ISOLATION OF COSMIC-RAY-PRODUCED NITROGEN IN METEORITIC SILICATES AND SOME IMPLICATIONS; J. S. Kim, Y. Kim, and K. Marti, Dept. of Chemistry 0317, University of California at San Diego, 9500 Gilman Dr., La Jolla, CA 92093-0317.

Abstract: We measured nitrogen isotopic signatures in meteoritic silicate separates of Enon, Brenham, and Forest Vale. Enon and Forest Vale silicates reveal almost pure cosmic-ray-produced nitrogen. Nitrogen in Brenham silicates is an isotopically equilibrated mixture of cosmogenic and trapped components. We used spallation nitrogen as a monitor for volume diffusion properties and found that trapped nitrogen in chondritic silicates sited in minor carrier phases rather than in the silicate lattice.

Recently, several studies of the nitrogen distribution and of nitrogen isotopic signatures in different meteorites played an important role in the understanding of the evolution of parent bodies and their genetic relationships, supplementing information provided by oxygen isotope signatures. However, sometimes cosmogenic stable isotopes mask information on the trapped components and it is necessary to correct the spallation component. Although the distribution of trapped noble gas has been constrained [1], the carbon-rich carrier phase does not account for all the gases. As part of our general study of carriers and of distribution of noble gases and of nitrogen in meteorites, we selected Enon (ungrouped), Brenham (pallasite), and Forest Vale (H4), because of their long cosmic exposure ages in an attempt to use the spallation component that is sited in silicate lattice as monitor for volume diffusion. We used metal and silicate separates and measured N and Xe isotopic signatures of gas extracted by a combination of combustion and pyrolysis steps.

The ratio of ^{14}N and ^{15}N are very different in trapped and cosmogenic components. We measure $^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$ molecules rather than atomic species. The isotopic exchange reaction between labeled N_2 molecules was observed with the use of catalysts [2]. Also, when mixtures of several distinct components are analyzed by mass spectrometry, the nitrogen molecules are dissociated and equilibrated isotopically [3, 4]. In our work on mineral separates, we considered three components (trapped, cosmogenic, and adsorbed air nitrogen). The trapped indigenous component is isotopically similar to air N but differs from cosmogenic N. Cosmogenic nitrogen is produced from oxygen in silicates. Therefore, the site of cosmogenic nitrogen is in the lattice of silicates. If two nitrogen components are released differentially from distinct carriers by stepwise extraction, it has to be expected that nitrogen is isotopically disequilibrated. As mentioned in [4], from the $^{29}N_2/^{28}N_2$ ratios of mechanical mixture and isotopic equilibrium, we can obtain isotopic signature for 2nd components, which is the mixture between cosmogenic and trapped nitrogen in the silicate lattice. This is a useful tool to measure very small amounts of trapped nitrogen. Hashizume and Sugiura [4] hypothesized that nitrogen released from bulk ordinary chondrite at high temperature steps was not isotopically equilibrated for trapped and cosmogenic N based on the time dependent changes in 29/28 ratio and mass 30 peak. However, Murty [5] criticized their hypothesis stating that cosmogenic N is produced in atomic form in the lattice of silicate, therefore, it is expected that N will isotopically exchange with trapped N in ordinary chondrite silicates.

Experimental: In nitrogen measurement, the main mass interference is from CO^+ ions. By monitoring mass 30, we can correct CO^+ contributions. Usually >50% of the mass 30 peak is due to CO^+, but $\delta^{15}N$ corrections are <5‰. Occasionally NO^+ interference is observed, that can cause a rapid decay of the mass 30 peak. In the melting step of Enon silicate, we observed mass 29 increased while mass 30 decreased with time in the mass spectrometer as shown in Fig. 1. We find isotopically disequilibrated molecular nitrogen in the following observations: 1) The magnitude of mass 30 intensity loss equals 50% of the gain of mass 29 peak. 2) The ratio 30/31 and its time dependence reflect the decay of $^{15}N^{15}N$. Other possible interferences (CO, NO and hydrocarbons) can be eliminated. An isotopic exchange reaction does not occur during our clean-up procedure. On the other hand, we extracted nitrogen from bulk Enon and did not observe isotopic disequilibrium. It is not clear how N isotopic equilibrium is achieved in the bulk sample. A possible mechanism is the catalytic reaction by metal or else nitrogen is released in different molecular form, but not only as N_2.

