation is predicted at 1550-1600K for C/O=1.05 and at 1870-1970K for C/O=2 [10]. That the low-density graphite contains less refractory internal phases (ORG1 RMN and SiC), greater turbostratic disorder [11] and higher O content [12], are all consistent with formation of low-density graphite at lower T from a gas with a lower C/O ratio (just above unity). For high density graphites, their more regular graphite ordering, more refractory internal phases, and lower O content are consistent with formation at higher C/O ratios.

If pRMNs were to form at similar temperatures, times, gas pressures and compositions as presolar TiCs and graphites [13], the low Os solar abundance would predict pRMN sizes ~3500x smaller than those observed. Thus pRMN formation must differ from that of other carbonaceous phases, through higher Os gas number densities and/or longer growth intervals [14]. Over-abundances of r-process Os of ~10x are possible in some carbonaceous grain-forming environments, but even larger deviations from solar abundances would probably cause pRMNs to deviate from the Fig. 2 curves [14]. Thus the pRMN sizes suggest formation in clumpy outflows with gas pressures approaching 10⁻³ atm but also likely require time intervals for formation of several decades (~10x longer than in [13]).

The chemical and structural similarities of mRMNs [9] with pRMNs (which are clearly direct condensates from the gas) strengthen the argument that isolated mRMNs may indeed be the some of the first condensates from the early solar nebula [2]. The finding of pRMNs also raises the possibility that some of the isolated mRMNs are actually presolar grains, and that pRMNs may be significant carriers of r-process rich Os.

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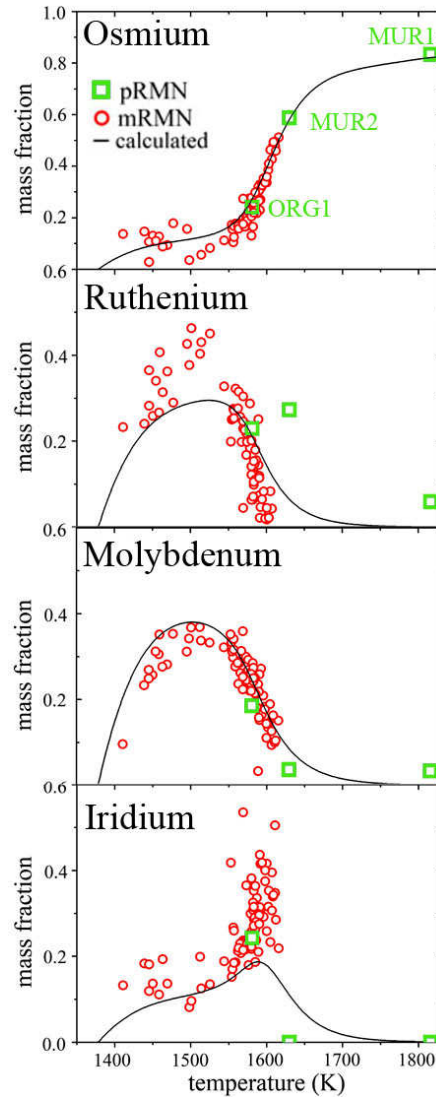


Fig. 2. Elemental compositions (wt. %) of pRMNs and mRMNs [2] plotted vs. an inferred temperature of last equilibration. Solid curves are calculated based on equilibrium condensation from a solar composition gas at 10⁻⁴ atm [3].

References: [1] El Goresy A. et al. (1978) *LPS IX*, 1279. [2] Berg T. et al. (2009) *Ap J*, 702, L172. [3] Palme H and Wlotzka F. (1976) *EPSL*, 33, 45. [4] Hutcheon, I.D. et al (1987) *GCA*, 51, 3175. [5] Amari S. et al. (1994) *GCA*, 58, 459. [6] Croat T.K. et al. (2005) *Ap J*, 631, 976. [7] Jadhav M. et al. (2006) *New Astron. Rev.* 50, 591. [8] Jadhav M. et al. (2012) *GCA (submitted)*. [9] Harries D. et al. (2011) *LPSC XLII, abstract #1837*. [10] Lodders, K. and Fegley, B. Jr. (1995) *Meteoritics*, 30, 661. [11] Croat et al. (2008) *Meteoritics & Planet. Sci.*, 43, 1497. [12] Hoppe et al. (1995) *GCA*, 59, 4029. [13] Bernatowicz et al. (2005) *ApJ*, 631, 988. [14] Croat et al. (2012) *Meteoritics & Planet. Sci. (submitted)*.