NITROGEN IN PLANETARY MATERIALS

Nitrogen forms a variety of compounds that are significant in the interstellar medium, star formation, planetary formation and the evolution of life. Through the study of planetary materials, we recognize three generations of nitrogen and nitrogen-bearing compounds: primary, secondary and tertiary. Species from different sources are recognized by characteristic isotopic compositions or specific modes of occurrence (e.g. Grady and Wright 2003).

PRIMARY NITROGEN

Primary nitrogen is nitrogen that has been inherited directly from the molecular cloud from which the Solar System evolved. The isotopic composition of primary nitrogen reflects the original source reservoirs and is preserved in presolar grains, organic molecules and high-temperature condensates.

Presolar grains are found in primitive meteorites. These grains originated from other regions of the molecular cloud, beyond the protoplanetary disk from which our Solar System formed ~4.567 billion years ago. Presolar grains were first recognized because they host isotopically unusual noble gases (Zinner 2007). Subsequent characterization has shown them mainly to be grains of silicon carbide (SiC) and graphite, plus oxides and, possibly, nanometre-sized diamonds. The isotopic composition of the grains themselves is often, but not always, unusual, because the grains come from stars which experienced different nuclear processes from our Sun (e.g. carbon-burning stars, supernovae). Their isotopic composition is related to the production of individual species in astrophysically distinct locations. Nitrogen is formed in stars through the CNO cycles (Fig. 1a), as a result of which the abundance of ^{14}N is gradually increased over that of ^{15}N. If a star reaches the end of the CNO cycles, it will attain a $^{14}N/^{15}N$ ratio of 5000, which corresponds to a $\delta^{15}N$ value of –945‰. In contrast, grains produced during nova outbursts are more enriched in ^{15}N, and reach a $^{14}N/^{15}N$ ratio ~ 5, which means a $\delta^{15}N$ value of +54,000‰.

Figure 1b is a summary of nitrogen (and carbon) isotope compositions of presolar grains; where fields overlap in C versus N space, the grains can be separated by silicon isotope composition (Nittler 2003). It is clear that the isotopic extremes generated by nucleosynthetic reactions in different types of stars are inherited by the materials produced within the stars, and these materials can be identified as discrete grains within meteorites. Figure 1b shows that we can identify the astrophysical location in which a particular group of presolar grains was produced. The presolar grains that have been extracted from meteorites are refractory materials, resistant to dissolution in acids and solvents. Their survival in interstellar space, transport and processing in the protoplanetary disk and their distribution through asteroidal parent bodies make it likely that presolar grains also survive alteration on the parent bodies of primitive meteorites.

Organic Material: The interstellar medium is rich in organic molecules formed by several different processes, such as ion–molecule reactions on the surface of icy grains. The effect of such reactions is to increase the heavier isotope over the lighter one, producing material with characteristic isotopic signatures (e.g. Herbst 2003). Inventories of interstellar molecules (e.g. www.astro.uni-koeln.de/cdms/molecules) indicate that there are ~60 N-bearing species, most of which are organic in nature. As a result, a variety of N-bearing organic species are available for incorporation into meteorite parent bodies, and these species may be subsequently altered during parent-body evolution. These interstellar species include molecules (e.g. ammonia, amines, carboxylic acids) that are important both as building blocks and as intermediates in the chain of evolution from simple to complex molecules, which ultimately led to the formation of DNA. Although precursor molecules have been identified, there have been no confirmed observations of amino acids in the interstellar medium. Glycine was thought to have been discovered in the interstellar medium (Kuan et al. 2003), but the conclusion was later overturned (Jones et al. 2007).

High-temperature condensates: Primary nitrogen is also present within highly reduced minerals thought to be grains that condensed at high temperatures as the presolar nebula cooled (Meibom et al. 2007; Feng et al. 2012). These minerals include osbornite (TiN), sinoite (Si_2N_2O) and nierite (Si_3N_4), and they occur in varying abundances within the primitive chondrite classes. They are characterized by an isotopically light nitrogen composition, and they are interpreted as having the original composition of the solar nebula (Meibom et al. 2007).

