NITROGEN ISOTOPES BY LASER PROBE EXTRACTION. I.A. Franchi, E.K. Gibson, Jr.*, I.P. Wright and C.T. Pillinger, Planetary Sciences Unit, Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, U.K. (* presently on leave from Experimental Planetology Branch, NASA Johnson Space Center, Houston, Texas 77058, U.S.A.).

Lasers were first used to extract noble gases from extraterrestrial materials in 1967 (1); the advantages which they offer in respect of sampling selectivity have been discussed on a number of occasions and applications involving $^{40}Ar/^{39}Ar$ dating well documented (eg. 2,3). Now that it is possible to measure stable isotopes at nanogram sensitivity levels, it seems appropriate to explore the possibility of using lasers to release other elements particularly nitrogen and carbon. Herein, we discuss preliminary results concerning nitrogen and evaluate some potential applications

Previously, it has been shown (4) that a Nd/glass pulsed laser (JK System 2000) could liberate nitrogen from mineral samples by focussing the beam onto fragments of lunar agglutinates encapsulated in evacuated quartz capillary tubes (these were subsequently opened in the inlet of a static vacuum mass spectrometer). The same laser has now been coupled directly to a dedicated mass spectrometer via a sample turret with facilities for reflected and transmitted light microscopic viewing and X,Y and Z coordinate control. The maximum size of the specimen which can be accommodated is ca 1 cm^3. Gases released by the laser beam may be processed to remove interfering species such as CO, CO_2, CH_4, C_2H_4, C_2H_6, H_2, H_2O etc and to convert any NH_3 or nitrogen oxides so that only "pure" nitrogen is taken for isotopic measurements. After a clean-up procedure and bake-out (250°C, 12 to 36 hr), the loaded turret has a negligible nitrogen outgassing rate (<0.01 ng/minute). A system blank has been established by firing 10-20 laser pulses into low nitrogen (<2ppm) steels. This activity produced essentially no additional nitrogen and demonstrates that surface adsorbed gas and interaction of the beam with the optical window, coverslip or reflections onto the turret walls do not contribute to the analysis.

In the first instance, because of the small cross section of the beam and the limitations of the mass spectrometer, the laser may only be applied to samples relatively rich in nitrogen and capable of yielding ca 10 ng of N_2 from a small number of pulses. Thus, an investigation of the nitrogen isotopic composition of individual nitride minerals would seem appropriate to a technique capable of providing spatial resolution. Iron meteorites have relatively low total nitrogen contents (2-50 ppm) although occasionally higher values have been reported (5). However, irons are known to contain nitride minerals, both carlsbergite (CrN) and roaldite (Fe_4N) having been identified. Carlsbergite is quite common in some meteorite groups (particularly IA, IIA and IIIA with low Ni abundance) when it occurs as small platelets (30x5x2 μm) in kamacite with a frequency of ca 25/mm^2 (6). In such cases, a major proportion of the nitrogen in the bulk sample must be implicated. Enstatite chondrites are relatively rich in nitrogen and contain the unusual minerals osbornite (TiN) and sinoite (Si_2N_2O).

In order to evaluate the applicability of the laser technique to specific minerals, a crystal (3 mm) of artificially produced titanium nitride was loaded into the sample chamber and subjected to single laser pulses (300 μ sec duration, ca 10^{10} W/cm^2). After purification, nitrogen was admitted to the static mass spectrometer and its yield assessed by comparison with the m/z 28 peak produced from metered amounts of a pure nitrogen reference gas; $\delta^{15}N$ values are reported relative to atmospheric nitrogen. The results given in Table 1 show that the yield of nitrogen from a single laser pulse is between

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30 and 49 ng. The presence of pits on the sample demonstrates that the laser beam causes local temperatures in excess of 3000°C, the melting point of TiN. Quantitative conversion of the laser excavated material into titanium and nitrogen requires production of a hemispherical pit around 50 um diameter given that TiN has a density of 5.22 g/cm^3. The observed pits are about this size (measured using a graticule eye piece) but appear to be conical in shape. Thus, we anticipate that the laser is producing almost quantitative yields of nitrogen. The isotopic composition of the nitrogen from TiN is around 0.8 ±2.5‰; a value of -10‰ was obtained (7) by stepped combustion of the same material. However, it must be emphasised that the maximum temperature attained during the combustion was only 1200°C and that the TiN was obtained by hand-picking several blast furnace slags, therefore, it is not inconceivable that some variability exists. We intend to combust the residue of the TiN chip after its usefulness for laser experiments has been exhausted. Two other observations can be made from the isotope data bearing in mind that the laser pits were created under identical firing conditions: (i) the lowest $\delta^{15}N$ values are observed with the highest nitrogen yields; it may be fortuitous but pits 1 and 4 gave almost identical nitrogen yields and $\delta^{15}N$ values and (ii) pits 1 to 3 which were induced by sequential firings of the laser at the same point on the crystal show an increasing yield of nitrogen and a regular change in $\delta^{15}N$ from +3.1 to -0.6‰.

Another application of the laser will be to investigate the location and distribution of various nitrogen species within samples where there is a prior knowledge of $\delta^{15}N$ values of components separated by chemical/physical means. To this end, we subjected chips from lunar breccia 10059 and the Murchison CM2 chondrite, samples known to contain 100-800 ppm nitrogen, to laser treatment. For the breccia, twenty shots were needed to provide 5 ng of nitrogen for an isotopic measurement; the $\delta^{15}N$ value obtained was low (-46.7‰) as might be expected but since it represents an average of several locations rather than a single site, the laser (in its present configuration) may have only limited usefulness with lunar materials. Murchison, however, looks much more promising as sufficient nitrogen for isotopic measurement could be obtained from only five pulses into the same pit in the matrix (Table 2). Interestingly, twice as many shots produced approximately double the quantity of gas although for such experiments the beam had to be refocussed on more than one location. The $\delta^{15}N$ values obtained are mostly greater than the value of ca 40‰ measured for Murchison by pyrolysis or combustion. Both light and heavy nitrogen components are known to exist in Murchison and it is possible that by confining the laser to the dark matrix locations during these experiments, we are discriminating between these two components. Further exploratory investigations are in progress.

References:
(1) Megrue (1967) Science, 157, 1555. (2) Plieninger and Schaeffer (1976) P7LSC, 2055. (3) Herzog et al (1980) P11LSC, 959. (4) Norris et al (1981) Meteoritics, 16, 369. (5) Gibson and Moore (1971) GCA, 35, 877. (6) Buchwald (1975) Handbook of Iron Meteorites, Univ. of California Press. (7) Carr and Pillinger (1984) LPS XV, 129.

TABLE 1. Nitrogen from TiN extracted by a single laser pulse

Pit	$\delta^{15}N_{AIR}$ (‰)	nitrogen yield (ng)
1	+3.1	30.1
2	+1.9	38.9
3	-0.6	47.3
4	+3.1	30.2
5	-3.5	48.8

TABLE 2. Nitrogen released from Murchison matrix by repeated laser firings

Pit	No. of pulses	$\delta^{15}N_{AIR}$ (‰)	nitrogen yield (ng)
1	5	+29.8	14.7
2	5	+59.6	12.6
3	10	+54.2	22.3
4	10	+50.6	19.7
5	9	+55.3	13.6

ACKNOWLEDGEMENTS: We are grateful to Drs. Bevan, Graham and Hutchison (BM-NH) for helpful discussions.