# RUTHENIUM ISOTOPE COMPOSITION OF TERRESTRIAL IMPACT ROCKS – A NEW TOOL FOR DEDUCING GENETIC SIGNATURES OF METEORITIC PROJECTILES

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**Introduction:** Many impact-related rocks and deposits are characterized by elevated abundances of platinum-group elements (PGE) that may derive from the meteoritic projectile [*e.g.*, 1]. One of the most prominent and well-studied examples for extraterrestrial PGE-enrichment in terrestrial rocks is the Cretaceous-Paleogene (K-Pg) boundary layer. In 1980 Alvarez et al. [2] reported elevated concentrations of Ir in Italian and Danish K-Pg boundary layers. This finding fostered the hypothesis that the latest major mass extinction event on Earth was triggered by an asteroid impact, at 66 Ma ago. In the following years, Ir concentrations exceeding normal crustal values were reported for an increasing number of K-Pg boundary sites [*e.g.*, 3].

Besides the K-Pg boundary layer, many other examples of elevated PGE concentrations in impact-related terrestrial rocks of various ages were documented. Consequently, PGE systematics such as inter-element PGE ratios and osmium isotope compositions were used to place constraints on the nature of meteoritic projectiles [*e.g.*, 4-6]. However, this approach relies on the assumption that relative PGE abundances were not fractionated during the impact itself, or during later processes affecting their host rocks. When using ratios of fluid-immobile PGE like Os, Ir, Ru, and Rh reliable constraints on the meteoritic component can be deduced. For instance, PGE analyses of impact rocks from the Popigai, Brent, Clearwater East and Morokweng impact structures yielded critical constraints on the type of meteoritic projectile that produced these craters [4-6].

Here we present a new tool for deducing the nature of the meteoritic component in impact-related terrestrial rocks and deposits that is based on the isotopic composition of the PGE ruthenium (Ru). Our approach builds on nucleosynthetic Ru isotope variations among different meteorite groups [*e.g.*, 7] that could serve as a genetic fingerprint for the meteoritic component in impact rocks. The advantage of this isotopic approach is that for terrestrial impact rocks such nucleosynthetic Ru isotope signatures will be preserved even if inter-element PGE ratios related to the meteorite component may become altered during the impact or by secondary processes.

We report the first Ru isotope data obtained for samples from the K-Pg boundary layer, and other Phanerozoic impact structures and craters (Brent, Clearwater East, Popigai, Rochechouart), as well as data for Archean spherule layers from the BARB-5 and CT3 drill cores (Barberton, South Africa).

**Methods:** The separation and purification of Ru was conducted according to the procedures described in [8]. In brief, Ru from powdered samples was pre-concentrated using a NiS fire assay technique. Ruthenium was separated from the sample matrix by cation exchange chromatography and further purified by distillation. Ruthenium isotopic compositions were measured on a Thermo Fisher NeptunePlus multi collector ICP-MS instrument at the University of Cologne. Isotopic data were normalized to $^{99}Ru/^{101}Ru$ and corrected for mass-dependent fractionation using the exponential law. The results are reported as ε-values representing the deviation in parts per 10,000 from the Ru laboratory standard solution (Cologne 4711 Ru).

**Results:** All analyzed impact-related samples exhibit well-resolved anomalies in $\varepsilon^{100}Ru$ (Fig. 1). Samples from the K-Pg boundary layer have the most negative $\varepsilon^{100}Ru$ anomalies that are indistinguishable from average carbonaceous chondrites (CC) and their associated iron meteorite groups (IID, IVB, Chinga). These compositions are clearly distinct from inner solar system material as represented by ordinary (OC) and enstatite chondrites (EC). In contrast, samples from other Phanerozoic impact structures and craters and Archean spherule layers from Barberton have less negative $\varepsilon^{100}Ru$ anomalies. Collectively, the Ru isotope compositions obtained for these samples are most similar to ordinary chondrites, IIE and IVA irons, and CI carbonaceous chondrites (Fig. 1).

**Discussion:** One important observation from our new Ru isotope data for impact rocks is that, as in the case of meteorites, Ru isotope anomalies of terrestrial impact-related rocks and deposits are systematic and can be assigned to variable deficits in Ru nuclides produced by s-process (slow neutron capture process) nucleosynthesis [*e.g.*, 8]. This observation underscores the validity of our new approach for using Ru isotopic variations among meteorites and terrestrial impact-related rock samples to deduce the nature of a meteoritic component.

