**RESONANT PHOTOIONIZATION MASS SPECTROMETER FOR DETERMINATION OF ISOTOPIC COMPOSITIONS OF KRYPTON IN EXTRATERRESTRIAL SAMPLES.** I. Strashnov[1], D. J. Blagburn and J. D. Gilmour, [1]School of Earth Atmospheric and Environmental Sciences, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK (Ilya.Strashnov@manchester.ac.uk).

**Introduction:** The isotope ratios of Krypton trapped in presolar SiC grains record the physical properties of s-process sites [1], while Kr isotopic measurements of small samples of primitive meteorites allow the irradiation environment of the early solar system to be investigated [2,3]. Extracting the maximum amount of information from such samples, especially those available in limited amounts such as material returned by the Genesis and Stardust missions, requires instrumentation with extremely high sensitivity (detection limit ~1000 atoms). Such an instrument that employs a resonant photoionisation mass spectroscopy method [4] is under development in our laboratory since 2007 [5]. The latest results are discussed.

**Experimental procedure:** The development of the time-of-flight mass spectrometer (TOF MS) benefits from its prototype 'RELAX (Refrigerator Enhanced Laser Analyser for Xenon)' [6] that has successfully been used for determination of isotopic ratios of Xe in various extraterrestrial samples [e.g. 7]. As a result of step-heating or laser probe the atoms are released from sample into a mass spectrometer volume where condensation at the localized cold spot (~75 K) occurs. After desorption of condensate by 1064 nm Q-switched Nd:YAG laser Kr atoms are ionized by a resonant photoionization laser system and detected by electron multiplier. For calibration and adjustment purposes the known aliquots of air contained $10^5$-$10^6$ atoms of interest can be used.
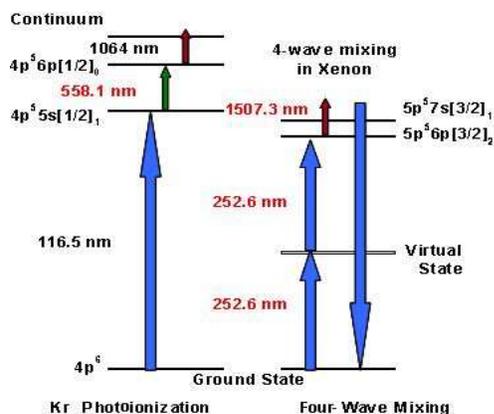


*Fig. 1: Kr photoionization scheme and Xe levels used for four-wave mixing.*

The Kr photoionization scheme (Fig. 1) employs resonant excitation from the ground state by 116.5 nm vuv light that is generated using four-wave non-linear mixing in Xe (described in details below). The second resonant step employs ~1 mJ/mm$^2$ at 558.1 nm from a dye laser (Sirah, Cobra) pumped by the second harmonic (532 nm) of a pulsed Nd:YAG laser (Continuum, Powerlight 9010, 10 Hz, ~5 ns pulse width). Part of the fundamental 1064 nm light from the same Nd:YAG laser (~2 mJ/mm$^2$) is used for the ionization step. We estimate that the ionization region is ~1 mm from the cold spot. All dye lasers are pumped by the same Nd:YAG laser system, beam delay lines being employed to ensure temporal overlap.

**VUV generation by four-wave mixing in Xe:** Our experimental architecture is adapted from that reported by Thonnard et al. [8]. The Xe levels used for 116.5 nm light generation are shown in Fig.1. The interaction of four coherent optical fields through the third order non-linear susceptibility known as four-wave mixing is well studied [9]. Because of energy and momentum conservation laws, radiation of frequency $\omega_4 = \omega_1 + \omega_2 + \omega_3$ is generated if the phase matching condition $\Delta k = k_4 - k_1 - k_2 - k_3 \approx 0$ is met ($k_i$ are wave vectors that depends on refractive index). To meet this condition a xenon-argon mixture can be used as a nonlinear medium. Xenon is negatively and argon positively dispersive in the spectral region near 116.5 nm, so by changing the partial pressures of gases to match the input laser frequencies an optimum condition for vuv light generation at the desired wavelength can be found. The intensity of generated light is given by

$$I(w_1 + w_2 + w_3) = N^2 \chi^2 F I(w_1) I(w_2) I(w_3),$$

were $I(w_i)$ is the intensity of the laser light at frequency $w_i$, $N$ is the concentration of atoms used in the mixing process, $\chi$ is the third order susceptibility and $F$ is a function having maximum when the gas media is phase matched.

