RUTHENIUM ISOTOPE COMPOSITION OF ALLENDE REFRACTORY METAL NUGGETS. M. Fischer-Gödde[1], D. Schwander[2], U. Ott[2], and T. Kleine[1]. [1]Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany. Correspondence: m.fischer-goedde@uni-muenster.de, [2]Institut für Physik, Universität Mainz, Staudingerweg 7, 55128 Mainz, Germany.

Introduction: Thermodynamic calculations predict that the first elements to condense from a gas of solar composition are the refractory siderophile elements (W, Re, Os, Ir, Mo, Ru, Pt and Rh) [1]. These elements occur as tiny refractory metal nuggets (RMNs) and as larger aggregates of metal, oxide, sulfide, phosphate and silicate phases [1,2] in primitive chondrites. The latter have been termed Fremdlinge or opaque assemblages and are thought to be the product of low-temperature parent body processes [3-5]. The precursors of Fremdlinge nevertheless probably had a condensation origin. More recently, Berg et al. [6] identified a large number of RMNs from Murchison, whose chemical composition was interpreted as being consistent with condensation from a solar gas.

As some of the first solid material formed in the cooling solar nebula, RMNs provide important information on the initial isotopic composition of the solar system and may have tapped an initial isotope heterogeneity at a very early stage of solar nebula evolution. Ruthenium is a promising element to study in this regard, because bulk meteorites exhibit nucleosynthetic Ru isotope anomalies. Ruthenium has two *p*-only (^{96}Ru, ^{98}Ru), one *s*-only (^{100}Ru) and one *r*-only isotope (^{104}Ru), making it possible to identify the distribution of the carriers of *p*-, *s*- and *r*-process nuclides through precise Ru isotope measurements. Relative to the Earth, all meteorites are characterized by a deficit in *s*-process Ru nuclides as is evident from lower-than-terrestrial ^{100}Ru/^{101}Ru ratios [12,13].

Hutcheon et al. [7] conducted the first Ru isotope study on Fremdlinge from Allende and found no resolvable Ru isotope anomaly at the ~1 % level. Here we report the first high-precision Ru isotope data for a RMN separate from the Allende CV3 meteorite.

Samples and Analytical Methods: A sample enriched in refractory metal nuggets (RMN) from a ~30 g piece of the Allende CV3 meteorite was prepared by sequential dissolution following the method of [8]. In addition to RMNs, the sample also contained presolar nanodiamonds and some Ca-rich mineral grains, most probably perovskite and spinel.

To achieve dissolution of the RMNs only, the sample was digested in a Carius tube in reverse aqua regia at 230°C. Using this technique the nanodiamonds should not be dissolved. A small aliquot of the sample solution was used to determine concentrations of Re, W, Ir, Mo, Ru, Pt and Pd by isotope dilution using the ThermoScientific X-Series II Q-ICMPS at the University of Münster.

From the remaining solution, Ru was purified by distillation of volatile RuO_4. Ruthenium isotopes were measured on a ThermoScientific Neptune *Plus* MC-ICPMS at the University of Münster, equipped with a Cetac Aridus II desolvating system. Isobaric interferences of Mo and Pd were corrected by monitoring ^{97}Mo and ^{105}Pd. Measured Ru isotope ratios were normalized to ^{99}Ru/^{101}Ru using the exponential law and are reported as ε^{i}Ru (parts per 10^4 deviation from the terrestrial Ru standard).

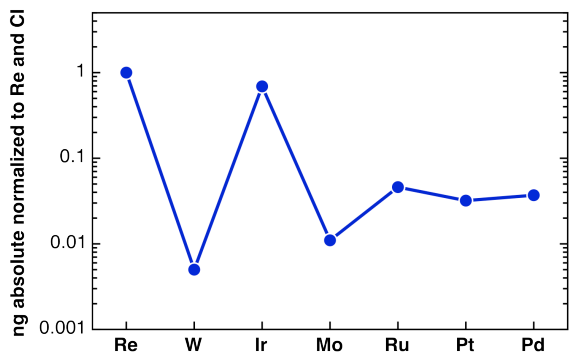

Fig. 1: Highly siderophile element pattern of the Allende RMN sample. Absolute amount of element [ng] present in sample normalized to Re and CI chondrite concentrations.

Results: The relative abundances of Re, W, Ir, Mo, Ru, Pt and Pd in the investigated RMN sample are shown in Fig. 1. Rhenium and Ir are enriched relative to the less refractory Mo, Ru, Pt and Pd. Molybdenum and W exhibit marked depletions relative to other siderophile elements of similar volatility. Overall, the abundance pattern of the siderophile elements in the RMN sample is similar to those observed previously for opaque assemblages in Allende [e.g. 9], although the Mo depletion observed here is somewhat larger than those reported in earlier studies.

