

NITROGEN IN THE EARTH: DEVELOPMENT OF THE $^{14}\text{N}(d,\alpha)^{12}\text{C}$ MICROPROBE TECHNIQUE: INITIAL RESULTS ON UPPER MANTLE MICAS; S. R. Sutton,^{1,2} J. V. Smith,^{1,2} K. W. Jones,² and J. B. Dawson³; ¹Department of the Geophysical Sciences, The University of Chicago, Chicago, IL; ²Department of Applied Science, Brookhaven National Laboratory, Upton, NY; ³Department of Geology, University of Sheffield, Sheffield, England.

Introduction: The geochemical migrations of nitrogen between the atmosphere, biosphere, and the sedimentary, metamorphic and igneous components of the Earth are relevant to a host of fundamental problems directly or indirectly related to human welfare. Bulk chemical and isotopic measurements are available for many upper crustal rocks, but for few samples of the lower crust and upper mantle. Contamination and alteration of xenoliths during transport to the Earth's surface is a problem for all bulk analyses, and detailed microprobe analyses on selected spots in well-preserved areas are desirable. The first order of business is development of an highly accurate microprobe technique using the $^{14}\text{N}(d,\alpha)^{12}\text{C}$ nuclear reaction. Preliminary results are yielding a detection level near 5 part-per-million for a 50 μm spot, and further technical development should halve these numbers. Exploitation of the new microprobe technique is just beginning, and exploratory results are presented for micas from well-described, upper-mantle samples transported by kimberlites. Until this study, the only known host for N in the upper mantle was diamond for which there is a huge literature [1-4] indicative of multiple origins and annealing conditions. Ammonium substitution is crystal-chemically plausible in all K-bearing minerals of which mica [5,6], amphibole and K-feldspar [7] are likely candidates. Also of interest are graphite (N substitution?), scapolite (NO_3^- ; [8]), glass, and high pressure carbonates. These potential substitutions will be controlled by complex multi-component fluid equilibria.

Experimental Technique: Specimens were excited with 2.0 MeV deuterons (1nA target current) generated by the 3.5 MV Research Van de Graaff Accelerator at Brookhaven National Laboratory, Upton, NY. An electrostatic quadrupole lens was used to focus the $^2\text{H}^+$ beam to a spot about 50 μm in diameter. Charged particles were detected with an annular silicon detector (450 mm^2 , Ortec A series, 100 μm depletion layer) The high Q-value (kinetic energy released in reaction) of 13.58 MeV results in the production of alpha particles of unusually high energy which can in principle be identified in charged particle spectra on this basis. Fe-Ni metal in iron meteorites have been studied by this reaction using a 1 mm beam with a detection limit of about 5 ppmw [9].

Two types of interferences must be considered, (1) nitrogen in surface contaminants and (2) alpha particles from competing reactions. Metal analyses tend to be complicated by contamination since surface chemistry is energetically favorable, whereas the reaction cross sections and Q-values are small for these relatively high Z major elements. Silicate analyses, on the other hand, are complicated primarily by competing reactions since these minerals contain relatively high concentrations of low Z elements (i.e., those elements with higher cross sections and Q-values). Important target atoms in silicates which efficiently produce competing high energy alpha particles are ^6Li (Q=22.37 MeV), ^{10}B (Q=17.82 MeV), ^{17}O (Q=9.81 MeV), ^{19}F (Q=10.04 MeV) and ^{31}P (Q=8.17 MeV). In the present experimental geometry, the maximum alpha particle energies for each of these target nuclei are 10.6, 12.1, 8.7, 9.1, and 8.6 MeV, respectively, compared to 10.9 MeV for ^{14}N . Alpha particle yields can be approximated by the product of the reaction cross section, elemental content and isotopic fraction. Yields relative to that from 10 ppm ^{14}N , estimated by the ratio of these products for each nuclei, are 0.1, 0.005, 5, 35, and 0.3, respectively (assumed elemental contents: 10 ppm Li, 1 ppm B, 50% O, 0.5% F, and 100 ppm P; Li, B, and F from [10]). Thus, ^{10}B interference can be inferred to be negligible on this basis. Alpha particles from ^{17}O , ^{19}F and ^{31}P can be avoided by setting an energy threshold at 9.3 MeV, i.e., slightly above the maximum alpha energy of these competing reactions. The remaining interference is Li. Previous ion microprobe analyses on micas suggest an upper limit of about 10 ppm Li for the upper mantle samples. Thus, significant problems are expected only for specimens with N contents below 10 ppm. Li analyses are desirable on each specimen to quantify this contribution.

Standardization was obtained using pure silica implanted with 100 keV $^{14}\text{N}^+$ ions to a dose of 1.0×10^{17} ions/ cm^2 . Figure 1 shows the charged particle spectrum obtained from this implanted glass. Elastically-scattered deuterons, protons from nuclear reactions on Si and O and pileup events dominate the spectrum below about 5 MeV. A prominent peak due to $^{16}\text{O}(d,p_1)^{17}\text{O}^*$ observed in all glass and mica spectra was used for normalization purposes. Two alpha peaks from ^{14}N were observed, one (10.9 MeV) from the reaction producing ^{12}C in the ground state and the other (7.3 MeV) ^{12}C in the first excited state. The implanted glass also served to establish that alpha particles detected from surface-

correlated nitrogen possess energies only between 9.9 and 10.9 keV in the present setup. The combination of competing alpha particles below 9.1 MeV and surface contributions above 9.9 MeV results in a narrow 800 keV energy window available for bulk nitrogen analysis. This energy contains alpha particles emitted from the depth range of 3 to 7 μm in silicates.

