NITROGEN AND NOBLE GASES IN A DIAMOND-BEARING PEBBLE FROM SW EGYPT.
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Introduction: Kramers *et al.* [1] recently reported the very unusual nature of a diamond-bearing pebble found in the area of SW Egypt where the Libyan Desert Glass (LDG) was produced by a likely impact event ~28 Myr ago. Based on carbon and noble gases isotopes they demonstrated an extraterrestrial origin for this pebble (called "Hypatia") and suggested that it may be a fragment of a cometary nucleus whose impact led to the formation of the LDG. This proposal was subsequently criticized [2]. Here we present a follow-up study confirming the extraterrestrial origin of this unique material. Our data shows no evidence for a cometary origin of Hypatia but puts new constraints on the cosmochemical origin of this rock.

Analytical: At ETH five mg-sized samples were analyzed for He, Ne and Ar isotopes by total extractions at 1800 ˚C, at CRPG three for Ne, Ar and N_2 isotopes by stepwise laser extractions (~600-2200 ˚C) and one sample for Ar, Kr and Xe isotopes by stepwise furnace extraction (~400-2200 ˚C).

Results: *Helium isotopes* The $^{3}He/^{4}He$ ratios obtained in all samples range between 1.4×10^{-4} - 2.1×10^{-4}, close to the isotopic composition of helium in phase Q, a major carrier of noble gases in primitive meteorites [3].

Neon isotopes All total extractions and temperature steps show an isotopic composition close to Ne-Q with a minor contribution of cosmogenic ^{21}Ne, corresponding to a nominal cosmic ray exposure age of ~0.1 Ma (assuming Hypatia to have been a ~m-sized body in space and using [4] to compute CRE ages). The excess ^{21}Ne cannot be nucleogenic, based on the $^{21}Ne/^{4}He$ ratio and cannot have been produced by cosmic rays on Earth as this would require an unreasonably long exposure at the find site of ~0.5-1 Gyr. We find no evidence for the presence of "exotic" Ne-G (essentially pure ^{22}Ne) in Hypatia, as had been reported in [1].

Argon isotopes Except for preliminary heating steps $^{40}Ar/^{36}Ar$ ratios in all analyzed samples vary between 2.2 – 3, well below the atmospheric value of 298.56, with a minimum value of 0.2 in one individual extraction step. Such very low values are only known for extraterrestrial material. The $^{38}Ar/^{36}Ar$ ratio (0.1871±0.0013 (2σ)) is very close to the composition of Ar-Q (0.1872 [3]). The very low $^{40}Ar/^{36}Ar$ ratios exclude a major contribution of atmospheric $^{36,38}Ar$. No cosmogenic Ar has been detected.

Xenon isotopes Two isotopic spectra for Xe released at low and high temperature are presented in Fig. 1a and 1b, respectively. Some atmospheric Xe seems to be released at 400°C but this represents only 2% of the total Xe in the sample. 50% of the total Xe is released at high temperature (1800-2200°C) with an isotopic composition matching almost perfectly Xe-Q [3] except for a substantial excess of radiogenic ^{129}Xe due to the decay of the extinct radioactive nuclide ^{129}I.

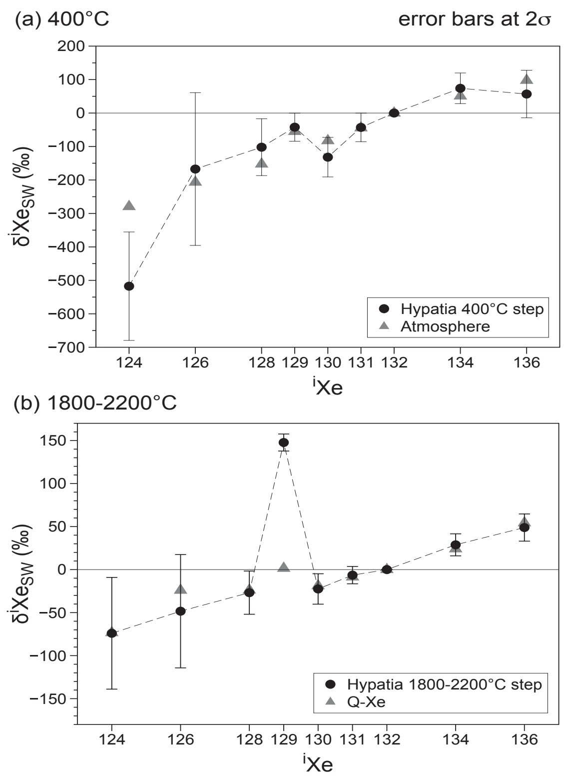

Fig. 1: Isotopic spectra of Xe released at low temperature (a) and at high temperature (b). Isotopic ratios are normalized to the solar wind composition measured by Genesis [5] and expressed with the delta notation.

Nitrogen isotopes The isotopic composition of nitrogen released during all three step-heating experiments reveals one heavy and one light component. Fig. 2 shows a representative example. A heavy component with $\delta^{15}N$ up to 25±3 ‰ is released during the first heating step (600-800 °C) and may be reminiscent to a similar heavy component contained in ureilites [6]. When temperature increases a very light component (-113±3 ‰) representing more than 60% of the total N_2 is released. In Fig. 2 we compare the Hypatia data with two prominent N components in ureilites [6] and with N observed in graphite nodules in iron meteorites [7].

