

DOE Award # DE-SC0016246

Sponsoring Program Office- Office of Science SC-1, US Department of Energy

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Project title: Storage and Diffusion of Carbon and Nitrogen in Crustal Materials, in collaboration with PIs Bruce Watson and Morgan Schaller, Rensselaer Polytechnic Institute

Abstract. Carbon (C) and nitrogen (N) are abundant at and near the Earth's surface, and essential for all life. The roles of these elements in the present-day biosphere and atmosphere are well understood, but much less is known about the amounts and locations of C and N stored deep in the Earth, and whether and how deep reservoirs might exchange these elements with the surface over geologic time. A key question concerns the possibility that C and N might be stored within the atomic structures of volumetrically dominant silicate minerals of Earth's crust at elevated pressures and temperatures. Recent studies propose that N stored in bedrock rivals atmospheric N inputs across major sectors of the global terrestrial environment (e.g., Houlton et al., 2018). To date, experimental studies and measurements of natural samples have not clearly determined concentrations of N in rock-forming minerals at depth in the crust. DOE Award # DE-SC0016246 provided funding to design, fabricate, and install a nitrogen purification extraction line for measuring N via static noble gas mass spectrometry in the Syracuse University Noble Gas Isotopic Research Laboratory. Additional required activities included hardware and software upgrades, and mineral standard development. The laboratory's expanded analytical capability allows for measurement of N and noble gas concentrations, and isotopic compositions extracted from silicate minerals in research projects that investigate crustal inventories and elemental (re)cycling models, and the capacity of crustal materials to capture, store, and retain a record of ancient atmospheric gases. This project was part of a larger collaborative effort to determine the amounts and locations of C and N stored in the crust, and whether and how crustal reservoirs might exchange these elements with the surface over geologic time.

PROJECT ACTIVITIES

This project enabled the establishment of new capabilities and experimental procedures in the Syracuse University Noble Gas Isotopic Research Laboratory for measuring N stored in crustal materials. Project activities focused on design modifications to the extraction lines and noble gas mass spectrometers to enable combined N and noble gas analyses in gas extracted from minerals. Development of protocols for coupled Ar and N measurements took place incrementally so as not to compromise the cleanliness and background of the magnetic sector noble gas mass spectrometer (Micromass 5400). Below we describe the various design modifications made possible by this award.

Ultrahigh vacuum nitrogen purification line. To achieve project goals, a dedicated ultrahigh vacuum (UHV) nitrogen purification system was designed, fabricated from a 3D prototype, and attached to an existing UHV extraction line in the Syracuse University Noble Gas Isotopic Research Laboratory. The N purification line is made of quartz glass and was connected to the existing stainless steel UHV extraction line. We chose a quartz line as metal lines tend to adsorb N during the purification process. The new glass line is isolated from the all-metal extraction line

using two manual valves. It consists of a CuO finger, a cold finger and a pressure gauge (Figures 1 and 2). The quartz line incorporates a MKS-390 modular vacuum gauge, to measure pressures in the range of 10^3 to 10^{-9} torr (i.e. from atmosphere to UHV). A cylindrical heater for the CuO finger was designed, constructed, and tested for purification of extracted N_2 using a Cu-CuO oxidation cycle (Figure 2). CuO wires, packed in Pt foil, are heated to oxidize CO and convert to CO_2 . This purification process is required to minimize CO interferences with N_2 measurements (e.g., $^{12}C^{16}O$ on $^{14}N^{14}N$, $^{13}C^{16}O$ on $^{15}N^{14}N$, $^{12}C^{18}O$ on $^{15}N^{15}N$). An oxygen atmosphere ($P_{O_2} \geq 0.1$ torr) is generated in the isolated volume by heating the CuO to temperatures $\geq 720^\circ C$. Organic compounds released from the heated sample (together with nitrogen and noble gases) are dissociated to oxide molecules (e.g., CO_2 , SO_2 , H_2O) in the presence of oxygen. These oxides are trapped on a cold finger kept at $-183^\circ C$ by an external liquid N_2 bath. After purification, the partial pressure of oxygen is lowered by reducing the temperature of the CuO wires to $\sim 400^\circ C$. The pressure inside the quartz line is monitored using the MKS pressure gauge during this purification process.