Results: Enon is an ungrouped meteorite which contains silicates of chondritic composition with more than 50% metal. It shows a undisturbed old K-Ar age and a cosmic ray exposure age of ~80My [6]. We measured N and Xe in bulk Enon, in metal and in silicates. The bulk sample reveals very low Xe concentrations (< 2.4×10^{-12}cc/g) and low N (0.3ppm) and the spallation component is visible in melting step ($\delta^{15}N$=228‰). The metal separate yields δ15N=5‰ and [N]=0.8ppm. We found almost pure cosmogenic nitrogen in Enon silicates. The measured high $\delta^{15}N$ >1500‰ in the melting step shows isotopic disequilibrium. From the $^{29}N_2/^{28}N_2$ ratios in the mechanical mixture, and after isotopic equilibrium we obtained cosmogenic nitrogen component with

$(^{15}N/^{14}N)_c > 0.87$. Since the theoretical value for $(^{15}N/^{14}N)_c$ is ≥ 1, the cosmogenic nitrogen in Enon silicates may have in part exchanged with either trapped, blank or adsorbed nitrogen during the extraction process.

An earlier nitrogen study [7] of Brenham revealed 21ppm of N with $\delta^{15}N$=-66‰ in metal and below the detection limit in silicate. We measured nitrogen to obtain the isotopic signature of trapped N from metal and the cosmogenic $[^{15}N_C]$ from olivine separates. Our data revealed 69ppm N in the metal with $\delta^{15}N$=-73‰, and 0.83ppm N in the olivine with $\delta^{15}N$=+47‰. The Brenham olivine data showed that cosmogenic nitrogen was isotopically equilibrated with trapped nitrogen. The Brenham olivine obiously contains trapped nitrogen in the silicate lattice which possibly was incoporated during metamorphism.

In the H-chondrite Forest Vale, we studied N and Xe isotopic signatures in silicates. Most of the silicates represent broken chondrules. Cosmogenic nitrogen was released above 1050°C, mostly in the melting step, and revealed isotopic disequilibrium corresponding to $(^{15}N/^{14}N)_c > 0.45$. On the other hand, trapped nitrogen was released in all temperature steps yielding a total [N]= 2.1ppm. Comparing Forest Vale, Enon and Brenham silicates, we note that chondritic silicates have a different carrier that contains most of the trapped nitrogen, but the silicate lattice itself may actually contain little trapped nitrogen. It is interesting to note that trapped Xe was released before the melting step (1200°C), while a considerable fraction of radiogenic $129Xe_r$ was released on the melting step (1500°C). The different release patterns of cosmogenic nitrogen and of trapped and radiogenic Xe again reveal different sites in the silicates. In fact, microscopic inclusions are typically observed in silicates.

Conclusions: The evidence for nitrogen isotopic disequilibrium in meteoritic silicates may depend on the trapped nitrogen in the silicates lattice. Enon silicates are extremely depleted in volatile and the nitrogen disequilibrium is seen in cosmogenic nitrogen. Brenham is not depleted in nitrogen, and silicates release isotopically equilibrated N_2 of trapped and cosmogenic nitrogen. The record in Forest Vale suggests that the observed disequilibrium may indicate that the silicate lattice carries little trapped nitrogen. Enon is an excellent sample for studies of volatile cosmogenic nuclides. We have identified the signature of cosmogenic nitrogen $(^{15}N/^{14}N)_c > 0.87$ in Enon silicates.

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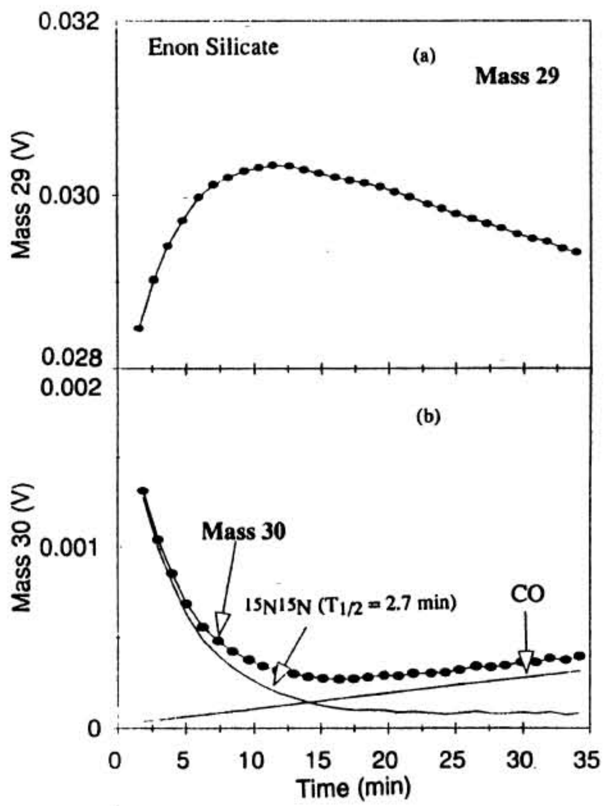

Fig.1. Peak height vs. time plots for (a) mass 29, (b) mass 30, and (c) the ratio 30/31 measured in the 1500°C fraction of Enon silicates. The ratio 30/31 was measured in an aliquot using the multiplier. The mass 28 peak (not shown) was normal (decreasing with time).