

## RIMSKI (RESONANCE IONIZATION MASS SPECTROMETER FOR KRYPTON ISOTOPES) APPLIED TO $^{81}\text{Kr}$ -Kr COSMIC RAY EXPOSURE AGE DETERMINATIONS OF EUCRITES.

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**Introduction:** The length of time a meteorite has been exposed to cosmic rays (cosmic ray exposure ages, CRE ages) can be determined by comparing the equilibrium concentration of radioactive  $^{81}\text{Kr}$  to the concentrations of stable cosmogenic Kr isotopes. Among the various types of methods  $^{81}\text{Kr}$ -Kr CRE ages appear the most reliable for eucrites because no adjustment is needed for shielding and the high concentration of target elements (Rb, Sr, Y, Zr) for spallation reactions [1]. Moreover the chemical composition of the sample does not have to be known, while isotopic ratios measurements are more precise than absolute gas concentrations.

Among ~200 known eucrites only a few  $^{81}\text{Kr}$ -Kr CRE ages have been reported. This is partly because low  $^{81}\text{Kr}$  concentrations in meteorites (several thousands atoms/mg) have imposed a requirement for gram-size samples [2-4]. O.Eugster and Th.Michel [5] assign known eucrite CRE ages to five clusters:  $6\pm 1$ ,  $12\pm 2$ ,  $21\pm 4$ ,  $38\pm 8$ , and  $73\pm 3$  My, that correspond to CRE age clusters for howardites and diogenites. This suggests these groups of meteorites are sourced from the same impacts on a common parent body (or group of bodies).

We are developing RIMSKI (Resonance Ionization Mass Spectrometer for Krypton Isotopes - formerly known as RISK [8] a time of flight mass spectrometer that can be used to reliably measure CRE ages on **mg-size** samples. Here we report recent determinations of the  $^{81}\text{Kr}$ -Kr ages of 4 eucrites (Stannern, Bereba, Pasamonte and Sioux County) that correspond to known literature values. More measurements are planned to better understand the exposure history of this group of meteorites.

The high sensitivity of RIMSKI will also allow determining  $^{81}\text{Kr}$ -Kr CRE ages of primitive meteorites that, in turn, may provide information about the irradiation environment of the early solar system and allow collision events to be dated [6,7]. Analyses of krypton trapped in presolar SiC grains are also planned.

**Experimental technique:** Samples are heated by focused CW laser radiation to release krypton into the gas phase. After gettering to remove active gases, the krypton is admitted to the mass spectrometer, where it continuously condenses onto a localized cold spot maintained at ~75 K in the back plate of the (Wiley-McLaren) ion source using a commercial liquid helium refrigerator system. Time-of-flight mass spectra are generated with a duty cycle of 10 Hz; accumulated atoms are first desorbed from the "cold finger" by a pulse from a Nd:YAG laser, and resonant photo-ionization takes place in the plume (116.5 nm, 558.1 nm and 1064 nm) after a delay of ~1 $\mu$ s when the concentration of sample atoms in the ionization volume is maximized [9]. Ions are accelerated into the flight tube and detected using a pair of chevron mounted microchannel plates.

**Blank, buildup and reproducibility:** Calibration samples ( $10^6$  krypton atoms) have been used for method characterization. The ionization signal from calibration

samples was compared with the krypton signal acquired when no sample was present and the mass spectrometer was isolated from the pumps. The blank of total ~6300 Kr atoms (~750  $^{83}\text{Kr}$  atoms) was deduced by the comparison of two signal heights determined for the time  $t=0$  and was isotopically consistent with atmospheric krypton. No  $^{81}\text{Kr}$  is registered. Due to degassing, the build up of ~1450  $^{83}\text{Kr}$  atoms is detected after 5 minutes.

