



# Earth's Nitrogen and Carbon Cycles

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## Abstract

Understanding the Earth's geological nitrogen (N) and carbon (C) cycles is fundamental for assessing the distribution of these volatiles between solid Earth (core, mantle and crust), oceans and atmosphere. This Special Communication about the Earth's N and C cycles contains material that is relevant for researchers who are interested in the Topical Collection on planetary evolution "Reading Terrestrial Planet Evolution in Isotopes and Element Measurements". Variations in the fluxes of N and C between these major reservoirs through geological time influenced the evolution and determined the unique composition of the Earth's atmosphere. Here we review several key geological aspects of the N and C cycles of which our understanding has significantly advanced during the last decade through field-based, experimental and theoretical studies. Subduction zones are the most important pathway of both N and C from the Earth's surface into the deep Earth. A key question in the flux quantification is how much of the volatile elements is stored in the downgoing slab and introduced into the mantle and how much is returned back to the surface and the atmosphere through arc magmatism. For N, the retention of N as  $\text{NH}_4^+$  in minerals has a major influence on fluxes between reservoirs. The temperature-dependent stability of  $\text{NH}_4^+$ -bearing minerals determines whether N is predominantly retained in the slab to mantle depths (in subduction zones with a low geothermal gradient) or devolatilized (in subduction zones with a high geothermal gradient). Several lines of evidence suggest that the mantle is regassing with respect to N due to a net influx of subducted N over time, but this issue is highly debated and evidence to the contrary also exists. Nevertheless, there is consensus that the majority of the planetary N budget is stored in the Earth's mantle, with the continental crust also constituting a significant N reservoir. For C, release from the subducting slab occurs through decarbonation reactions, dissolution and formation of carbonatitic liquids, but reprecipitation of C in the slab or the forearc mantle wedge may limit the effectiveness of direct return of C into the atmosphere. Carbon release through regional metamorphism in collision zone orogens also has potentially profound effects on C release into the atmosphere and consensus has emerged that such orogens are sources rather than sinks of atmospheric  $\text{CO}_2$ . On shorter timescales, contact metamorphism through interaction of mantle-derived magmas with C-bearing country rocks, and the resulting release of large quantities of  $\text{CH}_4$  and/or  $\text{CO}_2$ , has been linked to global warming events.

**Keywords** Nitrogen cycle · Carbon cycle · Planetary atmospheres · Planetary evolution

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Reading Terrestrial Planet Evolution in Isotopes and Element Measurements  
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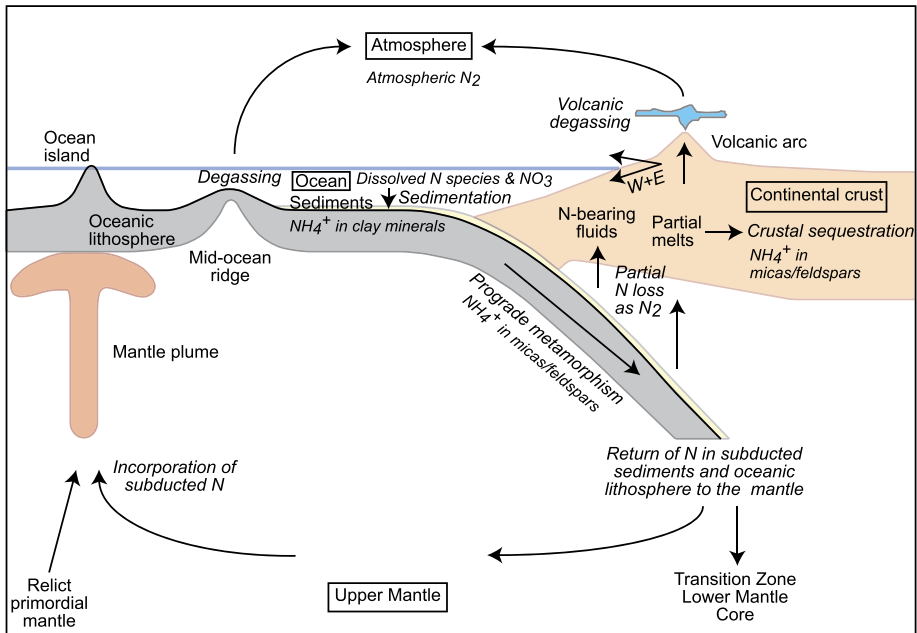
# 1 The Deep Nitrogen Cycle on Earth

The Earth's N-cycle links to observations from planetary and extraterrestrial N-reservoirs and to near-surface nutrient cycling and palaeoenvironmental investigations of ancient Earth. Regarding the evolution of the Earth's atmosphere, a key aspect is whether the Earth's mantle is presently degassing or regassing and whether this balance has shifted in the Earth's history (Zhang and Zindler 1993). One approach to constrain the whole-Earth N distribution is based on using existing observations about the sizes of the Earth's N-reservoirs based on data in key rock types and geotectonic settings (Javoy 1997; Tolstikhin and Marty 1998; Johnson and Goldblatt 2015, 2017a,b; Bebout et al. 2016; Zerkle and Mikhail 2017; Hirschmann 2018). Our understanding of the geologic processes responsible for distributing N has further improved thanks to the experimental work on mineral-fluid-melt N partitioning (Roskosz et al. 2006; Mysen and Fogel 2010; Mallik et al. 2018; Mysen 2018) and theoretical calculations on the speciation of N as a function of P-T conditions and pH (Mikhail and Sverjensky 2014; Mikhail et al. 2017), one can focus here on the following key areas for the distribution and cycling of N on Earth:

1. Subduction zones, which play an essential role for the transport of N from the Earth's surface to the deep interior of the Earth and its subsequent partial return via a "short circuit" through arc magmatism or a "longer loop" through incorporation into mantle plumes.
2. Earth's continental crust, which it appears could contain a large fraction of whole-Earth N (perhaps ~15%; Goldblatt et al. 2009; Johnson and Goldblatt 2017a,b).
3. The Earth's mantle and core, which together contain large amounts of N outweighing those of atmosphere and crust.

