SEARCH FOR *R*-PROCESS ^{244}PU IN THE K-PG BOUNDARY LAYER.

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Introduction: The K-Pg (Cretaceous–Paleogene) boundary at 66 Ma marks one of five major mass extinctions in Earth's fossil history. Based on strong enrichments of the platinum-group elements in the boundary layer, Alvarez et al. [1], in 1980, suggested that the impact of a large asteroid was responsible for the K/Pg event.

Earlier, other possible causes for the mass extinction, e.g., a nearby supernova(SN)-explosion, were also discussed, and indeed also Alvarez et al. initially considered this option to explain the high Ir concentration. However, to explain the observed Ir content, the distance for a SN would have to be less than one light-year. To exclude the SN option for the K-Pg event, they searched for a specific long-lived radionuclide, ^{244}Pu, which has a half-life of 81 Myr and does not exist naturally on Earth. Assuming that this radionuclide is predominantly produced and ejected in SNe, its presence could indicate a nearby SN. No ^{244}Pu at required levels was detected, leaving an impact as the most plausible cause (which was later confirmed by the discovery of shocked minerals and also a source crater, Chicxulub).

However, since 1980, strong evidence evolved that the heavy *r*-process elements, e.g., actinides such as ^{244}Pu, are produced in rare explosive events (ca. 1000 times less frequent than common type II core-collapse SNe in the galaxy) [2]. Neutron star mergers are potential candidates or rare subsets of SNe. Thus, the common core-collapse SNe might not have contributed significantly to actinide nucleosynthesis for the past few 100 Myr. This assumption agrees also with recent observations following the gravitational-wave event GW170817 [3]. Furthermore, by searching deep-sea archives for interstellar signatures we confirmed recently that nucleosynthesis yields of ^{244}Pu are much lower (possibly a factor of 100) than expected if SNe dominate heavy isotope r-process nucleosynthesis [4-6]. However, the detection of a significant ^{244}Pu influx above background into these terrestrial archives suggests the possibility of a nearby explosive event within the past few hundred millions years, possibly from a rare event. Thus, a small *r*-process contribution to actinide production from SNe is still a possibility. In general, site and frequency of *r*-process events are still strongly debated [2].

Thus, in contrast to the assumption of Alvarez et al. [1], it is not clear that non-detection of ^{244}Pu excludes a nearby supernova explosion at 66 Ma. Despite the overwhelming evidence for an asteroid impact, a new method for direct atom counting has emerged with superior detection efficiency for ^{244}Pu: since the original work by Alvarez et al. in 1980, the ^{244}Pu detection-sensitivity has improved by more than a factor of a million by applying the method of Accelerator Mass Spectrometry (AMS) [5,7,8]. This enormous gain in abundance sensitivity prompted us to reinvestigate the ^{244}Pu concentration in the K-Pg boundary layers. Here we present first results for a set of samples covering this transition period from the Cretaceous to the Paleogene.

Samples: We studied various samples from the same location in Italy (Gubbio) that was analyzed by [1]. Samples were taken from the clay-like sedimentary layer that contains the enhanced iridium concentrations, as well as rock samples from above and below. The latter serve as background samples.

Sample preparation: Sample preparation requires the chemical separation of ^{244}Pu, potentially by the dissolution of the sample. In short, ^{244}Pu is extracted together with a ^{242}Pu spike and co-precipitated with iron hydroxide to produce an oxide powder sample for the subsequent AMS measurement.

Gentle leaching or the standard dissolution procedures used for AMS of soil or sediment samples may not extract all plutonium from the relevant fractions of these samples. Major work was therefore devoted to confirm the quantitative extraction of any potential extraterrestrial ^{244}Pu present.

The samples were ground in an agate mortar and subsequently dried prior to digestion. Different digestion protocols using combinations of nitric acid, hydrochloric acid and hydrofluoric acid were used and compared in order to study the effect of potential refractory oxides, which may incorporate Pu and could be lost for the analysis.

After leaching or digestion, anion exchange chromatography using DOWEX 1x8 resin in nitric acid medium was used to separate the Pu from the matrix elements. The Pu eluate was dried down and eventually co-precipitated with 3 mg Fe added to the solution. After drying, the precipitate containing also the Pu was ignited at 600°C to form Fe_2O_3 and pressed into Al cathodes for AMS.