SECONDARY NITROGEN

Second-generation nitrogen-bearing species are those produced on parent bodies by alteration (aqueous or thermal) of primary nitrogen-bearing species. Such processes may lead to modification of the primary species, for example, the graphitization of amorphous carbon during metamorphism, and may or may not alter the original isotopic compositions. The most primitive types of meteorites, the CI, CM and CR chondrites (Fig. 2), contain ~500–5000 ppm nitrogen, with overall $\delta^{15}N$ ranging from +15‰ to +150‰ (see Fogel and Steele 2013 this issue).

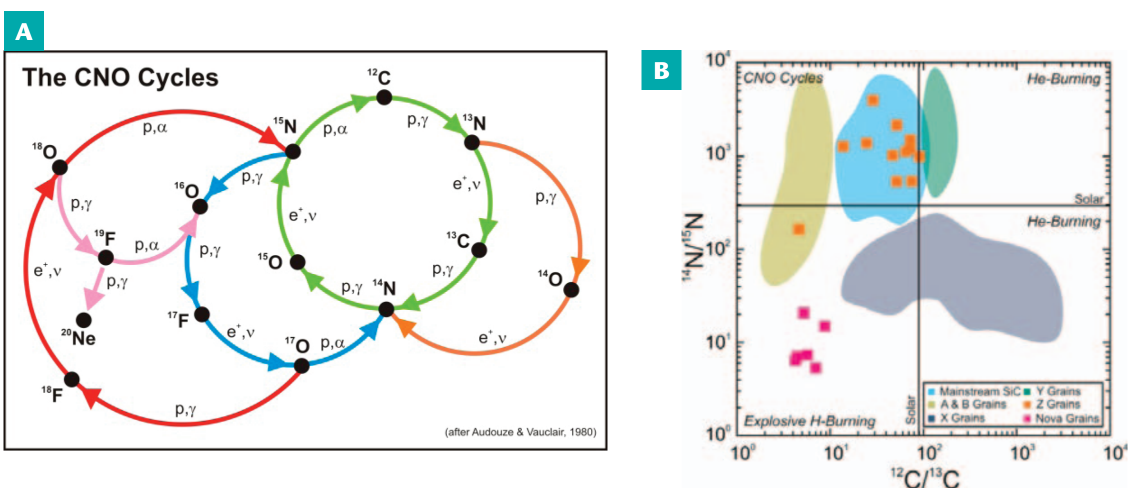

Figure 1 Relationship between astrophysical processes and presolar grains. (**A**) Schematic of CNO cycles showing production of ^{14}N and ^{15}N (adapted from Audouze and Vauclair 1980) (**B**) Isotopic composition of SiC grains from the Murchison primitive carbonaceous chondrite. The four quadrants are labelled according to the fields in which the products of specific astrophysical processes would fall. Figure adapted from Zinner (2007) and sources therein

FIGURE 2 The Murchison meteorite, which fell in 1969, contains ~2 wt% organics, some of which appear to derive directly from interstellar organic compounds. Specimen is ~15 cm across.

TERTIARY NITROGEN

Tertiary nitrogen species are introduced into meteorites by implantation, mainly during exposure to cosmic and solar radiation, during both residence at the parent-body surface and transit in interplanetary space.

Cosmogenic (or spallation) nitrogen is produced by the interaction of cosmic rays with silicate minerals, where the main target elements are ^{16}O and ^{24}Mg. Both ^{14}N and ^{15}N are produced, with a ^{14}N/^{15}N ratio of approximately 1 (Reedy 1981; Silberberg et al. 1998), which translates to a δ^{15}N value of +270,000‰. The abundance of cosmogenic nitrogen is related to the length of time that material is exposed to radiation – the cosmic ray exposure age of a sample – and is generally very low, at the parts per billion level.