Much of the N in Earth's lithosphere owes its existence to its biogeochemical processing and fixation into organic matter, then transfer into low-temperature mineral phases such as the clay minerals (Boyd 2001; Bebout et al. 2013b; Busigny and Bebout 2013). Once it is stored as  $\text{NH}_4^+$  in silicate phases (see Fig. 1), N can be retained at impressive levels even in rocks experiencing partial melting (Jia 2006; Palya et al. 2011) and this retention in  $\text{NH}_4^+$ -bearing phases (e.g., micas, feldspars) likely plays a key role in determining the sizes of deep-Earth reservoirs and cycling among these reservoirs (Yang et al. 2017; Mikhail et al. 2017). Of all the different lithologies in subduction zones, marine sediments have the highest concentrations of N with concentrations of up to several hundred ppm (Sadofsky and Bebout 2014). Early diagenetic breakdown of organic matter (Sadofsky and Bebout 2003; Li et al. 2007) leads to an increase in  $\text{NH}_4^+$  in sediment pore waters, which is then at greater depths incorporated into clays (Schroeder and McLain 1998). Reworking of sediment and organic matter (Junium et al. 2015) and diagenesis (Williams et al. 1995) affect the distribution of N within the sediments, resulting in a large variability in N concentration and isotopic composition. Extremely heterogeneously distributed N is also present in hydrothermally altered oceanic crust and mantle rocks (Busigny et al. 2005; Li et al. 2007; Halama et al. 2014). Because of the very large volume of oceanic crust and mantle being subducted, even very small concentrations of N added during alteration can produce a subducting N inventory rivalling that in the overlying sediment sections (Li and Bebout 2005; Busigny et al. 2011; Halama et al. 2014).

Subduction zone thermal structure determines the stability of N-bearing mineral phases and hence the efficiency of the deep subduction of N (Bebout and Fogel 1992; Busigny et al. 2003; Bebout et al. 2013a, 2016; Halama et al. 2017). During subduction zone metamorphism, preservation of pre-subduction heterogeneities in high-P/T metamorphosed rocks



**Fig. 1** Schematic representation of the geological nitrogen cycle (based on Bebout et al. 2013a,b; Cartigny and Marty 2013). W + E = Weathering and erosion

has been observed in some metasedimentary rocks (Sadofsky and Bebout 2003; Pitcairn et al. 2005; Bebout et al. 2013a), metabasaltic rocks (Halama et al. 2010; Busigny et al. 2011) and serpentinites (Philippot et al. 2007). In these rocks, the effects of devolatilization are variably masked by the initial heterogeneity related to seafloor alteration over wide ranges in temperature and at highly variable fluid/rock ratios. Only in subduction-related metamorphic rocks that formed under a relatively warm geothermal gradient has significant N devolatilization been observed, resulting in decreasing N contents with increasing grade (Bebout and Fogel 1992). The behaviour of N during partial melting is largely unknown (see Jia 2006; Palya et al. 2011), but for the mantle wedge above the subducting slab, thermodynamic calculations indicate relatively oxidising conditions under which N is likely to degas as N<sub>2</sub> in fluids (Mikhail and Sverjensky 2014). The behaviour of N during fractional crystallization of mantle-derived melts in the arc is also poorly constrained. However, studies of N fluxes in volcanic arcs can provide constraints on the efficiency of N recycling through the subduction cycle (see Hilton et al. 2002; Sano et al. 2001).

A study by Fischer et al. (2002) for the Central American margin concluded that almost 100% of sedimentary N is returned to the surface via arc volcanism. However, subsequent investigations updated this consideration employing data for the specific sediments subducting into that margin and demonstrated that, for some margins, the altered oceanic crust can be as important for the N input flux as the sediments (Li and Bebout 2005; Elkins et al. 2006; Li et al. 2007; Mitchell et al. 2010). If N stored in the altered oceanic crust is taken into consideration, the return of subducted N via arc volcanism is far less efficient, yielding values of 15–40% at the Central American margin and 4–17% at the Izu-Bonin arc. These calculations suggest that a large amount of N is transported to beyond sub-arc depths into mantle depths greater than 150–200 km.

Nitrogen-bearing material that has been subducted can be traced in plume-derived magmas using a combination of N elemental and isotopic systematic in combination with noble gas data (Marty and Dauphas 2003). Systematic differences in the N isotope composition of rocks derived from a plume mantle source compared to those from a depleted MORB mantle source suggest the presence of a recycled crustal component in the Iceland and Reunion plumes (Halldórsson et al. 2016; Barry and Hilton 2016). These data were interpreted to reflect regassing of the mantle, which can explain the imbalance between input and output N fluxes at volcanic arcs. If correct, regassing of the mantle over geological timescales also implies the presence of a more N-rich atmosphere before the initiation of subduction (Barry and Hilton 2016).

Estimation of the N concentration and isotopic composition of N in Earth's continental crust have been plagued by the fragmentary dataset for various materials likely to make up this highly heterogeneous reservoir (see Johnson and Goldblatt 2017a,b). The extremely wide range of lithologies in continental crust complicates any assessment of the size and isotopic composition of this reservoir (see Rudnick and Gao 2014) and estimates have been based on analyses of individual rock types (e.g., Palya et al. 2011) weighted by proportions in the crust. Johnson and Goldblatt (2017a) presented measurements of N concentration in glacial tills through time as a proxy for the upper continental crust and, building on arguments made earlier by Goldblatt et al. (2009), suggested that N in the early-Earth atmosphere was uptaken via biological processes and conveyed into (and stored in) continental crust. Johnson and Goldblatt (2017a) suggested that the isotopic composition of N shows no obvious secular variation.

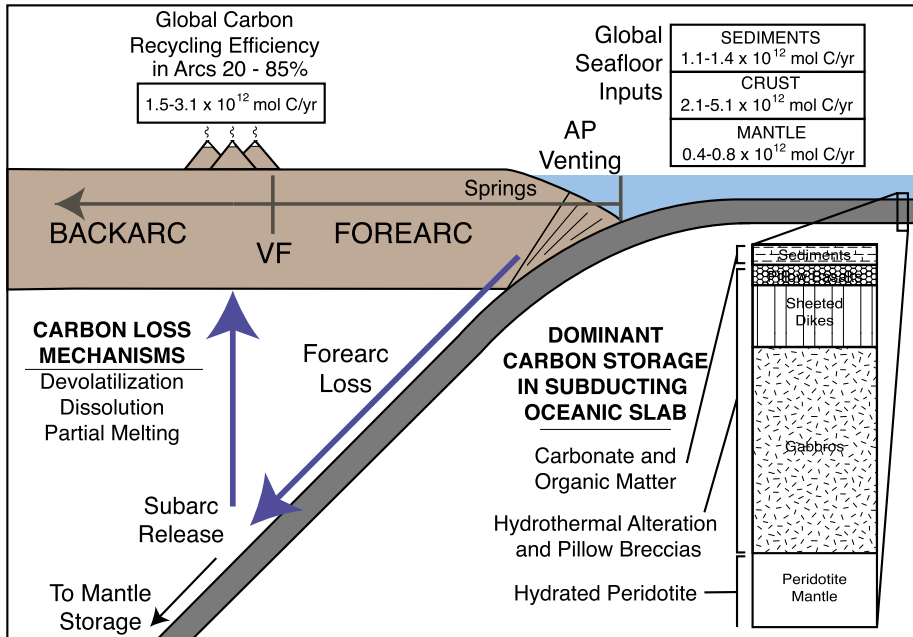
Several recent experimental studies have investigated the distribution and behaviour of N in the deep mantle and the core (Cartigny and Marty 2013; Li et al. 2013; Li and Keppler 2014; Yoshioka et al. 2018; Li et al. 2016; Dalou et al. 2017). Despite the generally low N concentrations in mantle minerals (Yokochi et al. 2009), most of the planetary budget of N is stored in the Earth's mantle (see the review by Johnson and Goldblatt 2015, and papers cited therein). A high N storage capacity of mantle minerals indicates that N released during subduction would be redissolved in the mantle minerals (Watenphul et al. 2010; Li et al. 2013). Nitrogen solubility data for major minerals in the Earth's transition zone and lower mantle suggest that these regions can store at least 33 times the mass of N presently in the atmosphere (Yoshioka et al. 2018).

