



The nitrogen budget of Earth

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ABSTRACT

We comprehensively compile and review N content in geologic materials to calculate a new N budget for Earth. Using analyses of rocks and minerals in conjunction with N–Ar geochemistry demonstrates that the Bulk Silicate Earth (BSE) contains $\sim 7 \pm 4$ times present atmospheric N (4×10^{18} kg N, or PAN), with $27 \pm 16 \times 10^{18}$ kg N. Comparison to chondritic composition, after subtracting N sequestered into the core, yields a consistent result, with BSE N between $17 \pm 13 \times 10^{18}$ kg to $31 \pm 24 \times 10^{18}$ kg N. Embedded in the chondritic comparison we calculate a N mass in Earth's core (180 ± 110 to $30 \pm 180 \times 10^{18}$ kg) as well as present discussion of the Moon as a proxy for the early mantle.

Significantly, our study indicates that the majority of the planetary budget of N is in the solid Earth. We suggest that the N estimate here precludes the need for a “missing N” reservoir. Nitrogen–Ar systematics in mantle rocks and primary melts identify the presence of two mantle reservoirs: MORB-source like (MSL) and high-N. High-N mantle is composed of young, N-rich material subducted from the surface and identified in OIB and some xenoliths. In contrast, MSL appears to be made of old material, though a component of subducted material is evident in this reservoir as well.

Taking into account N mass and isotopic character of the atmosphere and BSE, we calculate a $\delta^{15}\text{N}$ value of $\sim 2\%$. This value should be used when discussing bulk Earth N isotope evolution. Additionally, our work indicates that all surface N could pass through the mantle over Earth history, and in fact the mantle may act as a long-term sink for N. Since N acts as a tracer of exchange between the atmosphere, oceans, and mantle over time, clarifying its distribution in the Earth is critical for evolutionary models concerned with Earth system evolution. We suggest that N be viewed in the same light as carbon: it has a fast, biologically mediated cycle which connects it to a slow, tectonically-controlled geologic cycle.

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1. Introduction

Nitrogen, the fifth most common element in the solar system, is the main component of the atmosphere, is a key nutrient for life, and has potential to be a tracer of processes linking the surface Earth to different reservoirs in the solid planet. Though N has long been known to exist geologically in fluid inclusions or as NH_4^+ in mineral lattices (e.g., Mayne, 1957), it was thought to predominantly reside in the atmosphere and biosphere (Baur and Wlotzka, 1969). It is now clear that N can indeed become incorporated into minerals and rocks in significant amounts and cycles over long time scales through the atmosphere, oceans, crust, and mantle. While the absolute concentration of N in rocks is low (often ~1 ppm, but up to ~100 or 1000 ppm), the great mass of the solid Earth compared to the atmosphere means that it has the potential to sequester large amounts of N. A picture of the behaviour of N in the Bulk Silicate Earth (BSE) has begun to emerge, but necessitates a new review and synthesis of available data (Fig. 1).

Similar to C (e.g., Holland, 1984), N is cycled in the Earth system in two ways: a fast, biologic cycle; and a slow, geologic cycle. Descriptions of biologic (e.g., Kelly, 2000) and geologic (e.g., Boyd, 2001; Holloway and Dahlgren, 2002; Kerrich et al., 2006) N cycles exist, but no adequate Earth system-wide picture of the fast and slow N cycles together is currently available. Briefly, the biologic cycle (for the modern Earth) is as follows: N_2 in the atmosphere dissolves in the ocean and is converted to a biologically available form by N-fixing bacteria. This process is termed N-fixation. Nitrogen-fixing bacteria are either consumed by other organisms, or release N in waste, primarily as NH_4^+ , which is quickly oxidized to NO_3^- in a

bacterially-mediated process called nitrification. The primary return flux of N to the atmosphere is via denitrification, where NO_3^- is used by certain bacteria as the terminal acceptor in the electron transport chain and converted to either N_2 or N_2O . Recently, the importance of an additional reaction, anaerobic ammonium oxidation or anammox has been recognized as a return flux of N to the atmosphere (Thamdrup, 2012, and references therein). This is another bacterially mediated process whereby NH_4^+ reacts with NO_2^- to produce N_2 and two H_2O molecules.

