Ruthenium isotope composition of Allende refractory metal nuggets

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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 called Fremdlinge or opaque assemblages in primitive chondrites [1-5].

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 sampled 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. 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 [7,8].

Ruthenium isotopes

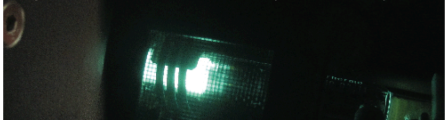
Pd98	Pd99	Pd100	Pd101	Pd102 1.02	Pd103	Pd104 11.14	Pd105	Pd106
Rh97	Rh98	Rh99	Rh100	Rh101	Rh102	Rh103	Rh104	Rh105
Ru96 5.52 *p*	Ru97	Ru98 1.88 *p*	Ru99 12.7 *r, s* [28.4%]	Ru100 12.6 *s* [95.3%]	Ru101 17.0 *r, s* [15.3%]	Ru102 31.6 *r, s* [43.03%]	Ru103	Ru104 18.7 *r, s* [2.74]
Tc95	Tc96	Tc97	Tc98 $t_{1/2}$ = 4.2 Ma β⁻	Tc99 $t_{1/2}$ = 0.2 Ma β⁻	Tc100	Tc101	Tc102	Tc103
Mo94	Mo95	Mo96 16.7	Mo97	Mo98 24.1	Mo99	Mo100 9.63	Mo101	Mo102

Analytical Methods

A sample enriched in refractory metal nuggets (RMNs) from a ~30 g piece of the Allende CV3 meteorite was prepared by sequential dissolution following the method of [9]. In addition to RMNs, the sample also contained presolar nanodiamonds and some Ca-rich mineral grains, most probably perovskite and spinel.

Digestion: Carius tube, HNO_3:HCl (2:1), 230°C

Ru purification: distillation in PFA unit (Mo/Ru < 2×10^{-5})



Measurements: ThermoScientific Neptune *Plus* MC-ICPMS

$$\varepsilon^iRu = \left\{\frac{(^iRu/^{101}Ru)_{sample}}{(^iRu/^{101}Ru)_{standard}} - 1\right\} \times 10^4$$

Internal normalization to $^{99}Ru/^{101}Ru$ and $^{100}Ru/^{101}Ru$

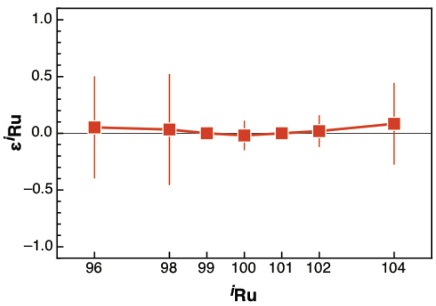
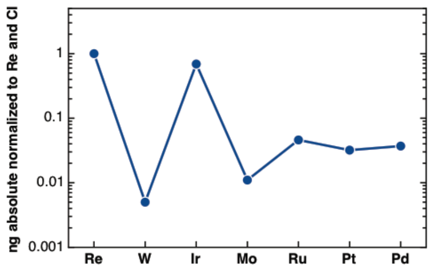


Fig. 1: External reproducibility (2sd) of Ru isotope measurements on the ThermoScientific Neptune Plus MC-ICPMS. Shown are Ru isotope data obtained for multiple digestions (n=8) of Ru doped NIST steel SRM 129C.

Concentrations of siderophile elements



- Re and Ir are enriched relative to the less refractory elements Mo, Ru, Pt and Pd.
- Mo and W exhibit marked depletions relative to other siderophile elements of similar volatility.
- The siderophile element composition of the RMN sample is similar to those of opaque assemblages [e.g. 10].

Fig. 2: Siderophile element composition of the Allende RMN sample. Absolute amount of element [ng] present in sample normalized to Re and CI chondrite concentrations.