From this brief summary, one can see that the N-cycle is a complex system that is interlinked to the planet's tectonic regime and hence its initial radioactive heat producing elements (O'Neil et al.) and even life (see Stüeken et al.; Lloyd et al.). Three review articles within this book (Avicé and Marty; Stüeken et al.; Lloyd et al.) summarize the latest knowledge of early Earth's nitrogen evolution based on constraints of a detailed analysis of early Earth's isotopic fingerprints.

## 2 A Tectonometamorphic Perspective on Carbon Cycling

For carbon cycling at the present day and in the Earth's geological past one can focus on three tectonic settings in which metamorphic processes play a key role in C cycling:

1. Subduction zones, which are fundamental for the return of material from the Earth's surface to the deep interior of the Earth and, largely (but not entirely) via arc volcanic degassing, into the atmosphere. The metamorphic processes in the subducting slab and the overlying lithosphere are essential to understand the balance between C input fluxes at trenches and the output via arc volcanism and forearc seeps.



**Fig. 2** Schematic illustration of an ocean-continent subduction zone, showing global-basis estimates of C fluxes discussed in the text (moles of C/year) and highlighting the uncertainties in the various flux estimates (from Cook-Kollars et al. 2014; other sources cited therein). Use of the fluxes shown here would suggest volcanic arc return efficiency (inputs/arc outputs) of  $\approx 15$  to 80%, indicating the need to examine C cycling in individual margins for which the input and output fluxes are better constrained. VF = volcanic front; AP = accretionary prism

2. Collision zone orogeneses, in which large quantities of C-bearing rocks undergo metamorphism with profound effects on C in the Earth's atmosphere.
3. Contact metamorphism, where the interaction of mantle-derived magmas with C in sedimentary layers is able to produce large amounts of  $\text{CO}_2$  and/or  $\text{CH}_4$ .

The key question in assessing C cycling in subduction zones is how much of the C stored in the downgoing slab is directly transferred back to the Earth's surface (Fig. 2). Published global estimates vary widely from  $\approx 15$ -80%, indicating that a significant proportion of C is not returned (see recent estimates by Dasgupta and Hirschmann 2010; Johnston et al. 2011; Collins et al. 2015). Detailed regional studies also show significant variations: In the Central American subduction zone,  $\text{CO}_2$  output calculations based on petrological estimates as well as hydrothermal and gas emissions only account for a maximum of 24% of the input (Freundt et al. 2014). More  $\text{CO}_2$  is released from arc volcanoes than the subducted C flux in sediments at the Sunda margin (Indonesia), requiring additional C sources in the subducting altered oceanic crust or perhaps the overriding plate (House et al. 2019). Aiuppa et al. (2017) suggested that, in some margins, decarbonation in the upper-plate crust (released by contact metamorphism) could contribute significantly to volcanic  $\text{CO}_2$  output. A recent review of subduction zone C fluxes by Kelemen and Manning (2015) provided a contrasting perspective that little C is recycled into the convecting mantle as the lithosphere in the overlying plate represents an important reservoir for C (cf. Collins et al. 2015). In this scenario, the subduction zone C cycle is nearly balanced over geologically short timescales of 5-10

million years and outgassing at mid-ocean ridges and within-plate volcanic centres provides a net flux of C to the Earth's surface.

Understanding C release from subducting slabs is crucial for evaluating the important effects on the global C cycle, palaeoatmospheric CO<sub>2</sub> concentrations and arc magmatism (Kerrick and Connolly 2001). There are three main mechanisms for C release from the subducting slab: metamorphic decarbonation reactions, dissolution of carbonates, and formation of carbonatitic liquids. Metamorphic decarbonation depends on the specific subduction geotherm. For subduction of limestones and marls, only modest amounts of devolatilization of C occur along low-temperature geotherms (Cook-Kollars et al. 2014) unless the decarbonation is driven by infiltration of the rocks by H<sub>2</sub>O-rich fluids (see Gorman et al. 2006; Collins et al. 2015). Similarly, a significant fraction of carbonate is retained to depths >200 km during the subduction of ophicarbonates (hydrothermally altered mantle rocks), providing a mechanism for carbonating the mantle (Kerrick and Connolly 1998; Collins et al. 2015). Hence, C is largely retained in the slab, in particular in relatively cool subduction zones (Gorman et al. 2006), explaining the discrepancy between input and output CO<sub>2</sub> fluxes. Even though the efficiency of C release from slab metamorphic decarbonation appears to be limited, dissolution of carbonate minerals by infiltrating fluids is a potentially voluminous pathway for slab decarbonation (Manning 2014). However, the magnitude of this release by carbonate dissolution, and whether it can impact margin-scale C cycling, have not yet been ascertained. In the exhumed Cycladic subduction complex, 60–90% of the initially present CO<sub>2</sub> was released adjacent to former fluid conduits (Ague and Nicolescu 2014) but extrapolation of this finding to scales of subducting slabs and overlying sediments will be problematic. Further evidence for fluid-mediated carbonate removal comes from diamond-bearing fluid inclusions with bicarbonate and carbonate ions in ultrahigh-pressure rocks from the Italian western Alps (Frezzotti et al. 2011). Theoretical modelling also shows that abundant dissolved organic and inorganic ionic C species are contained in subducted slab fluids, which can then be transported from the slab into the mantle wedge (Sverjensky et al. 2014). Ultimately, the removal of carbonate via dissolution is dependent upon the degree of infiltration of the rocks by fluids capable of dissolving and transporting the carbonate. Where studied in detail, carbonate-rich metasedimentary rocks that experienced high- or ultrahigh-pressure conditions can show only minimal petrologic and isotopic evidence for infiltration by far-traveled fluids (e.g., Cook-Kollars et al. 2014). An additional pathway for the release of C from subducted slabs is via the formation of carbonatitic liquids. Experimental data show that carbonatitic liquids can be produced at temperatures of 870–900 °C corresponding to ~120 km depth underneath arcs when the presence of water depresses the solidus for hydrous carbonate gabbro and limestone (Poli 2015). At even greater depths of 300–700 km, transport of C into the lower mantle is prevented by the formation of carbonatite melts when the slab geotherms intersects the melting curve of carbonated oceanic crust (Thomson et al. 2016). Whereas carbonatite melts at depths approaching the transition zone will metasomatise the overlying mantle and form diamonds, the sub-arc carbonatitic liquids provide a CO<sub>2</sub> source for subduction zone magmatism.