The Ru isotope composition of the RMN sample is shown in Fig. 2 and reveals large, mass-independent isotope anomalies of nucleosynthetic origin. For normalization to ^{99}Ru/^{101}Ru, the RMN sample shows apparent excesses in all other Ru isotopes. Overall, this Ru isotope pattern is consistent with a deficit in *r*-process nuclides as calculated using the stellar model of nucleosynthesis from [10] (Fig. 2a). Compared to this model, the observed ^{96}Ru- and ^{98}Ru-excesses are

somewhat smaller than those expected for a pure *r*-deficit, however. This slight mismatch may reflect coupled *p*- and *s*-excesses of different magnitude (which would be different from a pure *r*-deficit).

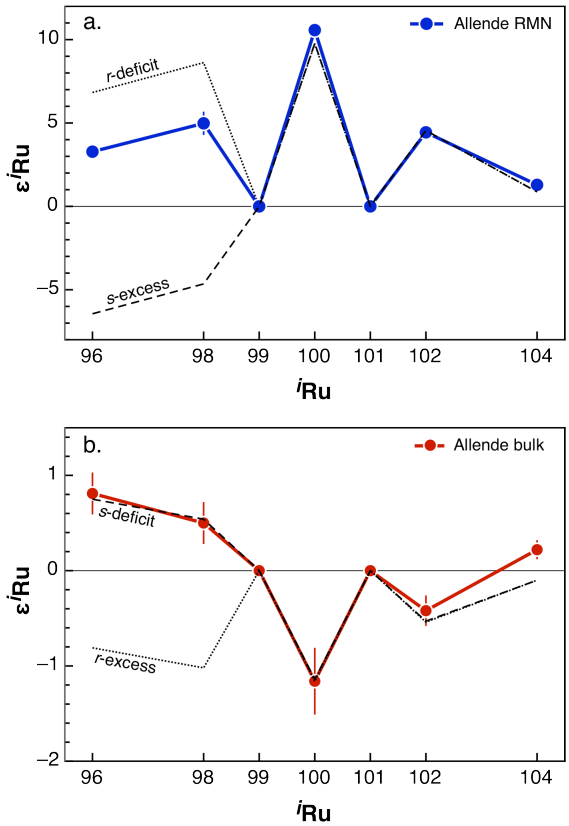

Fig. 2: Ruthenium isotope composition of Allende RMN (a.) and bulk Allende (b.) in comparison to isotopic patterns calculated for a deficits and excesses in *r*-process (dotted lines) and *s*-process nuclides (dashed lines) using the stellar model of Arlandini et al. [10].

Although the SiC content of Allende is very low (<0.02 ppm [11]), some SiC might have been present in the RMN sample investigated here. The slight mismatch between the model and the measured Ru isotope composition of the RMN sample could, therefore, in principle also reflect the addition of *s*-process Ru released from SiC during dissolution of the RMN-enriched sample. This possibility is considered unlikely, however, because our Carius tube digestion method is not expected to dissolve SiC. Likewise, the observed *r*-deficit in the RMN sample suggests that the nanodiamonds present in the separated RMN fraction were not attacked during Carius tube digestion. This is because nanodiamonds are enriched in *r*-process nuclides, and so, leached Ru from the nanodiamonds should show an *r*-excess rather than an *r*-deficit.

We have also determined the Ru isotope composition of a bulk Allende sample taken from a homogenized ~100 g powder, using an alkaline fusion digestion and the same analytical techniques as for the RMN sample. The Ru isotope results indicate that bulk Allende exhibits an *s*-deficit pattern, in stark contrast to the *r*-deficit pattern observed for the RMN sample (Fig. 2b).

Discussion: In an earlier study, Hutcheon et al. [7] concluded that the absence of large (i.e., ≥ 1%) Ru isotope anomalies in opaque assemblages from Allende preclude a presolar origin of these samples. Berg et al. [6] also concluded that the absence of large Os isotope anomalies in RMNs from Murchison rule out a presolar origin. Our results are consistent with these previous studies, because the Ru isotope anomalies of the RMN sample, although being large compared to those in bulk meteorites, are very small compared to anomalies expected for presolar components.

Since Ru in the RMNs is among the first elements expected to condense from a gas of solar composition, the most straightforward interpretation of the Ru isotope data is that they reflect an early isotope heterogeneity of the solar nebula. It is noteworthy that bulk CAIs seem to exhibit much smaller Ru isotope anomalies than the RMNs, and are characterized by ^{100}Ru deficits [12]. To account for the contrasting ^{100}Ru anomalies in RMNs and bulk CAIs, *r*-process Ru nuclides, therefore, must have been added to the CAI after condensation of the RMNs.

There are two important differences between the Ru isotope patterns of the Allende RMNs and those of bulk Allende and most other bulk meteorites. First, the Allende RMNs show an excess in ^{100}Ru, whereas most bulk meteorites exhibit ^{100}Ru-deficits. Second, while the Allende RMNs reveal an *r*-deficit pattern, bulk meteorites are characterized by *s*-deficit patterns. Thus, the composition of bulk Allende and other bulk meteorites is not easily obtained by adding *r*-process Ru to a composition sampled by the Allende RMNs. Instead, a more complicated scenario is required, which involves the addition of both *r*- and *p*-process Ru nuclides to obtain the composition of bulk meteorites.

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