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An ultra sensitive laser resonance ionisation mass spectrometer for krypton isotopic analysis.

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Abstract

An ultra sensitive mass spectrometer for krypton isotopic analysis has been developed. Tunable pulsed lasers are used for resonance ionisation of Kr atoms that are later detected by time of flight. Non-linear four wave mixing in a gaseous medium is used to generate tunable near 116.5 nm radiation for efficient excitation of the first atomic transition. Two other pulsed beams (558.1 nm and 1064 nm) complete the ionisation scheme. The method sensitivity is demonstrated by successful detection of radiogenic ^{81}Kr from noncumulate eucrite Stannern. Routine isotope ratios measurements of atmospheric samples containing 10^6 krypton atoms demonstrate precision better than 2%

1. Introduction

Krypton isotope structures in extraterrestrial material record the physical properties of s-process sites and the irradiation history of the early solar system.

Measurements of ^{81}Kr/^{stable}Kr isotope ratios of e.g. primitive meteorites allows cosmic ray exposure times (CRE ages) to be determined that, in turn, may provide information about the irradiation environment of the early solar system and allow collision events to be dated [1]. Moreover, krypton isotopes trapped in presolar SiC grains record the physical properties of s-process sites such as the temperature and neutron flux [2].

Extracting the maximum amount of information from such samples requires instrumentation with extremely high sensitivity (<1000 atoms detection limit). Such an instrument has been developed in our laboratory.

2. The apparatus

The ion source of the mass spectrometer is a Wiley-McLaren design. After focusing by einzel lens down a 65 cm flight tube the ions are detected by time of flight in a simple linear mode.

Meteorites are heated by CW laser radiation, releasing noble gas atoms into the mass spectrometer according to the diffusion properties of their host phase. Using a commercial refrigerator system a stainless steel substrate placed inside the mass spectrometer's ion source is cooled down to ~75 K. Sample atoms condense for 0.1 s and later are desorbed by a pulsed laser radiation. Desorbed atoms are resonantly excited (see below) and ionized by 1064 nm photons from a Nd:YAG laser (nanosecond laser pulses >0.2 J/cm^2 are used). Ions are mass-separated by time of flight.

Krypton atoms initially excited by 116.5 nm photons that are generated by nonlinear four wave sum frequency mixing in a xenon-argon mixture. Xenon atoms are excited by a two-photon absorption transition into a $5p^5(^2P°_{3/2})7s$ J=1 level (two photons of 252.5 nm are used) which provides the dipole polarization necessary for mixing. Phase matching is achieved by controlling the refractive index by varying the partial pressures of xenon and argon.

A second 558.1 nm beam (>85 mJ/cm^2) further excites the atoms into the $4s^24p^5(^2P°_{3/2})6p$, J=0 level, from which 1064 nm light (>0.2 J/cm^2) completes the ionization process.

3. Capability of the Method

The instrument sensitivity can be demonstrated by using e.g. noncumulate eucrite Stannern. The absolute concentration and isotopic ratios of Kr trapped in Stannern have been measured using a conventional mass spectrometer (>330 mg samples were required [3]). We used an 18 mg grain such that stepwise heating releases might be expected to produce roughly 10^3-10^4 atoms of ^{81}Kr.

The grain was step-heated by DC current for 3 min. 6 temperature steps were made and time-of-flight (TOF) spectra were repeatedly recorded after gettering. In Fig. 1a) a TOF spectrum is presented. The inset is an enlarged *m*/*z*=81 region. The signal disappeared when one of the lasers was detuned by a few nm from the resonant wavelength demonstrating that this is ^{81}Kr. Pulse counting at this mass revealed that the peak was created by ~270 ions. Thus the sensitivity is such that 1 cps (1 count per second) is produced by ~1000 atoms.

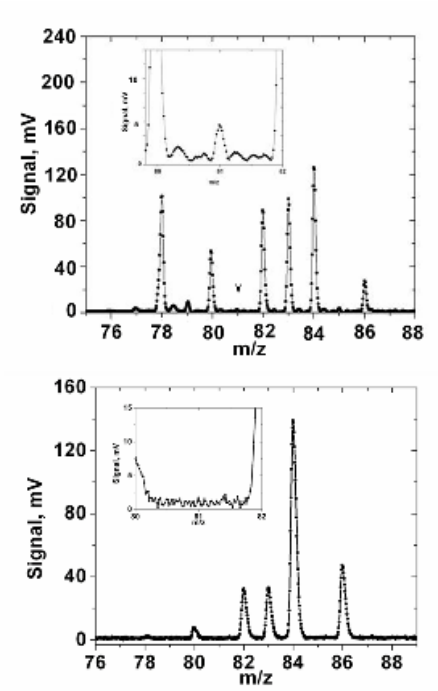

Figure 1: a) Integrated over 5 minutes (3000 desorption laser shots) TOF spectra of a Stannern meteorite measured using stepwise heating technique. The peak at m/z=81 (inset) corresponds to radiogenic ^{81}Kr. b) A TOF spectra of 10^6 atoms of atmospheric krypton and enlarged m/z=81 mass region. As expected no ^{81}Kr is detected in this case.

As expected the Kr isotope ratios of Stannern dramatically differ from terrestrial samples. An example of the TOF spectra of air sample containing ~10^5 atoms of ^{84}Kr is presented in the Fig.2b).

In principle, the minimum sample size which can be measured is limited only by blank, which is currently ~1800 atoms of ^{84}Kr and isotopically atmospheric. The maximum sample size of 10^7 atoms is considered practical. The bigger amounts of atoms lead to increase of the charge density in the ion source reducing the mass resolution dramatically and significant reduction of channel plate detector sensitivity.

Each analysis takes 5 min during which 3000 TOF spectra are collected (the condensation-ionization process occurs at 10 Hz). It has been determined that ~5 s takes for halve of the sample atoms to be collected at the cold spot, thus several multiple analysis of the same is performed. Routine isotope ratios measurements of atmospheric samples containing 10^6 krypton atoms demonstrate the precision below 2% [4].

4. Summary

An ultrasensitive mass spectrometer for measurements of isotope ratios of krypton has been developed. A krypton gas can be extracted from solid samples by laser heating. The mass spectrometer blank is ~1800 atoms of ^{84}Kr and has purely atmospheric composition.

Successful measurements of radiogenic ^{81}Kr in 18 mg grain of Stannern meteorite suggests the method capable of detection of <1000 atoms of particular isotope. The precision of the isotope ratios determination below 2% has been demonstrated.

References

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