The slow geologic cycle begins when dead organic matter sinks and settles in oceanic sediment. Organic N breaks down in the sediment via hydrolysis reactions, and converts to NH_4^+ (Hall, 1999). Since NH_4^+ has the same charge and a similar ionic radius as K^+ , it substitutes into mineral lattice sites that are normally occupied by K^+ . Clay minerals, micas, and K-feldspars are important mineral hosts of N. Once entrained in oceanic sediments and crust, N is carried into subduction zones, where it is either volatilized and removed from the down-going plate or carried into the mantle past the subduction barrier. In general, subduction zones with high geothermal gradients favour volatilization (e.g., Elkins et al., 2006), while cooler subduction zones favour N retention (e.g., Mitchell et al., 2010). Volatilized N either oxidizes to N_2 and escapes via arc volcanism or is incorporated into intrusive igneous rocks. Nitrogen that is not returned to the surface becomes entrained in mantle circulation. Basalts at both mid-ocean ridges (MORB) (Marty, 1995) and ocean islands (OIB) (Mohapatra et al., 2009) show evidence for this surface-derived N, through either positive $\delta^{15}\text{N}$ values¹.

While the general outline of the geologic N cycle is known, in order to more fully quantify this cycle and describe changes in it over Earth history, we calculate a thorough inventory of the N on Earth. This is a necessary step to accurately portray the Earth-system nature of the N cycle. To achieve this goal we present two approaches: “top-down” and “bottom-up” budget estimates. The “top-down” approach uses the composition of planetary building blocks and analogues to bracket total Earth N content. We then subtract the amount of N in the core to estimate BSE N content. For the “bottom-up” approach, we compile analyses of N in terrestrial rocks and minerals. We use these to estimate N concentration in various reservoirs: oceanic and continental sediments, oceanic and continental crust, and the mantle. We also use observed relationships between N and Ar from basalts to estimate the mantle N content. In addition, we briefly discuss the behaviour of N in specific reservoirs. Our approach differs from past attempts (e.g., Table 1) by utilizing an extensive literature compilation in conjunction

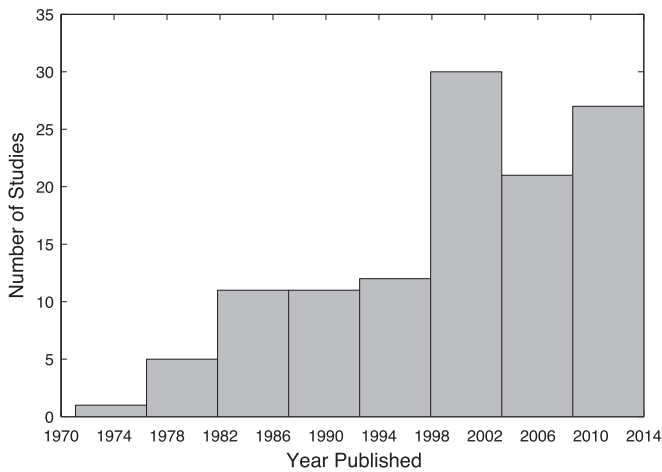


Fig. 1. Number of studies measuring N in geologic materials since 1975. The number of studies has increased as detection capability improves. Data produced after the mid-1990s have not been incorporated into a broad, Earth system perspective on the N cycle.

¹ Stable isotope notations are in per mil (‰) notation, where E is element of interest, X is heavy isotope, x is light isotope. $\delta^{13}\text{C}$ standard is V-PDB and the $\delta^{15}\text{N}$ standard is N_2 in air, which have a $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$ value of 0‰ by definition. (OIB) or correlation with radiogenic Ar (Sec. 4.5.1).

$$\delta^X E(0/00) = \left(\frac{X E^X E_{\text{sample}}}{X E^X E_{\text{standard}}} - 1 \right) * 1000$$

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