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SPECIAL COMMUNICATION

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 NH_4^+ in minerals has a major influence on fluxes between reservoirs. The temperature-dependent stability of 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 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 CH_4 and/or 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 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 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 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

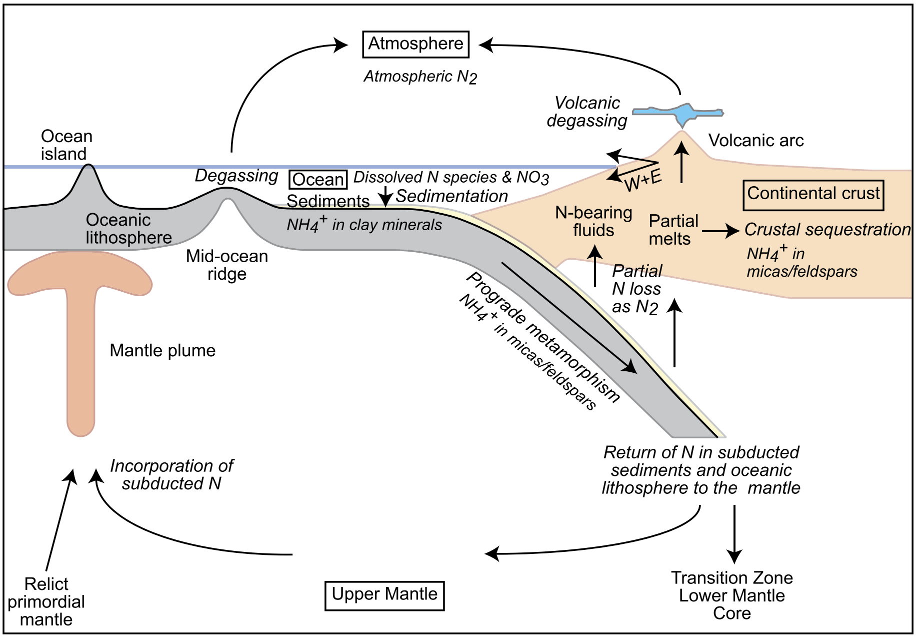

Fig. 1 Schematic representation of the geological nitrogen cycle (based on Bebout et al. 2013a,b; Cartigny and Marty 2013). W + E = Weathering and erosion

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_2 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 (Avice 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.

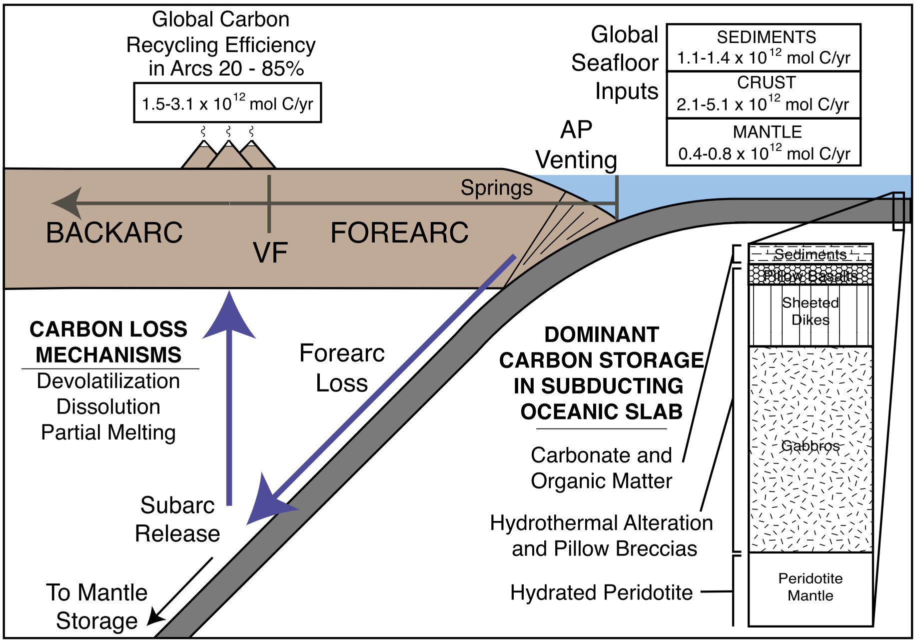

Fig. 2 Schematic illustration of an ocean-continent subduction zone, showing global-basis estimates of C fluxes discussed in the text (moles of C/year) and highlighting the uncertainties in the various flux estimates (from Cook-Kollars et al. 2014; other sources cited therein). Use of the fluxes shown here would suggest volcanic arc return efficiency (inputs/arc outputs) of ≈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 CO_2 and/or 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 ≈ 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, 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 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 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_2 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_2O-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_2 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_2 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 $\sim$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_2 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_2 degassing from the Cordilleran belt has been linked to Eocene global warming (Kerrick and Caldeira 1998) and CO_2 flux for the Himalayan orogeny carrying large fluxes of CO_2 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_2 in a wide range of orogenic settings during collisional metamorphism (Ague 2000; Groppo et al. 2013). The quantitative calculation of CO_2 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_2 (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_2 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_2 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_2 (Skelton 2011; Evans et al. 2008). On geological timescales, metamorphic degassing during collisional metamorphism and orogeneses will create pulses of CO_2 relative to the slow silicate weathering that eventually sequesters CO_2 (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_4 and CO_2 around igneous intrusions (Svensen and Jamtveit 2010; Aiuppa et al. 2017). Addition of volatiles including CO_2 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 volcaniclastic 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_2, CH_4) 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 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 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 CO_2 fluxes in subduction zones.
4. Release of 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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