Even though there is widespread field evidence for mobilization of C in subduction-related metamorphic rocks via decarbonation and/or dissolution, this C is not necessarily recycled back into the atmosphere via arc magmatism. Precipitation of C can occur via vein formation or replacement mechanisms (Piccoli et al. 2016), enabling sequestration of C in the forearc and/or in crustal and mantle lithologies of the slab (Jaeckel et al. 2018; Scambelluri et al. 2016; van der Straaten et al. 2012). These high-pressure carbonates carry isotopic signals of mixed organic-inorganic C sources (van der Straaten et al. 2012). Carbonate destabilization in subduction zones may also be counterbalanced by carbonate reduction and the

formation of graphite under reducing conditions (Galvez et al. 2013). Additional redistribution of C in the slab takes place via abiotic methanogenesis in ultramafic rocks during alteration (Vitale Brovarone et al. 2017). In summary, although there is a plethora of metamorphic processes operating in subduction zones that could impact carbon cycling, these processes have been demonstrated at only local (in some cases single outcrop) scales and their influence on regional (scales of individual margins) and global C recycling remains largely unconstrained.

The effects of C release during collisional orogeneses are less well studied than C cycling in subduction zones, but the magnitude of C release into the atmosphere via this pathway could be profound. For instance, CO<sub>2</sub> degassing from the Cordilleran belt has been linked to Eocene global warming (Kerrick and Caldeira 1998) and CO<sub>2</sub> flux for the Himalayan orogeny carrying large fluxes of CO<sub>2</sub> derived from metamorphic reactions was calculated to represent 7–60% of the global flux from volcanic arcs (Evans et al. 2008). Prograde metamorphism of carbonate-bearing sedimentary sequences will form calc-silicate rocks and release CO<sub>2</sub> in a wide range of orogenic settings during collisional metamorphism (Ague 2000; Groppo et al. 2013). The quantitative calculation of CO<sub>2</sub> release for the Himalayan orogeny through the study of calc-silicate rocks in the metamorphosed sedimentary sequences yielded a production of 1–3 Mt CO<sub>2</sub> (Groppo et al. 2017). Carbon fluxes during greenschist facies metamorphism alone were calculated to exceed C uptake by silicate weathering in orogenic belts (Skelton 2011). Whether the released CO<sub>2</sub> reaches the Earth's surface or is sequestered through carbonate or graphite precipitation is uncertain (Groppo et al. 2017), but the C sequestered by carbonate vein formation appears insignificant compared to the total amount of CO<sub>2</sub> released (Kerrick and Caldeira 1998) and cross-layer transport even allows for decarbonation during cooling (Ague 2000). There appears to be consensus that the orogenic belts are a source rather than a sink of atmospheric CO<sub>2</sub> (Skelton 2011; Evans et al. 2008). On geological timescales, metamorphic degassing during collisional metamorphism and orogeneses will create pulses of CO<sub>2</sub> relative to the slow silicate weathering that eventually sequesters CO<sub>2</sub> (Evans 2011).

A third metamorphic aspect of C release from crustal rocks relates to contact metamorphism, which can produce a high flux and volume of CH<sub>4</sub> and CO<sub>2</sub> around igneous intrusions (Svensen and Jamtveit 2010; Aiuppa et al. 2017). Addition of volatiles including CO<sub>2</sub> through shallow crustal sources via contact metamorphism has been observed for individual volcanoes such as Merapi (Indonesia) as they are located on thick sequences of limestones, marls and volcanoclastic deposits (Troll et al. 2012; Whitley et al. 2019). On a larger scale, the emplacement of voluminous mantle-derived melts in C-rich sedimentary strata (carbonates, evaporates, coal and organic-rich shales) generates large quantities of gases (CO<sub>2</sub>, CH<sub>4</sub>) that are vented directly into the atmosphere or rise as plumes through the water column into the atmosphere (Svensen et al. 2004; Ganino and Arndt 2009). For several large igneous provinces, this release of sediment-derived gases has been linked to global warming and mass extinctions (Ganino and Arndt 2009).

### 3 Conclusions

Field-based, experimental, and theoretical studies have greatly advanced our understanding of the Earth's geological N and C cycles and the distribution of these volatiles between the Earth's major reservoirs. Assessing key geological aspects of both the N and C cycles, we conclude:

1. The incorporation of N as  $\text{NH}_4^+$  in minerals is crucial for N subduction and release upon breakdown of the host minerals. Cold subduction causes preferential N transport into the deep mantle, whereas warm subduction favours N recycling into the atmosphere through greater loss in forearcs and via arc magmatism.
2. Both the continental crust and the mantle are important N reservoirs. Long-term storage of N in continental crust appears to be largely as  $\text{NH}_4^+$  in silicate minerals such as the micas. Despite low N contents in mantle minerals, N stored in the mantle outweighs N in the other Earth reservoirs and significantly more N can be stored in the mantle given its large N storage capacity.
3. Subducted C is released from the slab via decarbonation, dissolution of carbonates and carbonatite liquid formation. However, long-term carbonation of the mantle is indicated by the discrepancy between input and output  $\text{CO}_2$  fluxes in subduction zones.
4. Release of  $\text{CO}_2$  into the atmosphere also occurs during regional metamorphism in collisional orogens and by interaction with mantle-derived magmas with C-bearing country rocks. Periods when these fluxes appear to have been enhanced can be linked to specific past global warming events.