Bakeout hoods for the entire UHV extraction line, were modified to accommodate the N purification line and MKS gauge. Bake-out of the full extraction line table was performed to achieve pressures $\sim 2 \times 10^{-9}$ torr. The glass N purification line is very fragile and was accidentally broken twice (by an electrician and a post-doc). A protective Plexiglas box was designed and constructed to protect the glass purification line from further accidental breakage.

Additional modifications to the existing extraction line. The addition of the new glass line increased the volume of the extraction lines, and this expansion as well as the N purification process required a larger, more efficient pumping system to return to ultra-high vacuum following sample loading and analysis. To efficiently achieve UHV on the noble gas and nitrogen extraction lines a ***HiCube 300H turbo pumping station*** was installed (funded separately by a SU Small Equipment grant). A ***quadrupole mass spectrometer*** was also added to the existing UHV extraction line for pre-analysis of gas aliquots. The QMS was repurposed from a separate He extraction line in the lab that was previously used for apatite (U-Th)/He studies. The QMS was installed on the table with design modifications to the stainless steel UHV extraction line as required. The bakeable Balzers quadrupole mass spectrometer is fitted with a Faraday Cup and Secondary Electron Multiplier (SEM), providing it with a wide dynamic range (1-100 amu). Maintenance included replacement of failed pneumatic valves (V5) and quadrupole filaments. Extensive helium leak testing was performed and components in the stainless steel extraction line volume were also replaced (i.e., close to the mass spectrometer inlet valve; Figure 2).

Gas extraction: A Cu planchette was designed and fabricated for extraction of N standards encapsulated in capillary tubes using a CO_2 laser prior to gas purification and analysis. A sample crusher attachment to the UHV extraction line can be used for applications involving extraction of gases from sample vesicles. These design modifications allow for maximum flexibility in terms of degassing samples via either furnace step heating, CO_2 laser heating, UV laser ablation, or crushing under UHV conditions, combined with purification prior to static gas source mass spectrometry. Dr. Morgan Schaller (RPI) provided N standards encapsulated in glass capillary tubes, as well as a sample crusher that can be attached to the UHV extraction line for applications involving extraction of gases from sample vesicles.

Additional hardware and software modifications to the Micromass 5400 noble gas mass spectrometer

Micromass 5400 mass spectrometer modifications: A new potentiometer, used to modify the trap current, was installed and calibrated to enable optimization of tuning parameters for N isotopic analyses. A new Ortec ion counter was installed to replace the 20+ year old Micromass ion counter.

Software development: LabVIEW® software was written to control the MKS pressure gauge as well as to monitor pressures in the glass N purification line. Software development included writing new generation software to control the Micromass 5400 as well as the newly installed Ortec ion counter. An alpha version of the new generation software to control the 5400 mass spectrometer (ngs54) was installed and tested. While a beta version of ngs54 is further developed we retained the capability of using the original (ng290) software (written in Modula 2) with the original Micromass ion counter. Having the old (ng290) and new (ngs54) software working provided flexibility during development of analytical protocols (delayed due to COVID). The software upgrade offers the following advantages: it removes the dependency on obsolete outdated computer and interface cards; it provides better ion counting stability and flexibility with the new generation ion counter set up including discriminator and amplifier; it provides comprehensive and well-organized mass spectrometer control, data acquisition and management under the latest Windows environment; it provides quicker and more reliable communication between the PC and the units of mass spectrometer (e.g., source, magnet and detectors) with better safety and diagnostic features; it provides a faster isotope measurement protocol tailored for our specific requirements with freedom to develop new analytical protocols; it provides real time isotope ratio graphical display during data acquisition to assess data quality during analysis; it provides embedded data reduction software, concurrent with data acquisition and yielding high quality data with a format that is compatible to further offline data analysis using Microsoft Excel and Matlab.

