

**EVOLUTION OF THE MARTIAN ATMOSPHERE: CLUES FROM NITROGEN AND NOBLE GAS ISOTOPIC SIGNATURES IN SNC METEORITES.** K. J. Mathew and K. Marti, Dept. of Chemistry, University of California, San Diego, La Jolla, CA 92093-0317, USA. e-mail-mkattath@ucsd.edu

Nitrogen, argon, and xenon isotopic signatures in separated shock-melted glass of the shergottite Zagami were shown to match those observed earlier in the glassy lithology of the Antarctic shergottite EETA79001, demonstrating that the observed signatures are characteristic to all shergottites and represent the trapped gases in these shock-melted glass (Becker and Pepin, 1984; Wiens et al. 1985; Swindle et al. 1986; Marti et al. 1995). The close resemblance of the measured 282‰ larger than terrestrial  $^{15}\text{N}/^{14}\text{N}$  ratio, of the  $^{129}\text{Xe}/^{132}\text{Xe} = 2.40$  and of the nitrogen/argon/xenon elemental ratios in glassy lithologies of shergottites to the Viking spacecraft data for the Martian atmosphere (Owen et al. 1977) provided the strongest evidence for a Martian origin of these meteorites.

natures of heavy Martian atmospheric nitrogen (Becker and Pepin, 1984; Marti et al. 1995; Murty and Mohapatra, 1997; Mathew et al. 1998), but the heaviest component observed so far is  $\delta^{15}\text{N} \leq 282\text{‰}$ , barely overlaps the N ratio measured by Viking. On the other hand shock-implantation experiments showed no fractionation of the noble gas components (Bogard et al. 1986). ALH84001 data also reveal a nitrogen component which is isotopically light ( $\delta^{15}\text{N} \leq -30\text{‰}$ ), presumably reflecting a mantle component. Furthermore, two distinct Xe components are observed in ALH84001, suggesting also a mantle component and an atmospheric component (Mathew et al. 1998). The isotopic composition of one component is consistent with solar-type Xe, as previously observed in Chassigny (Ott, 1988).

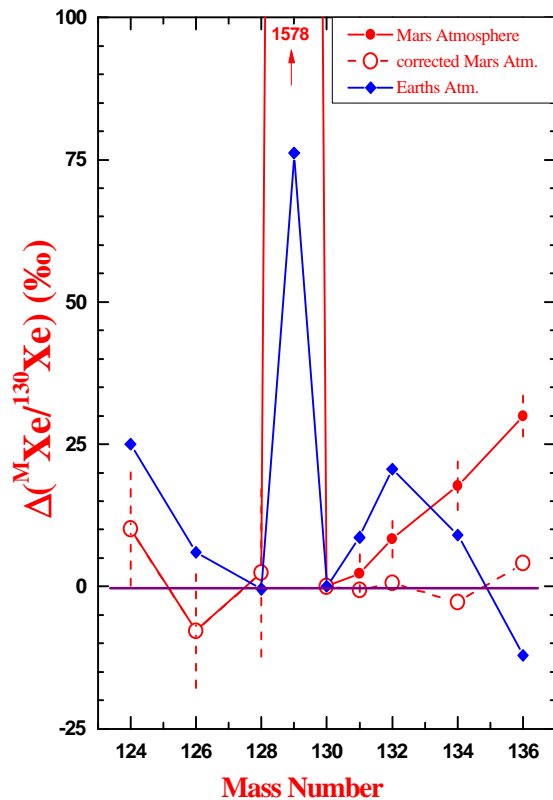


Fig. 1 Martian and terrestrial atmospheric Xe signatures relative to mass fractionated solar Xe. The  $\Delta=0$  line corresponds to a 37.7‰ per amu fractionation of solar Xe.  $^{129}\text{Xe}$  excesses due to decay of extinct  $^{129}\text{I}$  are observed on both planets and the concentrations per gram planet mass are rather similar.

The heavy nitrogen components in ALH84001, EETA79001 and Zagami agree with sig-

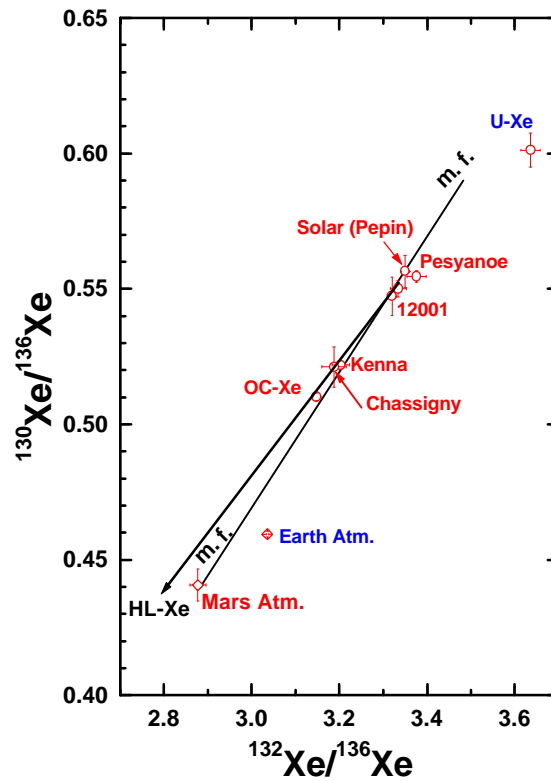


Fig. 2. Xenon isotopic systematics in various solar system reservoirs. Chassigny data shown is the average measured composition from this work. Deviations expected by mass fractionation and by addition of HL-Xe are indicated.