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## References

- J.J. Ague, Release of  $\text{CO}_2$  from carbonate rocks during regional metamorphism of lithologically heterogeneous crust. *Geology* **28**, 1123–1126 (2000). [https://doi.org/10.1130/0091-7613\(2000\)28<1123:ROCFCR>2.0.CO;2](https://doi.org/10.1130/0091-7613(2000)28<1123:ROCFCR>2.0.CO;2)
- J. Ague, S. Nicolescu, Carbon dioxide released from subduction zones by fluid-mediated reactions. *Nat. Geosci.* **7**, 355–360 (2014). <https://doi.org/10.1038/ngeo2143>
- A. Aiuppa, T.P. Fischer, T. Plank, P. Robidoux, R. Di Napoli, Along-arc, inter-arc, and arc-to-arc variations in volcanic gas  $\text{CO}_2/\text{ST}$  ratios reveal dual source of carbon in arc volcanism. *Earth-Sci. Rev.* **168**, 24–47 (2017). <https://doi.org/10.1016/j.earscirev.2017.03.005>
- P. Barry, D. Hilton, Release of subducted sedimentary nitrogen throughout Earth's mantle. *Geochem. Perspect. Lett.* **2**, 148–159 (2016). <https://doi.org/10.7185/geochemlet.1615>
- G.E. Bebout, M.L. Fogel, Nitrogen-isotope compositions of metasedimentary rocks in the Catalina Schist, California - implications for metamorphic devolatilization history. *Geochim. Cosmochim. Acta* **56**, 2839–2849 (1992). [https://doi.org/10.1016/0016-7037\(92\)90363-N](https://doi.org/10.1016/0016-7037(92)90363-N)
- G.E. Bebout, P. Agard, K. Kobayashi, T. Moriguti, E. Nakamura, Devolatilization history and trace element mobility in deeply subducted sedimentary rocks: evidence from Western Alps HP/UHP suites. *Chem. Geol.* **342**, 1–20 (2013a). <https://doi.org/10.1016/j.chemgeo.2013.01.009>
- G.E. Bebout, M.L. Fogel, P. Cartigny, Nitrogen: highly volatile yet surprisingly compatible. *Elements* **9**, 333–338 (2013b). <https://doi.org/10.2113/gselements.9.5.333>
- G.E. Bebout, K.E. Lazzari, C.A. Geiger, Pathways for nitrogen cycling in Earth's crust and upper mantle: a review and new results for microporous beryl and cordierite. *Am. Mineral.* **101**, 7–24 (2016). <https://doi.org/10.2138/am-2016-5363>
- S.R. Boyd, Nitrogen in future biosphere studies. *Chem. Geol.* **176**, 1–30 (2001). [https://doi.org/10.1016/S0009-2541\(00\)00405-8](https://doi.org/10.1016/S0009-2541(00)00405-8)
- V. Busigny, G.E. Bebout, Nitrogen in the silicate Earth: speciation and isotopic behavior during mineral–fluid interactions. *Elements* **9**, 353–358 (2013). <https://doi.org/10.2113/gselements.9.5.353>



- V. Busigny, P. Cartigny, P. Philippot, M. Ader, M. Javoy, Massive recycling of nitrogen and other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP oceanic metasediments of the Schistes Lustrés nappe (Western Alps, Europe). *Earth Planet. Sci. Lett.* **215**, 27–42 (2003). [https://doi.org/10.1016/S0012-821X\(03\)00453-9](https://doi.org/10.1016/S0012-821X(03)00453-9)
- V. Busigny, C. Laverne, M. Boniface, Nitrogen content and isotopic composition of oceanic crust at a superfast spreading ridge: a profile in altered basalts from ODP site 1256, Leg 206. *Geochem. Geophys. Geosyst.* **6**(12), Q12001 (2005). <https://doi.org/10.1029/2005GC001020>
- V. Busigny, P. Cartigny, P. Philippot, Nitrogen isotopes in ophiolitic metagabbros: a reevaluation of modern nitrogen fluxes in subduction zones and implication for the early Earth atmosphere. *Geochim. Cosmochim. Acta* **75**, 7502–7521 (2011). <https://doi.org/10.1016/j.gca.2011.09.049>
- V. Busigny, J. Chen, P. Philippot, S. Borensztajn, F. Moynier, Insight into hydrothermal and subduction processes from copper and nitrogen isotopes in oceanic metagabbros. *Earth Planet. Sci. Lett.* **498**, 54–64 (2018). <https://doi.org/10.1016/j.epsl.2018.06.030>
- P. Cartigny, B. Marty, Nitrogen isotopes and mantle geodynamics: the emergence of life and the atmosphere-crust-mantle connection. *Elements* **9**, 359–366 (2013). <https://doi.org/10.2113/gselements.9.5.359>
- N.C. Collins, G.E. Bebout, S. Angiboust, P. Agard, M. Scambelluri, L. Crispini, T. John, Subduction zone metamorphic pathway for deep carbon cycling: II. Evidence from HP/UHP metabasaltic rocks and ophi-carbonates. *Chem. Geol.* **412**, 132–150 (2015). <https://doi.org/10.1016/j.chemgeo.2015.06.012>
- J. Cook-Kollars, G.E. Bebout, N.C. Collins, S. Angiboust, P. Agard, Subduction zone metamorphic pathway for deep carbon cycling: I. Evidence from HP/UHP metasedimentary rocks, Italian Alps. *Chem. Geol.* **386**, 31–48 (2014). <https://doi.org/10.1016/j.chemgeo.2014.07.0123>
- C. Dalou, M.M. Hirschmann, A. von der Handt, J. Mosenfelder, L.S. Armstrong, Nitrogen and carbon fractionation during core-mantle differentiation at shallow depth. *Earth Planet. Sci. Lett.* **458**, 141–151 (2017). <https://doi.org/10.1016/j.epsl.2016.10.026>
- R. Dasgupta, M.M. Hirschmann, The deep carbon cycle and melting in Earth's interior. *Earth Planet. Sci. Lett.* **298**, 1–13 (2010). <https://doi.org/10.1016/j.epsl.2010.06.039>
- L.J. Elkins, T.P. Fischer, D.R. Hilton, Z.D. Sharp, S. McKnight, J. Walker, Tracing nitrogen in volcanic and geothermal volatiles from the Nicaraguan volcanic front. *Geochim. Cosmochim. Acta* **70**, 5215–5235 (2006). <https://doi.org/10.1016/j.gca.2006.07.024>
- K.A. Evans, Metamorphic carbon fluxes: how much and how fast? *Geology* **39**, 95–96 (2011). <https://doi.org/10.1130/focus012011.1>
- M.J. Evans, L.A. Derry, C. France-Lanord, Degassing of metamorphic carbon dioxide from the Nepal Himalaya. *Geochem. Geophys. Geosyst.* **9**, Q04021 (2008). <https://doi.org/10.1029/2007GC001796>
- T.P. Fischer, D.R. Hilton, M.M. Zimmer, A.M. Shaw, Z.D. Sharp, J.A. Walker, Subduction and recycling of nitrogen along the Central American Margin. *Science* **297**, 1154–1157 (2002). <https://doi.org/10.1126/science.1073995>
- A. Freundt, I. Grevenmeyer, W. Rabbel, T.H. Hansteen, C. Hensen, H. Wehrmann, S. Kutterolf, R. Halama, M. Frische, Volatile (H<sub>2</sub>O, CO<sub>2</sub>, Cl, S) budget of the Central American subduction zone. *Int. J. Earth Sci.* **103**, 2101–2127 (2014). <https://doi.org/10.1007/s00531-014-1001-1>
- M.L. Frezzotti, J. Selverstone, Z.D. Sharp, R. Compagnoni, Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps. *Nat. Geosci.* **4**, 703–706 (2011). <https://doi.org/10.1038/ngeo1246>
- M.E. Galvez, O. Beyssac, I. Martinez, K. Benzerara, C. Chaduteau, B. Malvoisin, J. Malavieille, Graphite formation by carbonate reduction during subduction. *Nat. Geosci.* **6**, 473–477 (2013). <https://doi.org/10.1038/ngeo1827>
- C. Ganino, N.T. Arndt, Climate changes caused by degassing of sediments during the emplacement of large igneous provinces. *Geology* **37**, 323–326 (2009). <https://doi.org/10.1130/G25325A.1>
- C. Goldblatt, M.W. Claire, T.M. Lenton, A.J. Matthews, A.J. Watson, K.J. Zahnle, Nitrogen-enhanced greenhouse warming on early Earth. *Nat. Geosci.* **2**, 891–896 (2009). <https://doi.org/10.1038/ngeo692>
- P.J. Gorman, D.M. Kerrick, J.A.D. Connolly, Modeling open system metamorphic decarbonation of subducting slabs. *Geochim. Geophys. Geosyst.* **7**(4), Q04007 (2006). <https://doi.org/10.1029/2005GC001125>
- J.A.D.
- C. Groppo, F. Rolfo, D. Castelli, J.A.D. Connolly, Metamorphic CO<sub>2</sub> production from calc-silicate rocks via garnet-forming reactions in the CFAS-H<sub>2</sub>O-CO<sub>2</sub> system. *Contrib. Mineral. Petrol.* **166**, 1655–1675 (2013). <https://doi.org/10.1007/s00410-013-0947-5>
- C. Groppo, F. Rolfo, D. Castelli, P. Mosca, Metamorphic CO<sub>2</sub> production in collisional orogens: petrological constraints from phase diagram modeling of Himalayan, scapolite-bearing, calc-silicate rocks in the NKC(F)MAS(T)-HC system. *J. Petrol.* **58**, 53–84 (2017). <https://doi.org/10.1093/petrology/egx005>
- R. Halama, G.E. Bebout, T. John, V. Schenk, Nitrogen recycling in subducted oceanic lithosphere: the record in high- and ultrahigh-pressure metabasaltic rocks. *Geochim. Cosmochim. Acta* **74**, 1636–1652 (2010). <https://doi.org/10.1016/j.gca.2009.12.003>