Mineral standard development

Air aliquots from standard tanks filled with atmospheric gas can be used to determine noble gas and N₂ (¹⁴N¹⁴N) sensitivities. Development of mineral standards for combined N and noble gas analyses took place incrementally. We first established procedures to prescreen silicate samples by measurement of N via electron microprobe analysis (EMPA) (Nachlas et al., 2019). We used tsaregorodtsevite (N(CH₃)₄)(AlSi₅O₁₂) to successfully develop N procedures via EMPA. Because tsaregorodtsevite also contains carbon (CH₃-groups), it cannot be considered as a mineral standard for noble gas mass spectrometry. We found that ammonioleucite (NH₄)(AlSi₂O₆) contains 8.7% (NH₄)₂O (equivalent to 4.68 wt% N) (Figure 3). However, the ammonioleucite sample we investigated was very heterogeneous, occurring as N-rich selvages on leucite, and within the ammonioleucite selvage itself there is heterogeneity in the N concentration (Nachlas et al., 2019). We are also pursuing LP 6 biotite as a possible mineral standard. Although intended as primarily a K-Ar dating standard, it is also used as an electron microprobe standard for potassium. Furthermore, abundant biotite separates are available for distribution to the community (Igami and Engells 1976).

Preliminary sample analyses

We found that the materials proposed to analyze as part of this project were analytically challenging for several reasons. The capacity of cherts to capture and retain ancient atmospheric gases was analytically challenging due to low [K] which precluded age determination and interferences on N. In addition, the chert samples investigated were found to be impossible to clean sufficiently prior to analysis due to considerable amounts of contaminating minerals (e.g, calcite, halite), and hydrocarbons. Analysis of N in cherts containing carbonates were risky due to the potential for hydrocarbon contamination on noble gases peaks (e.g., ^{40}Ar (C_3H_4), ^{39}Ar (C_3H_3), ^{38}Ar (H^{37}Cl , C_3H_2), ^{36}Ar (H^{35}Cl)).

In order to preserve the integrity of the system we focused our efforts on silicate minerals that contained N, potassium (i.e., minerals dateable using the $^{40}\text{Ar}/^{39}\text{Ar}$ method), and other noble gases. White mica samples from the ultrahigh pressure metamorphic terrane of Papua New Guinea were targeted because they yielded hydrogen and deuterium results indicating crystallization in presence of seawater during subduction (depths >70km; PNG03088b eclogite) versus meteoric water (due to interaction with the surface and therefore N atmospheric compositions; PNG03-076a quartzofeldspathic gneiss). $^{40}\text{Ar}/^{39}\text{Ar}$ analysis of white mica PNG03-076a yielded a plateau age of 2.54 ± 0.16 with an atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ trapped component. In contrast PNG 03-088B white mica yielded a complex saddle shaped $^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum with apparent ages ranging from 14 to 6 Ma. These $^{40}\text{Ar}/^{39}\text{Ar}$ measurements were obtained using the Micromass 5400 in peak-jumping, monocollection mode. Measurable N via EMPA was not detected in Ir-coated mica epoxy mounts of these mica samples (Figure 3), and therefore we have targeted these samples for N analysis via noble gas mass spectrometry. We have identified silicate minerals that can be used in the design of our experiments while ensuring that the cleanliness of the noble gas mass spectrometer is not compromised (in progress; delayed due to COVID).

Acknowledgement of Federal support and a disclaimer appears in the publication stemming from this award. There are no limitations on public release of the report.



Figure 1: Photo of the Syracuse University Noble Gas Isotopic Research Laboratory showing the N purification line (with perplex cover; center left), noble gas extraction lines (covered in Al foil), Prisma quadrupole (white; left middle foreground) and Micromass 5400 noble gas mass spectrometer (right portion of photo). DOE Award # DE-SC0016246 provided funding for the fabrication and installation of the N purification line and modifications to the existing extraction line and mass spectrometers.