When comparing these two signatures xenon in the Martian atmosphere is found to be strongly fractionated by 37.7‰ per amu relative to solar Xe, favoring the heavy isotopes (Fig. 1). The isotopic composition

of Xe in the Martian atmosphere may have been modified by outgassing of fission Xe, mainly due to  $^{244}\text{Pu}$ , if a chondritic  $^{244}\text{Pu}/^{238}\text{U}$  ratio applies to Mars. However, a detailed analysis of this component (Mathew et al. 1998) indicates only a minor contribution (2.5% at  $^{136}\text{Xe}$ ). Possibly a significant portion of such fission component was retained in the Martian interior. The fission-corrected Martian atmospheric Xe plots close to the fractionation line inferred for terrestrial atmospheric Xe. For the Martian atmosphere, Swindle et al (1986) also inferred a composition similar to terrestrial atmospheric Xe.

Xenon isotopic signatures in SNC's, presumed to represent the Martian mantle, show a component of solar-type Xe (Fig. 2), which is also characterized by an elementally very strongly fractionated reservoir (Ott, 1988; Mathew et al. 1999). An additional component, also elementally fractionated, reveals signatures close to OC-Xe (Lavielle and Marti, 1992). Nitrogen isotopic signatures observed in ALH84001 were interpreted as evidence for an evolution of Martian atmospheric nitrogen components (Murty and Mohapatra, 1997; Grady et al. 1998) but new data are consistent with variable mixtures of mantle and atmospheric components. Isotopic fractionation mechanisms need to be reconsidered in the light of evidence that Xe isotopic fractionation in the Martian and terrestrial atmospheres are consistent.

The set of elemental ratios  $^{36}\text{Ar}/^{132}\text{Xe}$  and  $^{84}\text{Kr}/^{132}\text{Xe}$ , as well as the  $^{14}\text{N}/^{15}\text{N}$ ,  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{132}\text{Xe}$  isotopic ratios in the Martian atmosphere differ from meteoritic components [Bogard and Johnson, 1983; Becker and Pepin, 1984; Wiens et al. 1985; Swindle et al. 1986; Ott and Begemann, 1985; Marti et al. 1995]. Furthermore, observed elemental and isotopic ratios in Chassigny and ALH84001 are distinct from those in the Martian atmospheric component [Ott, 1988; Swindle et al. 1995; Miura et al. 1995; Murty and Mohapatra, 1997], and are not consistent with simple two component mixtures of inferred Martian mantle and atmospheric components. These isotopic signatures suggest an additional "crustal" reservoir, which was not in isotopic equilibrium with the recent Martian atmosphere. The light N component in SNC meteorites is confirmed by new studies on ALH84001, Chassigny and Nakhla and can be constrained to be  $\delta^{15}\text{N} \leq -30\%$ , consistent with that predicted based on a correlation of the  $\delta^{15}\text{N}$  with  $^{40}\text{Ar}/^{14}\text{N}$  ratios in shock-produced glasses of Zagami and EETA79001 (Marti et al. 1995). It may be also noted that Chassigny shows a significant crustal component. A light N component is also present in Nakhla. The  $^{84}\text{Kr}/^{132}\text{Xe}$  and  $^{36}\text{Ar}/^{132}\text{Xe}$  ratios in Nakhla were interpreted to represent Martian weathering products [Musselwhite et al. 1991; Drake et al. 1994].

Such a process which may fractionate the elemental composition without fractionating the isotopic ratios may explain some of the Chassigny and ALH84001 data. However, the radiometric ages of these meteorites are different, and no heavy atmospheric N is observed in Nakhla. This contrasts with the Xe isotopic signatures which are consistent with the Martian atmosphere.

A suggestion that the measured Xe signatures in ALH84001 signal a crustal component takes significance when we are also considering the old age of this meteorite. This may suggest that portions of the planet are not degassed and the observed fractionation in this old Martian crustal rock may correspond to the fractionation in pre-accretionary and early accretionary stages of the planet history (processes such as large impacts) as opposed to loss due to mechanisms such as hydrodynamic escape which operates in the early stages of the planet history but after it has been assembled to more or less its present size. The large  $^{129}\text{Xe}$  excesses and fission excesses in ALH84001 also suggest fractionation in early processes. It may also indicate a common isotopic fractionation mechanism for the terrestrial and Martian atmospheres. We note that whereas in the case of Martian atmosphere the excesses at the heavy Xe isotopes are consistent with a  $^{244}\text{Pu}$  fission component, this is not the case with earth [Marti and Mathew, 1998].

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