In Table 1 we summarize results from 5 days (spread over 9 – the instrument was not run on the other 4 days) during each of which between 9 and 11 analyses were made of our standard calibration sample. On each day the instrument was tuned to maximum sensitivity before analyses commenced and then parameters were not changed during the sequence of analyses. These results thus demonstrate the reproducibility the instrument can achieve when applied to analyses of samples in its current configuration, where unknown ratios would be calibrated with reference to the day's air calibrations.

We calculate isotope ratios relative to  $^{84}\text{Kr}$  and define the delta values in standard way in parts per thousands (permil, ‰). Within each day's analyses, the standard deviation of the delta values for the major isotope is comparable to the average calculated error, indicating that our data reduction process (see below) generates reliable uncertainties on derived ratios. For the major even isotopes measured precision is close to the limit achievable by counting statistics for 5 minutes' analysis, where the measured lifetime against detection (25 minutes) and a quantum efficiency of 50% for the MCP detector have been assumed).

Somewhat worse reproducibility for  $^{83}\text{Kr}$ , and a noticeably higher variance in the standard deviation, can be

**Table 1: Measured, Calculated and Theoretical Limit on Precision.**

Ratio	Ave. S.D. <sup>1</sup>	Var. S.D. <sup>1</sup>	Ave. Err. <sup>2</sup>	Limit <sup>3</sup>
$^{78}\text{Kr}/^{84}\text{Kr}$	830.0	700.0	103.0	56.6
$^{80}\text{Kr}/^{84}\text{Kr}$	27.5	8.9	23.3	22.5
$^{82}\text{Kr}/^{84}\text{Kr}$	9.8	3.6	10.4	10.7
$^{83}\text{Kr}/^{84}\text{Kr}$	14.6	6.2	10.0	11.5 <sup>4</sup>
$^{86}\text{Kr}/^{84}\text{Kr}$	8.9	1.6	9.3	9.1

<sup>1</sup>Average and variance of "within day" standard deviations of delta values over 5 days' analyses of standard air calibrations ( $10^6$  atoms total Kr). <sup>2</sup>Average error calculated by data reduction software over 5 days' analyses. <sup>3</sup>Theoretical limit on precision achievable in 5 minutes' analysis of an initial  $10^6$  krypton atoms assuming a lifetime against ionization of 25 minutes and 50% detection efficiency of ions. <sup>4</sup>20% less efficient ionization of  $^{83}\text{Kr}$  compared to  $^{84}\text{Kr}$  has been assumed, in accordance with experimental observation. All units are permil (‰).

explained by nuclear spin induced spectroscopic effects [9]. For this isotope ratio it may be necessary to make a minor correction to calculated uncertainties to reflect actual within-day variation in ionization efficiency.  $^{78}\text{Kr}$  is something of a special case. There are fewer than 4000 atoms of this isotope in the calibration sample, and an isobaric interference with benzene ( $\text{C}_6\text{H}_6$ ) occurs. The main sources of this compound in the system are vapors of turbo pump oil and impurities in the solvents used for cleaning of vacuum parts. It has been found that the interference is negligible at the beginning of the day rising up to  $\sim 300\%$  of the total  $m/z=78$  peak height after about 5 hours of operation (the cold spot is allowed to return to ambient temperature overnight). For this isotope correction of the peak height can be performed by repeatedly determining the signal at mass 78 in blanks and interpolating.

**CRE ages and sensitivity:** Our measurements of the  $^{81}\text{Kr}$ -Kr ages of Stannern, Bereba, Pasamonte and Sioux County eucrites are summarize in Table 2 and compared with the literature values. The ages were calculated according to:

$$T_{81}(\text{My}) = 0.152 \left[ \left( \frac{^{80}\text{Kr}}{^{81}\text{Kr}} \right)_c + \left( \frac{^{82}\text{Kr}}{^{81}\text{Kr}} \right)_c \right] [6]$$