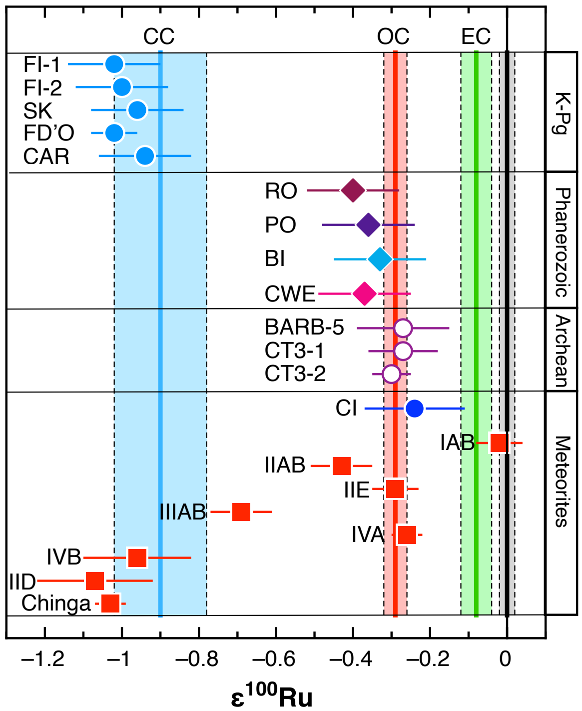


**Fig. 1:** $\varepsilon^{100}$Ru data for terrestrial impact-related rocks (FI: Fishclay, SK: Stevns Klint, FD'O: Fonte D'Olio, CAR: Caravaca, RO: Rochechouart, PO: Popigai, BI: Brent, CWE: Clearwater East, BARB-5 & CT3: Archean spherule layers) in comparison to group averages of meteorite data [7]. Colored areas indicate average values of enstatite (EC), ordinary (OC) and carbonaceous (CC) chondrites and the modern terrestrial mantle (grey area [8]) – with 95% conf. interval uncertainties; CI: CI chondrite; iron meteorite groups: IAB, IIAB, IID, IIE, IIIAB, IVA, IVB and Chinga (ungrouped).

Moreover, the Ru isotope signature of a given impact rock or deposit more directly corresponds to the meteoritic component because the Ru in these rocks will almost quantitatively be derived from the impactor. This is because crustal target rocks have very low Ru concentrations compared to meteorites. In contrast, as shown in previous work (*e.g.*, for K-Pg samples), the Cr isotope composition imparted by the impactor is much more readily diluted by Cr contributions from crustal target rocks [9,10]. In this case the identification of the projectile is only possible via extrapolation using data from various K-Pg sites. This is not the case for Ru because samples from different locations yield uniform and homogeneous Ru isotope anomalies and this isotopic signature directly relates to the impactor composition. Therefore, Ru isotope analyses of impact-related rocks and deposits represent a new tool for deducing the nature of the meteoritic component and its cosmochemical origin.

Our new, still limited Ru isotope data for terrestrial impact structures in conjunction with previously reported PGE concentration data [*e.g.*, 3,5,6] reveal that the projectiles for most Phanerozoic impacts derive from a population of extraterrestrial bodies that formed from an inner solar system reservoir, best represented by ordinary chondrites. This is in line with the fact that the majority of meteorite falls and finds are ordinary chondrites. So far, the one and only exception from this composition are samples from the K-Pg boundary layer. These samples clearly have carbonaceous chondrite-like Ru isotope compositions (Fig. 1). This is consistent with previous constraints from Cr isotopes [9,10].

It might be speculative, but maybe the disastrous consequences of the K-Pg impact may also in part relate to the rather exotic carbonaceous chondrite nature of the projectile. Nevertheless, our new Ru isotope data clearly reveal that the K-Pg impactor represents one of the rare cases that involves the impact of a body that derives from an outer solar system reservoir.

**Outlook:** Future work will be directed to determine Ru isotope signatures of other terrestrial and lunar impact rocks. Ruthenium isotope analyses of the Morokweng structure and for additional K-Pg sites are currently being conducted and will be reported at the conference. In case of the Moon, so far only a few Ru isotope data have been reported for impact rocks [11]. Because some 3.9-4.2 Ga old lunar impact rocks bear evidence for a carbonaceous chondrite-like impactor composition [12], this could be tested with Ru isotopes. As shown with the example of K-Pg boundary layer samples, carbonaceous chondrite-like compositions in impact rocks can be well distinguished owing to the more negative $\varepsilon^{100}$Ru values of carbonaceous chondrite groups (Fig. 1). As such, new Ru isotope data for lunar impact rocks may help to address the question whether volatile-rich material was added to the Earth-Moon system during its late accretion period.

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