Initial Nitrogen Results: Six mica megacrysts from kimberlite matrices and four sections of glimmerite and MARID-rocks containing mica from Bultfontein and Roberts Victor mines, South Africa, were doubly polished, mounted on pure silica slides and carbon coated. Preliminary nitrogen concentrations for the macrocrysts were at the present detection limit of 5 ppm and between 100 and 200 ppm for the micas from the Bultfontein and Roberts Victor kimberlites. Precision was limited to 15% (1σ) for 100 ppm samples primarily by the deuteron current limitations imposed by pulse pileup interference. More efficient pileup rejection circuitry should permit greater beam currents and, thus, count rates to be used. Uncertainties in the ion-implantation dose limited accuracy to about $\pm 25\%$. These results suggest that micas are generally minor sources of N in the upper mantle but can occasionally contain up to several hundred ppm N. Attention is specifically drawn to the high N content of glimmerites (interpreted as upper mantle pegmatites); nonetheless, the bimodal N distribution in these rocks points to possible different concentration processes or crystallo-chemical controls. Whether the higher concentrations of N are related to upper mantle metasomatism, or subducted oceanic crust, or both, will be explored in further studies.

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References: [1] Harris, G. D. (1984) *Diamond*, Adam Hilger, Bristol, 255p.; [2] Javoy, M., Pineau, F., Demaiffe, D. (1984) *EPSL* 68, 399-412; [3] Melton, C. E., and Giardini, A. A. (1974) *Amer. Mineral.* 59, 775-782; [4] Katern, A., Bergemeister, E. A., Westendorp, J. F. M., Roosendaal, H. E. (1983) *Materials Letters* 2, 71-3; [5] Duit, W., Hansen, J. B. H., Van Breemen, A., Bos, A. (1986) *Am. J. Sci.* 286, 702-32; [6] Itihara, Y., Honma, H. (1983) In, S. S. Augustithis (ed.) *The significance of trace elements in solving petrogenetic problems and controversies*, 431-444; [7] Smith, J. V. and Brown, W. L. (1987) *Feldspar Minerals*. 2nd edition, Springer, Berlin; [8] Goldsmith, J. R., Newton, R. C., Moore, P. B. (1974) *Amer. Mineral.* 59, 768-74; [9] Herzog, G. F., et al. (1986) *EOS*, *Trans. Am. Geophys. Union* 67, 401; [10] Jones, A. P. and Smith, J. V. (1984) *N. Jb. Miner. Mh.* 5, 228-240.

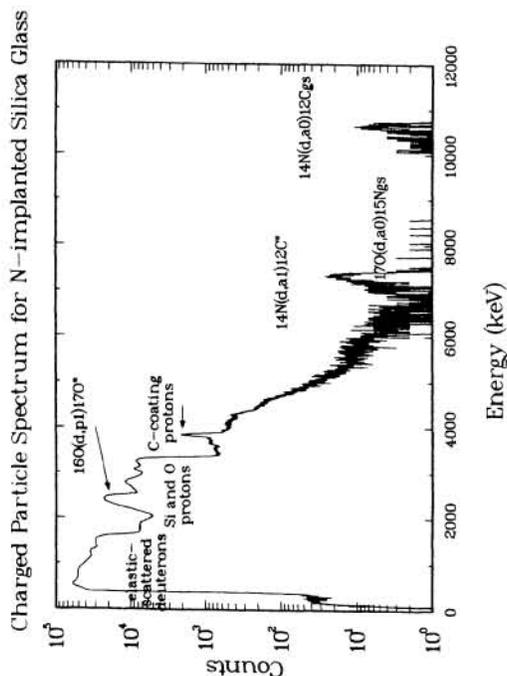


Table 1: Nitrogen Contents in Micas

Specimen	Source	Concentration (ppm)
Silica blank		< 5
BD 1380	macrocryst (Monastery, S. Africa)	8 \pm 4
BD 1823	macrocryst (Excelsior, S. Africa)	4 \pm 4
BD 1083	macrocryst (Wesselton, S. Africa)	7 \pm 4
BD 35	microijolite macrocryst (Oldoinyo Lengai, Tanzania)	14 \pm 6
BD 82	neph. syn. macrocryst (Oldoinyo Lengai, Tanzania)	19 \pm 7
BD 1118	macrocryst (Jagersfontein, S. Africa)	21 \pm 9
BD 1165	pyroxene-glimmerite (Roberts Victor, S. Africa)	85 \pm 20
BD 3089	diopside member (Bultfontein, S. Africa)	90 \pm 16
BD 1158	ilmenite glimmerite (Bultfontein, S. Africa)	210 \pm 33
BD 1159	amphibole glimmerite (Bultfontein, S. Africa)	240 \pm 40