- R. Halama, G.E. Bebout, T. John, M. Scambelluri, Nitrogen recycling in subducted mantle rocks and implications for the global nitrogen cycle. *Int. J. Earth Sci.* **103**, 2081–2099 (2014). <https://doi.org/10.1007/s00531-012-0782-3>
- R. Halama, G.E. Bebout, H.R. Marschall, T. John, Fluid-induced breakdown of white mica controls nitrogen transfer during fluid-rock interaction in subduction zones. *Int. Geol. Rev.* **59**, 702–720 (2017). <https://doi.org/10.1080/00206814.2016.1233834>
- S.A. Halldórsson, D.R. Hilton, P.H. Barry, E. Füri, K. Grönvold, Recycling of crustal material by the Iceland mantle plume: new evidence from nitrogen elemental and isotope systematics of subglacial basalts. *Geochim. Cosmochim. Acta* **176**, 206–226 (2016). <https://doi.org/10.1016/j.gca.2015.12.021>
- D.R. Hilton, T.P. Fischer, B. Marty, Noble gases and volatile recycling at subduction zones. *Rev. Mineral. Geochem.* **47**, 319–370 (2002). <https://doi.org/10.2138/rmg.2002.47.9>
- M.M. Hirschmann, Comparative deep Earth volatile cycles: The case for C recycling from exosphere/mantle fractionation of major (H<sub>2</sub>O, C, N) volatiles and from H<sub>2</sub>O/Ce, CO<sub>2</sub>/Ba, and CO<sub>2</sub>/Nb exosphere ratios. *Earth Planet. Sci. Lett.* **502**, 262–273 (2018). <https://doi.org/10.1016/j.epsl.2018.08.023>
- B.M. House, G.E. Bebout, D.R. Hilton, Carbon cycling at the Sunda margin, Indonesia: a regional study with global implications. *Geology* **47**, 483–486 (2019). <https://doi.org/10.1130/G45830.1>
- K. Jaeckel, G.E. Bebout, S. Angiboust, Deformation-enhanced fluid and mass transfer along Western and Central Alps paleo-subduction interfaces: significance for carbon cycling models. *Geosphere* **14**(6), 2355–2375 (2018). <https://doi.org/10.1130/GES01587.1>
- M. Javoy, The major volatile elements of the Earth: their origin, behavior, and fate. *Geophys. Res. Lett.* **24**, 177–180 (1997). <https://doi.org/10.1029/96GL03931>
- Y.F. Jia, Nitrogen isotope fractionations during progressive metamorphism: a case study from the Paleozoic Cooma metasedimentary complex, southeastern Australia. *Geochim. Cosmochim. Acta* **70**, 5201–5214 (2006). <https://doi.org/10.1016/j.gca.2006.08.004>
- B. Johnson, C. Goldblatt, The nitrogen budget of Earth. *Earth-Sci. Rev.* **148**, 150–173 (2015). <https://doi.org/10.1016/j.earscirev.2015.05.006>
- B. Johnson, C. Goldblatt, A secular increase in continental crust nitrogen during the Precambrian. *Geochem. Perspect. Lett.* **4**, 24–28 (2017a). <https://doi.org/10.7185/geochemlet.1731>
- B.W. Johnson, C. Goldblatt, EarthN: a new Earth system nitrogen model. *Geochem. Geophys. Geosyst.* **19**(8), 2516–2542 (2017b). <https://doi.org/10.1029/2017GC007392>
- F.K.B. Johnston, A.V. Turchyn, M. Edmonds, Decarbonation efficiency in subduction zones: implications for warm Cretaceous climates. *Earth Planet. Sci. Lett.* **303**, 143–152 (2011). <https://doi.org/10.1016/j.epsl.2010.12.049>
- C.K. Junium, M.A. Arthur, K.H. Freeman, Compound-specific  $\delta^{15}\text{N}$  and chlorin preservation in surface sediments of the Peru Margin with implications for ancient bulk  $\delta^{15}\text{N}$  records. *Geochim. Cosmochim. Acta* **160**, 306–318 (2015). <https://doi.org/10.1016/j.gca.2014.12.018>
- P.B. Kelemen, C.E. Manning, Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. *Proc. Natl. Acad. Sci. USA* **112**(30), E3997–E4006 (2015). <https://doi.org/10.1073/pnas.1507889112>
- D.M. Kerrick, K. Caldeira, Metamorphic CO<sub>2</sub> degassing from orogenic belts. *Chem. Geol.* **145**, 213–232 (1998). [https://doi.org/10.1016/S0009-2541\(97\)00144-7](https://doi.org/10.1016/S0009-2541(97)00144-7)
- D.M. Kerrick, J.A.D. Connolly, Subduction of ophiicarbonates and recycling of CO<sub>2</sub> and H<sub>2</sub>O. *Geology* **26**, 375–378 (1998). [https://doi.org/10.1130/0091-7613\(1998\)026<0375:S00ARO>2.3.CO;2](https://doi.org/10.1130/0091-7613(1998)026<0375:S00ARO>2.3.CO;2)
- D.M. Kerrick, J.A.D. Connolly, Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle. *Nature* **411**, 293–296 (2001). <https://doi.org/10.1038/35077056>
- L. Li, G.E. Bebout, Carbon and nitrogen geochemistry of sediments in the Central American convergent margin: insights regarding subduction input fluxes, diagenesis, and paleoproductivity. *J. Geophys. Res.* **110**, B11202 (2005). <https://doi.org/10.1029/2004JB003276>
- Y. Li, H. Keppler, Nitrogen speciation in mantle and crustal fluids. *Geochim. Cosmochim. Acta* **129**, 13–32 (2014). <https://doi.org/10.1016/j.gca.2013.12.031>
- L. Li, G.E. Bebout, B.D. Idleman, Nitrogen concentration and  $\delta^{15}\text{N}$  of altered oceanic crust obtained on ODP Legs 129 and 185: insights into alteration-related nitrogen enrichment and the nitrogen subduction budget. *Geochim. Cosmochim. Acta* **71**, 2344–2360 (2007). <https://doi.org/10.1016/j.gca.2007.02.001>
- Y. Li, M. Wiedenbeck, S. Shcheka, H. Keppler, Nitrogen solubility in upper mantle minerals. *Earth Planet. Sci. Lett.* **377–378**, 311–323 (2013). <https://doi.org/10.1016/j.epsl.2013.07.013>
- Y. Li, B. Marty, S. Shcheka, L. Zimmermann, H. Keppler, Nitrogen isotope fractionation during terrestrial core-mantle separation. *Geochem. Perspect. Lett.* **2**, 138–147 (2016). <https://doi.org/10.7185/geochemlet.1614>
- A. Mallik, Y. Li, M. Wiedenbeck, Nitrogen evolution within the Earth's atmosphere-mantle system assessed by recycling in subduction zones. *Earth Planet. Sci. Lett.* **482**, 556–566 (2018). <https://doi.org/10.1016/j.epsl.2017.11.045>