This formula combines  $^{83}\text{Kr}/^{81}\text{Kr}$  cosmogenic ratio with  $P_{81}/P_{83}$  production rate ratio; the factor 0.152 is a multiplication of  $^{81}\text{Kr}$  decay constant ( $T_{1/2}$  0.303 My) to isobaric fraction yield of  $^{81}\text{Kr}$  determined from irradiation experiments of the main meteoritic target elements with high-energy protons. Because of  $^{86}\text{Kr}$  yields from spontaneous fission of  $^{244}\text{Pu}$  [11] as well as from spallation [12] are low it is assumed that  $^{86}\text{Kr}$  belongs to trapped component. Hence, cosmogenic  $(^{80}\text{Kr}/^{81}\text{Kr})_c$  and  $(^{82}\text{Kr}/^{81}\text{Kr})_c$  ratios can be easily calculated from measured isotope ratios which are a mixture of cosmogenic and trapped components. The cosmogenic isotope ratios used in CRE ages calculations are presented at the three-isotope plot in Fig.1. As expected they are higher for the meteorites with bigger ages. The data nicely fit a linear function with a slope of 0.61 which is a  $P_{80}/P_{82}$  production rate ratio (in literature  $P_{80}/P_{82}=0.64$  [6]).

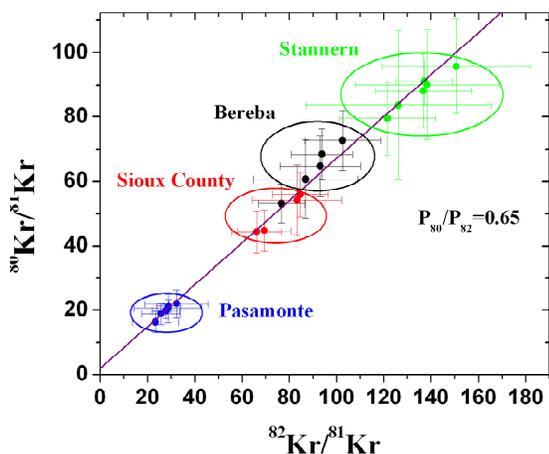


Fig.1 Three-isotope plot of cosmogenic  $^{80}\text{Kr}/^{81}\text{Kr}$  and  $^{82}\text{Kr}/^{81}\text{Kr}$  ratios of measured eucrites.

Our data reduction software integrates the peak areas with baseline subtraction and calculates the peak area errors that account for the baseline noise and the counting statistics. A linear least squares fit is used to determine the isotope ratios at inlet time. The errors on CRE ages are dominated mainly by  $^{81}\text{Kr}$  errors. The measured CRE ages of Bereba, Pasamonte, Sioux County and Stannern meteorites in a very good agreement with the literature values. The measurement uncertainties ( $<11\%$ ) in most cases are bigger than that of a literature data ( $<8\%$ ). However the weight of the samples discussed in this work are almost 3 orders of magnitude smaller (a gramm-size samples required for conventional apparatus's). E.g. 1.2 mg sample of Pasamonte meteorite contains only 3500 atoms of  $^{81}\text{Kr}$ . Thus we expect to be able to apply this ultra sensitive method for variety of discussed above exciting applications of planetary science in near future.

**Table 2: Measured  $^{81}\text{Kr}$ -Kr cosmic-ray exposure ages for eucrites (in Ma)**

Meteorite	$T_{81}, \text{My}$ this work	$T_{81}, \text{My}$ Literature
<b>Bereba</b> (2-5 mg)	<b>23.6±2.7</b>	<b>26.1±2.2</b> [2] <b>23.9±0.9</b> [10] <b>21.0±1.6</b> [4]
<b>Pasamonte</b> (1-4 mg)	<b>7.3±1.5</b>	<b>7.4±0.5</b> [2] <b>8.2±0.7</b> [10]
<b>Sioux County</b> (2-5 mg)	<b>19.1±2.2</b>	<b>20.6±1.3</b> [2] <b>18.9±1.4</b> [10] <b>20.6±0.9</b> [4]
<b>Stannern</b> (2-4 mg)	<b>33.9±3.9</b>	<b>35.6±0.9</b> [4] <b>34.6±0.6</b> [4] <b>36.9±2.9</b> [10]

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