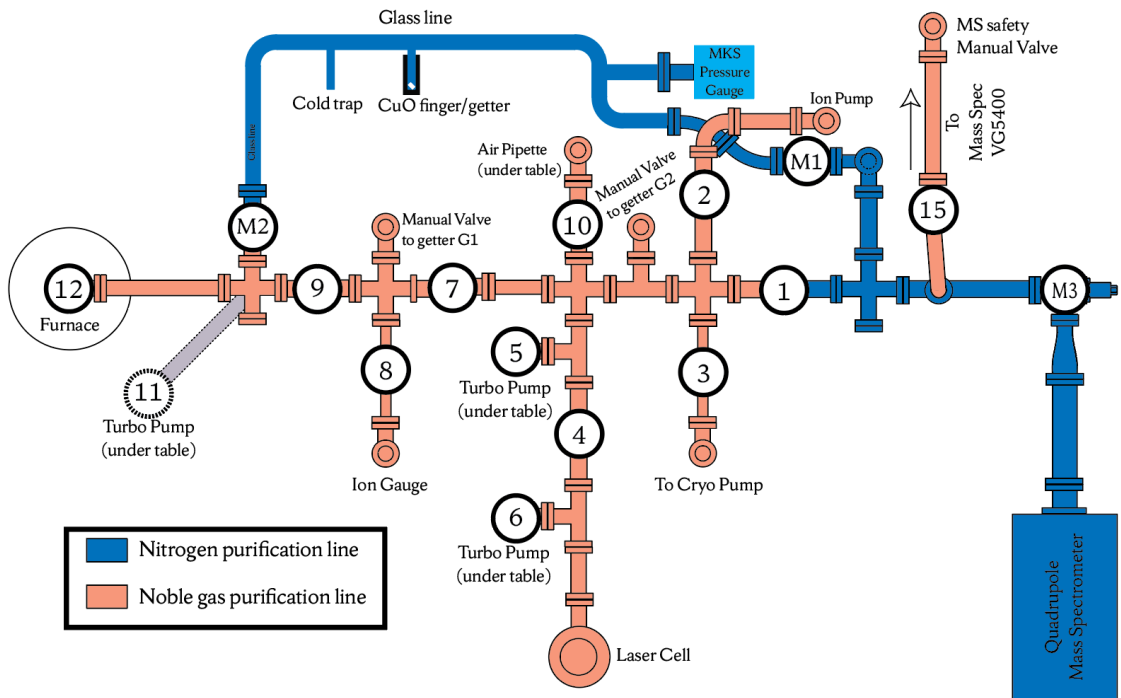


Figure 2: Schematic of the extraction lines connected to the Micromass 5400 noble gas mass spectrometer. View is looking down on top of the table shown in Figure 1 (i.e., bird’s eye view). Numbers refer to air actuated valves; M1-3 are manual valves. Extraction line modifications included installation of a N purification line (in blue) and quadrupole mass spectrometer. See text for details.

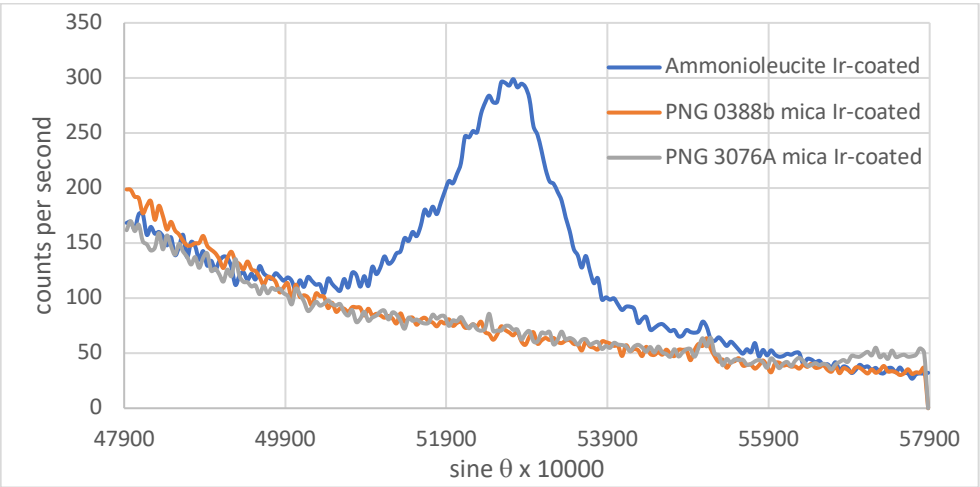


Figure 3: Nitrogen measurements of silicates by EMPA. Comparison of N analyses on potential mineral standards (ammonioleucite and white micas). Measurable N via EMPA was not detected in the micas, whereas the ammonioleucite gave ~300 cps using a very high beam current of 200

nA. Because the micas do not contain high measureable [N] on the electron microprobe, these samples are suitable for N analysis using the ion counting electron multiplier on the Micromass 5400.

References cited

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