- C.E. Manning, A piece of the deep carbon puzzle. *Nat. Geosci.* **7**, 333–334 (2014). <https://doi.org/10.1038/ngeo2152>
- B. Marty, N. Dauphas, The nitrogen record of crust-mantle interaction and mantle convection from Archean to present. *Earth Planet. Sci. Lett.* **206**, 397–410 (2003). [https://doi.org/10.1016/S0012-821X\(02\)01108-1](https://doi.org/10.1016/S0012-821X(02)01108-1)
- S. Mikhail, D.A. Sverjensky, Nitrogen speciation in upper mantle fluids and the origin of Earth's nitrogen-rich atmosphere. *Nat. Geosci.* **7**, 816–819 (2014). <https://doi.org/10.1038/NNGEO2271>
- S. Mikhail, P.H. Barry, D.A. Sverjensky, The relationship between pH and the deep nitrogen cycle. *Geochim. Cosmochim. Acta* **209**, 149–160 (2017). <https://doi.org/10.1016/j.gca.2017.04.007>
- C. Mitchell, T.P. Fischer, D.R. Hilton, E.H. Hauri, A.M. Shaw, J.M. de Moor, Z.D. Sharp, K. Kazahaya, Nitrogen sources and recycling at subduction zones: insights from the Izu–Bonin–Mariana arc. *Geochem. Geophys. Geosyst.* **11**(2), Q02X11 (2010). <https://doi.org/10.1029/2009GC002783>
- B. Mysen, Mass transfer in the Earth's interior: fluid-melt interaction in aluminosilicate–C–O–H–N systems at high pressures and temperature under oxidizing conditions. *Prog. Earth Planet. Sci.* **5**, 6 (2018). <https://doi.org/10.1186/s40645-017-0161-6>
- B. Mysen, M.L. Fogel, Nitrogen and hydrogen isotope compositions and solubility in silicate melts in equilibrium with reduced (N+H)-bearing fluids at high pressure and temperature: effects of melt structure. *Am. Mineral.* **95**, 987–999 (2010). <https://doi.org/10.2138/am.2010.3364>
- A.P. Palya, I.S. Buick, G.E. Bebout, Storage and mobility of nitrogen in the continental crust: evidence from partially melted metasedimentary rocks, Mt. Stafford, Australia. *Chem. Geol.* **281**, 211–226 (2011). <https://doi.org/10.1016/j.chemgeo.2010.12.009>
- P. Philippot, V. Busigny, M. Scambelluri, P. Cartigny, Oxygen and nitrogen isotopes as tracers of fluid activities in serpentinites and metasediments during subduction. *Mineral. Petrol.* **91**, 11–24 (2007). <https://doi.org/10.1007/s00710-007-0183-7>
- F. Piccoli, A. Vitale Brovarone, O. Beyssac, I. Martinez, J.J. Ague, C. Chaduteau, Carbonation by fluid-rock interactions at high-pressure conditions: implications for carbon cycling in subduction zones. *Earth Planet. Sci. Lett.* **445**, 146–159 (2016). <https://doi.org/10.1016/j.epsl.2016.03.045>
- I.K. Pitcairn, D.A.H. Teagle, R. Kerrich, D. Craw, T.S. Brewer, The behavior of nitrogen and nitrogen isotopes during metamorphism and mineralization: evidence from the Otago and Alpine Schists, New Zealand. *Earth Planet. Sci. Lett.* **233**, 229–246 (2005). <https://doi.org/10.1016/j.epsl.2005.01.029>
- S. Poli, Carbon mobilized at shallow depths in subduction zones by carbonatitic liquids. *Nat. Geosci.* **8**, 633–636 (2015). <https://doi.org/10.1038/ngeo2464>
- M. Roskosz, B.O. Mysen, G.D. Cody, Dual speciation of nitrogen in silicate melts at high pressure and temperature: an experimental study. *Geochim. Cosmochim. Acta* **70**, 2902–2918 (2006). <https://doi.org/10.1016/j.gca.2006.03.001>
- R.L. Rudnick, S. Gao, Composition of the continental crust, in *Treatise on Geochemistry, Volume 4: The Crust*, ed. by H.D. Holland, K.K. Turekian (Elsevier, Amsterdam, 2014), pp. 1–51. <https://doi.org/10.1016/B978-0-08-095975-7.00301-6>
- S.J. Sadofsky, G.E. Bebout, Record of forearc devolatilization in low-T, high-P/T metasedimentary suites: significance for models of convergent margin chemical cycling. *Geochem. Geophys. Geosyst.* **4**(4), 9903 (2003). <https://doi.org/10.1029/2002GC000412>
- S.J. Sadofsky, G.E. Bebout, Nitrogen geochemistry of subducting sediments: new results from the Izu–Bonin–Mariana margin and insights regarding global nitrogen subduction. *Geochem. Geophys. Geosyst.* **5**(3), Q03115 (2014). <https://doi.org/10.1029/2003GC000543>
- Y. Sano, N. Takahata, Y. Nishio, T.P. Fischer, S.N. Williams, Volcanic flux of nitrogen from the Earth. *Chem. Geol.* **171**, 263–271 (2001). [https://doi.org/10.1016/S0009-2541\(00\)00252-7](https://doi.org/10.1016/S0009-2541(00)00252-7)
- M. Scambelluri, G.E. Bebout, D. Belmonte, M. Gilio, N. Campomenosi, N. Collins, L. Crispini, Carbonation of subduction-zone serpentinite (high-pressure ophicarbonate; Ligurian Western Alps) and implications for the deep carbon cycling. *Earth Planet. Sci. Lett.* **441**, 155–166 (2016). <https://doi.org/10.1016/j.epsl.2016.02.034>
- P.A. Schroeder, A.A. McLain, Illite-smectites and the influence of burial diagenesis on the geochemical cycling of nitrogen. *Clay Miner.* **33**, 539–546 (1998). <https://doi.org/10.1180/000985598545877>
- A. Skelton, Flux rates for water and carbon during greenschist facies metamorphism. *Geology* **39**, 43–46 (2011). <https://doi.org/10.1130/G31328.1>
- H. Svensen, B. Jamtveit, Metamorphic fluids and global environmental changes. *Elements* **6**, 179–182 (2010). <https://doi.org/10.2113/gselements.6.3.179>
- H. Svensen, S. Planke, A. Malthe-Sørenssen, B. Jamtveit, R. Myklebust, T. Rasmussen Eidem, S.S. Rey, Release of methane from a volcanic basin as a mechanism for initial Eocene global warming. *Nature* **429**, 542–545 (2004). <https://doi.org/10.1038/nature02566>
- D.A. Sverjensky, V. Stagno, F. Huang, Important role for organic carbon in subduction-zone fluids in the deep carbon cycle. *Nat. Geosci.* **7**, 909–913 (2014). <https://doi.org/10.1038/ngeo2291>