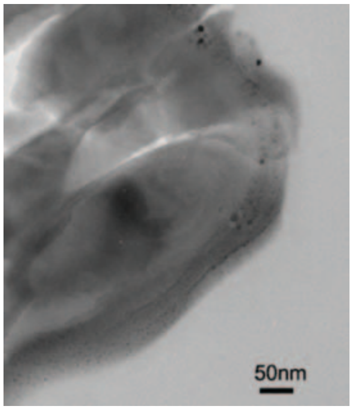

FIGURE 3 Glassy rim on the surface of a grain of lunar soil. The rim is produced by solar wind and cosmic ray bombardment. IMAGE COURTESY OF SARAH NOBLE, NASA/MARSHALL SPACE FLIGHT CENTER (HTTP://LUNARNETWORKS.BLOGSPOT.CO.UK/2010/03/UNDERSTANDING-REACTIVITY-OF-LUNAR-DUST.HTML)

Solar nitrogen: The solar wind is a stream of highly energetic particles that "blows" from the surface of the Sun. The energetic nature of the particles causes them to become implanted within grains when they impact a planetary surface. Two types of material have acted as collection surfaces for the solar wind from which measurements have been made: lunar soils and collectors from NASA's Genesis mission. Examination of mineral grains from Apollo soil samples revealed that they had glassy rims (FIG. 3) produced by a combination of cosmic and solar radiation. Nitrogen from these grains had δ^{15}N values as low as about –240‰ (Frick et al. 1988; Hashizume et al. 2000), which was inferred to have been implanted by radiation.

The Genesis mission exposed an array of collector plates (FIG. 4) to the solar wind for a period of just over 2 years. Analysis of nitrogen in the plates found that the solar wind was depleted in ^{15}N, with δ^{15}N about –400‰ (Marty et al. 2011). This finding fits well with the nitrogen isotope composition of the second-largest nitrogen reservoir in the Solar System: the atmosphere of Jupiter, which has δ^{15}N values of about –375 ± 100‰ (Owen et al. 2001). It also confirmed that the nitrogen implanted into the outer layers of grains from the lunar regolith was almost certainly from the solar wind.

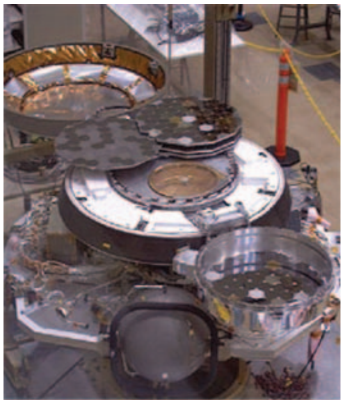

FIGURE 4 The Genesis spacecraft during integration, showing the different arrays of collectors. IMAGE COPYRIGHT NASA (HTTP://CURATOR.JSC.NASA.GOV/SEH/GENESIS.CFM)

An additional, and so far unique, example of tertiary nitrogen is that which occurs in many Martian meteorites, where clasts of glass act as hosts of gases trapped from the Martian atmosphere (see Fogel and Steele 2013).

SUMMARY

Through the study of nitrogen in meteorites, we can identify and track several generations of nitrogen-bearing species. Primary material formed in stars and molecular clouds and became incorporated into the protoplanetary nebula from which the Sun and Solar System formed. Secondary nitrogen resulted from the alteration of primary species on parent bodies. Some meteorites also contain tertiary nitrogen implanted by solar or cosmic radiation. Lunar and asteroidal surfaces also record tertiary nitrogen, and Martian meteorites carry samples of the planet's atmosphere, trapped inside grains/melt pockets at the time the meteorite was ejected from the surface of Mars by impact. On Earth, the structural and isotopic signatures of original parental materials have been modified by tectonic cycling and biological processing. Only in meteorites can we look back through the different generations of nitrogen to understand the reservoirs from which planetary nitrogen was originally sourced.

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