In our experiment two collinear 252.6 nm (~1.5 mJ/mm$^2$) and 1507.3 nm (<1mJ/mm$^2$) beams pass through the mixing cell (a stainless steel tube 19x180 mm filled with Xe-Ar mixture) that is attached to the ion source of mass-spectrometer via magnesium fluoride viewport. From the other side there are two cells also divided by magnesium fluoride viewport that works as proportional counters. One is filled with ~20
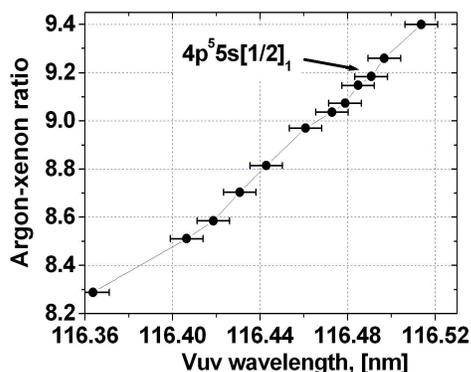
*Fig. 2: Experimental argon-xenon ratios of phase matched gas mixture for the wavelengths in the vicinity of the first Kr transition used in excitation scheme. The xenon partial pressure was kept constant 60 Torr.*
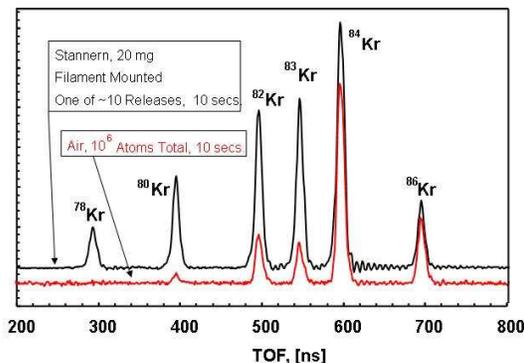


*Fig. 3: TOF spectra of Krypton measured for air samples and Stannern meteorite. In both cases the total Kr content was $10^6$ atoms. In the air spectrum the $^{84}Kr$ peak corresponds to $5.7 \times 10^5$ atoms and $^{80}Kr$ peak to $2.3 \times 10^4$ atoms.*

Torr of Kr for off-line spectroscopic measurements; another cell contains ~ 10 Torr of nitric oxide (NO) that is easily ionized by vuv and thus used for vuv generation monitoring.

The dependence of optimum Ar/Xe ratio on output vuv wavelength at constant Xe pressure is shown in Fig. 2. The Xe partial pressure was set to 60 Torr and small amounts of Ar were added into the gas mixture. At each new Ar/Xe ratio, the IR laser was tuned until the VUV signal measured in the NO cell was maximized. Peak generation shifts towards longer wavelengths as the Ar/Xe ratio increase; as the partial pressure of argon increases, contributing positive dispersion, the phase mismatch introduced into the system can be compensated for by shifting towards longer wavelengths where the refractive index of xenon is smaller.

The optimal ratio of partial pressures obtained within our experiments is $P_{Ar}/P_{Xe} \approx 9.2$ ($P_{Xe} \approx 60$ Torr; $P_{Ar} \approx 550$ Torr) (Fig.2). At this value the intensity of generated 116.5 nm light is at maximum and the first Kr transition is saturated. The fine tuning of the first transition can be achieved by changing the wavelength of the IR laser beam.

**Ultra trace amounts of Krypton detection:** The easiest way to probe the developed method for the first time was to use an air as the isotopic ratios are precisely known. A noncumulate eucrite Stannern was used as a reference extraterrestrial material.

Having optimized the experimental conditions we observed stable generation of VUV beam. The green and IR beams were aligned into the ion source to complete the ionization process. The cold finger was operated at 75 K. The VUV power density was estimated <1 μJ/mm². The power densities used for the

second and the third ionization steps were 1 mJ/mm² and 2 mJ/mm² respectively.

Aliquots of air containing $10^6$ atoms of krypton were gettered to remove active gases and then introduced into the mass spectrometer and the time-of-flight signal recorded.

The absolute concentration and isotopic ratios of Kr trapped in Stannern has been measured by Y.N. Miura et al. [10] using conventional mass spectrometer technique (320 mg sample was required). We used a 20 mg sample such that step heating releases might be expected to produce roughly the same amount of Kr as in the air samples ($10^6$ atoms). The grain was mounted onto the filament and step-heated for 5 min. The TOF signal was repeatedly recorded after gettering.

An example of air and Stannern Kr TOF spectra that are the signal sum from 100 laser shots that corresponds to ~10 sec. collection time is presented in Fig.3. In both cases the Kr yields are high taking in account relatively short collection time. This indicates the instrument capability of lower Kr amounts detection. As expected the Kr isotope ratios of Stannern dramatically differ from terrestrial samples, but our isotope ratios agree with those determined in the literature study.

**References:**[1] Lewis et al., Geochim.Cosmochim.Acta, **(1994)** 58(1),471-494.[2] Eugster et al., MAPS 37, **(2002)** 1345-1360.[3] Polnau et al., GCA 65, **(2001)** 1849-1866.[4] Letokhov VS **(1987)** In: Laser Photoionization spectroscopy, Acad Press.[5] I.Strashnov et al. **(2008)** Opt.Commun., doi:10.1016/j.optcom.2008.11.035. [6] Gilmour J. D. et al. **(1991)** Measurement Science & Technology 2(7), 589-595. [7] Gilmour J. D et al. **(2006)** Meteoritics & Planetary Science **41**(1), 19-31. [8] Thonnard N. et al. **(1992)** Inst. Phys. Conf. Ser. No 128, 27-30. [9] N.Bloembergen **(1981)** In: noble lecture.[10] Y.N.Miura et al. (**1998**) Geochim. Cosmochim. Acta 62 (13), 2369-2387.