- A.R. Thomson, M.J. Walter, S.C. Kohn, R.A. Brooker, Slab melting as a barrier to deep carbon subduction. *Nature* **529**, 76–79 (2016). <https://doi.org/10.1038/nature16174>
- I.N. Tolstikhin, B. Marty, The evolution of terrestrial volatiles: a view from helium, neon, argon and nitrogen isotope modeling. *Chem. Geol.* **147**, 27–52 (1998). [https://doi.org/10.1016/S0009-2541\(97\)00170-8](https://doi.org/10.1016/S0009-2541(97)00170-8)
- V.R. Troll, D.R. Hilton, E.M. Jolis, J.P. Chadwick, L.S. Blythe, F.M. Deegan, L.M. Schwarzkopf, M. Zimmer, Crustal CO<sub>2</sub> liberation during the 2006 eruption and earthquake events at Merapi volcano, Indonesia. *Geophys. Res. Lett.* **39**, L11302 (2012). <https://doi.org/10.1029/2012GL051307>
- F. van der Straaten, R. Halama, T. John, V. Schenk, F. Hauff, N. Andersen, Tracing the effects of high-pressure metasomatic fluids and seawater alteration in blueschist-facies overprinted eclogites: implications for subduction channel processes. *Chem. Geol.* **292–293**, 69–87 (2012). <https://doi.org/10.1016/j.chemgeo.2011.11.008>
- A. Vitale Brovarone, I. Martínez, A. Elmaleh, R. Compagnoni, C. Chaduteau, C. Ferraris, I. Esteve, Massive production of abiotic methane during subduction evidenced in metamorphosed ophicarbonates from the Italian Alps. *Nat. Commun.* **8**, 14134 (2017). <https://doi.org/10.1038/ncomms14134>
- A. Watenphul, B. Wunder, R. Wirth, W. Heinrich, Ammonium-bearing clinopyroxene: a potential nitrogen reservoir in the Earth's mantle. *Chem. Geol.* **270**, 240–248 (2010). <https://doi.org/10.1016/j.chemgeo.2009.12.003>
- S. Whitley, R. Gertisser, R. Halama, K. Preece, V.R. Troll, F.M. Deegan, Crustal CO<sub>2</sub> contribution to subduction zone degassing recorded through calc-silicate xenoliths in arc lavas. *Sci. Rep.* **9**, 8803 (2019). <https://doi.org/10.1038/s41598-019-44929-2>
- L.B. Williams, R.E. Ferrell Jr., I. Hutcheon, A.J. Bakel, M.D. Walsh, H.R. Krouse, Nitrogen isotope geochemistry of organic matter and minerals during diagenesis and hydrocarbon migration. *Geochim. Cosmochim. Acta* **59**, 765–779 (1995). [https://doi.org/10.1016/0016-7037\(95\)00005-K](https://doi.org/10.1016/0016-7037(95)00005-K)
- Y. Yang, V. Busigny, Z. Wang, Q. Xia, The fate of ammonium in phengite at high temperature. *Am. Mineral.* **102**, 2244–2253 (2017). <https://doi.org/10.2138/am-2017-6094>
- R. Yokochi, B. Marty, G. Chazot, P. Burnard, Nitrogen in peridotite xenoliths: lithophile behavior and magmatic isotope fractionation. *Geochim. Cosmochim. Acta* **73**, 4843–4861 (2009). <https://doi.org/10.1016/j.gca.2009.05.054>
- T. Yoshioka, M. Wiedenbeck, S. Shcheka, H. Keppler, Nitrogen solubility in the deep mantle and the origin of Earth's primordial nitrogen budget. *Earth Planet. Sci. Lett.* **488**, 134–143 (2018). <https://doi.org/10.1016/j.epsl.2018.02.021>
- A.L. Zerkle, S. Mikhail, The geobiological nitrogen cycle: from microbes to the mantle. *Geobiology* **15**, 343–352 (2017). <https://doi.org/10.1111/gbi.12228>
- Y. Zhang, A. Zindler, Distribution and evolution of carbon and nitrogen in Earth. *Earth Planet. Sci. Lett.* **117**, 331–345 (1993). [https://doi.org/10.1016/0012-821X\(93\)90088-Q](https://doi.org/10.1016/0012-821X(93)90088-Q)

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