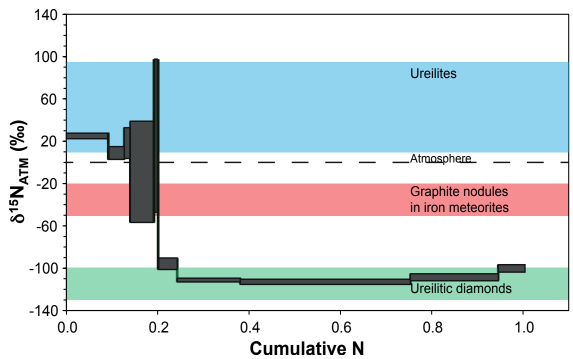

Fig. 2: Isotopic composition of nitrogen released during CO_2 laser step-heating. Isotopic compositions of N_2 in Graphite nodules in the iron meteorite Canyon Diablo [7], in ureilites and ureilitic diamonds [6] are shown as references. Errors at 1σ.

Elemental abundances Figure 3 shows the ranges of elemental abundances of noble gases and nitrogen in Hypatia and in some reference materials: a range of bulk ureilites and carbon-rich acid-resistant ureilite residues [8] (with the two ureilite bulk samples of Almahata Sitta [9] and Goalpara [8] highlighted) and a graphite nodule in Canyon Diablo [9]. Abundances in Hypatia are broadly consistent with abundances measured in bulk ureilites and — except for ^{4}He — the Canyon Diablo graphite.

An extraterrestrial sample The results presented here confirm [1] the extraterrestrial origin of this unique rock. The isotopic compositions of trapped noble gases in Hypatia are very close to the Q component found in primitive meteorites, and isotopically light N is also inconsistent with a terrestrial origin. ^{40}Ar/^{36}Ar ratios are much lower than in terrestrial samples and the cosmogenic ^{21}Ne must have been produced in space.

Origin of the sample Hypatia cannot be directly associated to any known extraterrestrial material. It is unusually rich in carbon (>70%) and its noble gas and nitrogen elemental and isotopic signatures present striking similarities with carbon-rich phases in ureilites and graphite inclusions in iron meteorites. Like Hypatia, both materials contain noble gases with Q-like composition [9, 10]. Particularly striking are the very similar δ^{15}N values found both in the high temperature extractions in Hypatia and in the carbon-rich veins of ureilites. More N analyses of graphite nodules in iron meteorites are needed to explore the full spread of δ^{15}N in such samples. However, the noble gas and N abundances in Hypatia are orders of magnitude lower than in C-rich phases in ureilites and closer to bulk ureilite values or concentrations in graphite inclusions in Canyon Diablo. Unlike Hypatia and graphite inclusions in iron meteorites, ureilitic Xe is also essentially free of radiogenic ^{129}Xe [11]. Taken together, the data presented here suggest the possibility that Hypatia and carbon-rich samples in meteorites discussed previously may have trapped noble gases and nitrogen from similar reservoirs. Our studies have not corroborated the presence of the "exotic" G component in primitive meteorites. This occurrence was taken as an argument for a cometary origin for Hypatia on the premise that material from the outer solar system should be rich in stellar debris. Thus this work does not support the proposed link of Hypatia with cometary material although it does not exclude either the possible link between comets and carbon-rich material. The very low nominal cosmic ray exposure age of ~0.1 Ma may suggest that Hypatia is actually a fragment of a body with a pre-atmospheric radius of at least several m leading a lower ^{21}Ne production rate that assumed here.

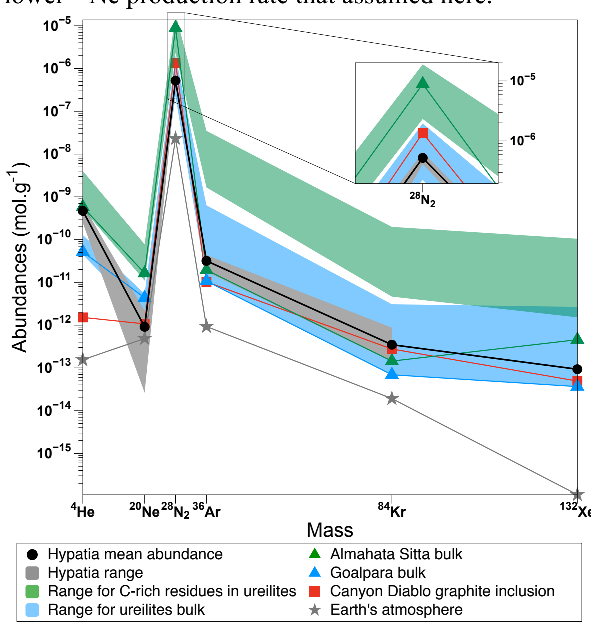

Fig. 3: Abundances of volatile elements in Hypatia. Some reference values are shown for comparison (see text for details).

References [1] Kramers J. D. et al. (2013) *EPSL, 382,* 21–31. [2] Reimold W. U. & Koeberl C. (2014) *Journal of Af. Earth. Sci., 93,* 57-175. [3] Busemann H. et al. (2000) *Meteoritics & Planet. Sci., 35,* 949-973. [4] Leya I. & Masarik J. (2009) *Meteoritics & Planet. Sci., 44*, **7**, 1061-1066. [5] Meshik A. et al. (2013) *GCA*, *127*, 326-347. [6] Rai V. K. et al. (2003) *Geochim. Cosmochim. Acta, 67*, **12**, 2213-2237. [7] Grady M. M. & Wright I. P. (2003) *Space Sci. Rev., 106,* 231-248. [8] Göbel R. et al. (1978) *JGR,* 83, **B2**, 855-867. [9] Murty S. V. S. et al. (2010) *Meteoritics & Planet. Sci., 45*, **10-11**, 1751-1764. [10] Matsuda J. -I. et al. (2005) *Meteoritics & Planet. Sci., 40,* **3**, 431-443. [11] Rai V. K. et al. (2003) *Geochim. Cosmochim. Acta, 67*, **22**, 4435-4456.