Ruthenium isotope composition

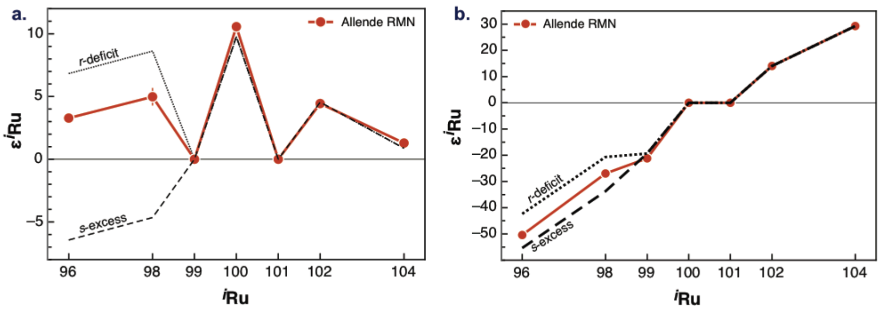


Fig. 3: Ruthenium isotope composition of Allende RMNs for normalization to $^{99}Ru/^{101}Ru$ (a.) and $^{100}Ru/^{101}Ru$ (b.) in comparison to isotopic patterns calculated for deficits and excesses in *r*- and *s*-process nuclides using the stellar model of Arlandini et al. [11].

- The Allende a RMN sample displays large mass-independent Ru isotope anomalies of nucleosynthetic origin (Fig 3).
- When normalized to $^{99}Ru/^{101}Ru$ the sample shows apparent excesses in all other Ru isotopes (Fig. 3a).
- Normalization to $^{100}Ru/^{101}Ru$ yields large negative anomalies for ^{96}Ru, ^{98}Ru and ^{99}Ru, and positive anomalies for ^{102}Ru and ^{104}Ru (Fig 3b).
- The Ru isotope patterns in both normalization schemes are consistent with a deficit in *r*-process nuclides.
- In case of the *p*-process isotopes ^{96}Ru and ^{98}Ru the anomalies are different from those expected for a pure *r*-deficit and might reflect coupled *p*- and *s*-excesses of different magnitude.
- The Ru isotope composition of bulk Allende and Allende CAIs exibit *s*-deficit patterns (Fig 4), in stark contrast to the *r*-deficit pattern observed for the RMN sample.

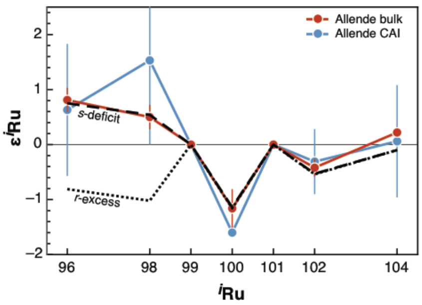


Fig. 4: Ruthenium isotope composition of bulk Allende [this study] and Allende CAIs [7] in comparison to isotopic patterns calculated for deficits and excesses in *r*- and *s*-process nuclides using the stellar model of Arlandini et al. [11].

Discussion

- In an earlier study Hutcheon et al. [12] concluded that the absence of large (> 1%) Ru isotope anomalies in opaque assemblages from Allende preclude a presolar origin. Similarly, a presolar origin of RMNs from Murchison was excluded based on the absence of large Os isotope anomalies [6].
  - → Our new Ru isotope data is consistent with these studies, because the Ru isotope anomalies in the RMN sample are small compared to anomalies expected for presolar phases.
- Ru isotope anomalies in the Allende RMNs most likely reflect an early isotope heterogeneity of the solar nebula when the first condensates formed.
- Bulk Allende and CAIs from Allende display *s*-deficit patterns (Fig. 4), while the Allende RMNs show an *r*-deficit pattern (Fig. 3).
  - → 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 mixing scenario is required, involving the addition of both *r*- and *p*-process Ru nuclides to obtain the composition of bulk meteorites.
- The Ru isotopic signature of Allende RMNs provides no evidence for effects from radiogenic decay of Tc.
  - → The chemical fractionation of Tc from Ru is a prerequisite to generate any measurable effect resulting from Tc decay.
  - → Depending on their respective condensation temperatures Tc/Ru fractionation may occur during condensation and evaporation processes in the solar nebula.

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