Measurement method: The most sensitive techniques for identifying longer-lived radionuclides are direct atom counting techniques, in particular Accelerator Mass Spectrometry (AMS) [7], allowing to identify radionuclides at their natural abundances, which can be 10 to 17 orders of magnitudes lower than those of the stable (terrestrial) nuclides. No naturally occurring stable isobar to ^{244}Pu exists and molecular isobaric interference is excluded in AMS.

The Pu contents were analyzed at the 1-MV AMS facility *Vega* at ANSTO, Sydney [9], which is optimized for high actinide measurement efficiency and isotope selectivity. *Vega* demonstrated a measurement efficiency for Pu detection of ~1 % [9,10]. Efficiencies of AMS samples originating from a complex matrix with multiple Pu separation and extraction steps, however, yield values that can be substantially lower.

AMS of ^{244}Pu is nearly background-free, meaning that for processing blanks typically no or only one detector event will be registered over several hours of counting time - which is the typical measurement time of an AMS sample. Accordingly, a significant ^{244}Pu signal above background measured in AMS can be as low as a few detection events per sample.

Results and Discussion: Several samples, processing blanks and reference samples were prepared at the chemistry laboratories at HZDR (Dresden), at ANU (Canberra) and at ANSTO (Sydney) and then measured with AMS using the *Vega* facility. Blanks (which contain only the spike material ^{242}Pu) served to test the background level of ^{244}Pu and ensure background-free measurement conditions, and reference materials verified the overall efficiency.

None of the analyzed samples contain any evidence for interstellar ^{244}Pu. Figure 1 shows preliminary results from the AMS measurements at *Vega*. Plotted are measured ^{244}Pu concentrations of samples from the K-Pg boundary, from adjacent rock layers, and from chemistry blanks.

Four samples representing the boundary layer were processed from masses between a few and up to 250 gram (black symbols). Between 0 and 3 detector events were registered for ^{244}Pu for all samples. There is no significant difference between the K-Pg boundary, the sections outside and processing blanks. The few detector events might reflect residual anthropogenic Pu in the chemical reagents or some memory effect in the AMS ion source that might result from Pu reference material. The error bars in Fig. 1 represent 1σ values using Poisson statistics for low small signals [11].

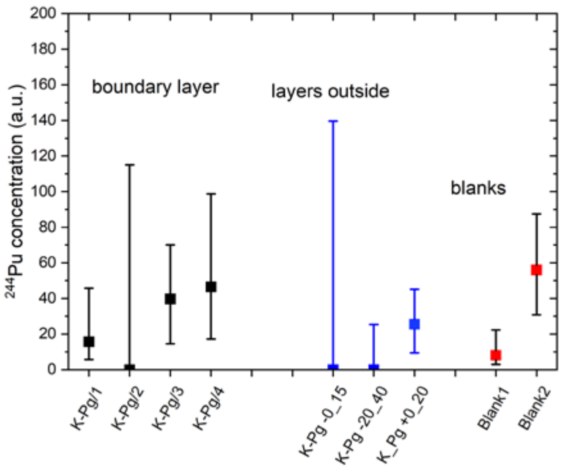

Fig. 1: AMS results (in arbitrary units) for ^{244}Pu measured at ANSTO: K-Pg samples 1 to 4 are from the boundary layer with different leaching and digestion protocols. The blue symbols represent layers above (0 – 20 cm) and below the boundary. Also plotted are two processing blanks.

These first results indicate ^{244}Pu concentration limits more than six orders of magnitude lower than those presented by Alvarez et al. [1]. Our data support the previous conclusion of no evidence being imprinted in the boundary for a close-by explosive event at that time. Considering also the recent shift in knowledge that the most probable *r*–process site changed from SNe to other rare event scenarios (neutron-star mergers or rare subsets of SNe), we do not find evidence that the K-Pg mass extinction is associated with such a scenario. We note that rare events scenarios would have much higher *r*-process yields per single event, which would allow to sample distances 10 to 100 times larger compared to the SN case (see above). Future work includes the determination of the absolute ^{244}Pu concentrations. We will also extend our work to additional mass extinction events.

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