



## GR Letter

# Volatiles in the mantle below Northern Antarctica: Insights from Deception Island volcano

Antonio Caracausi<sup>a,b,\*</sup>, Antonio Polo-Sánchez<sup>a</sup>, Antonio M. Álvarez-Valero<sup>a</sup>, Jabrane Labidi<sup>c</sup>, Edward D. Young<sup>d</sup>, Hirochika Sumino<sup>e</sup>, Conxita Àvila<sup>f</sup>, Dario Buttitta<sup>b</sup>, Adelina Geyer<sup>g</sup>, Paolo Randazzo<sup>b</sup>

<sup>a</sup> Departamento de Geología, Universidad de Salamanca, Plaza de la Merced s/n, 37008 Salamanca, Spain

<sup>b</sup> Istituto Nazionale di Geofisica e Vulcanologia (INGV), sezione di Palermo. Via Ugo La Malfa, 153. 90146 Palermo, Italy

<sup>c</sup> Institut de Physique du Globe de Paris, Université de Paris, CNRS, 1 Rue Jussieu, 75005 Paris, France

<sup>d</sup> Department of Earth, Planetary and Space Sciences, UCLA, 595 Charles E Young Dr, 90095 Los Angeles, USA

<sup>e</sup> Research Center for Advanced Science and Technology, University of Tokyo 153-8904 Tokyo, Japan

<sup>f</sup> Departament de Biologia Evolutiva, Ecologia i Ciències Ambientals, Universitat de Barcelona, Av. Diagonal 643, 08028 Barcelona, Spain

<sup>g</sup> Geosciences Barcelona (GEO3BCN), CSIC, Lluís Solé i Sabarís s/n, 08028 Barcelona, Spain



## ABSTRACT

The incomplete knowledge of the pristine composition of the Earth's interior along with the variable impact of shallow ecosystems on the mantle over geological time severely restrict the ability to assess the volatiles budget in the Earth's deep reservoirs and how geodynamics controls mantle heterogeneity. We present the results of a geochemical exploration at Deception Island volcano in Antarctica, whose fluids provide the rare opportunity to investigate the mantle at very high latitudes. This region is characterized by a paucity of data due to its remoteness and not easy to reach to explore and collect samples in the field. Helium isotopes combined with the carbon-isotope composition of carbon dioxide in fluids emitted at Deception Island match the composition of the convective Mid Oceanic Mantle Reservoir (MORB-type). In contrast, the nitrogen  $^{15}\text{N}^{15}\text{N}$  isotopologues surprisingly indicate an excess of nitrogen respect to a MORB-type Earth mantle. We conclude that this is due to the subduction of shallow crustal materials with low carbon/nitrogen ratios—typical of high-latitude regions—down into the mantle. Our results therefore highlight the impact of the surface environment on the Earth's interior by revealing a convincing match between the low carbon/nitrogen ratios of the lowest latitude surface environment and of the mantle-derived fluids. These findings offer novel perspectives into the role of diverse latitudinal surface ecosystems in shaping the heterogeneity of the Earth's mantle and their implications for carbon and nitrogen cycles.

## 1. Introduction

The Earth's mantle contains traces of the primordial volatiles stored in the Earth since its formation (e.g., Mukhopadhyay, 2012; Bekaert et al., 2019; Broadley et al., 2020 and references therein), and the complex mantle geochemistry also reflects its global evolution over time (e.g., Allègre et al., 1980; Zindler and Hart, 1986; Hofmann, 1997; Bekaert et al., 2021 and references therein). Carbon (C) and nitrogen (N) arrived on Earth with accretionary materials (e.g., Marty et al., 2020 and references therein). Beyond being key nutrients for supporting life, these two elements also offer the potential to trace processes linking the planet's surface to various reservoirs in the Earth's interior. Billions of years of plate tectonics have modified at least part of the volatiles budget, by redistributing elements among surface environments, the terrestrial atmosphere, and the crust and mantle (e.g., Mukhopadhyay, 2012; Bekaert et al., 2019; Broadley et al., 2020; Hu et al., 2024). This

has resulted in mantle-derived minerals and fluids at the Earth's surface containing traces of C and N cycling through the Earth's shallow and deep reservoirs (Stachel et al., 2022), allowing assumptions to be made about how the surface biology might influence mantle heterogeneity (e.g., Doucet et al., 2021; Kurokawa et al., 2022; Hu et al., 2023; Aitchison et al., 2025).

Carbon and nitrogen are fundamental constituents of the terrestrial atmosphere, and both are drivers of planetary habitability (e.g., Zerkle and Mikhail, 2017; Foley and Smye, 2018; Labidi et al., 2020 and references therein). Nitrogen is the most-abundant component of the atmosphere and carbon is one of the main elements contributing to the greenhouse effect. Primordial volatiles inherited during the accretion of the planet continuously escaped towards the atmosphere mainly via magmatic degassing and volcanic eruptions (e.g., Labidi et al., 2020; Marty et al., 2020; Bekaert et al., 2024). Mantle reservoirs are also contaminated by the recycling of shallow materials at depth due to

\* Corresponding author.

E-mail addresses: [antonio.caracausi@ingv.it](mailto:antonio.caracausi@ingv.it) (A. Caracausi), [aav@usal.es](mailto:aav@usal.es) (A.M. Álvarez-Valero).

<https://doi.org/10.1016/j.gr.2026.03.018>

Received 18 August 2025; Received in revised form 25 March 2026; Accepted 29 March 2026

Available online 28 April 2026

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subduction at the boundaries of converging plates (e.g., Bekaert et al., 2021 and references therein). Therefore, while the abundances of C and N in major deep terrestrial reservoirs might be strongly linked to subduction, they are still not well constrained (e.g., Marty and Zimmermann, 1999; Barry et al., 2014; Marty et al., 2020 and references therein) due to the paucity of natural fluids at the Earth's surface reflecting a deep origin without contaminations by the atmosphere in shallow crustal layers (e.g., Marty et al., 2020; Bekaert et al., 2024). This situation indicates the need for more investigations of volatiles from different geodynamics settings and in different regions of the planet in order to characterize the volatiles budget in the deep major terrestrial reservoirs (e.g., Labidi et al., 2021; Labidi, 2022; Bekaert et al., 2021 and 2024).

Moreover, the existing data that are used to explore the amounts and isotope compositions of volatiles (e.g., C, N and noble gases) in the Earth's mantle come largely from magmatic systems in low-latitude regions (oceanic and continental). This means that mantle volatiles remain unexplored in vast regions of our planet (e.g., the polar regions), and so new explorations are mandatory to characterize the mantle heterogeneity and the budget of volatiles such as C and N on Earth. The extreme weather conditions and geographical remoteness of Antarctica have made it the least-explored continent on our planet. Nonetheless, the technological advancements in the last two decades have allowed scientists to extend the challenging exploration of this continent and its surrounding sea regions (Smellie et al., 2021). Fluids trapped in minerals of magmatic rocks from continental and submarine volcanic systems in Antarctica have offered rare opportunities to investigate the volatiles (e.g., light noble gases) in the mantle below the cold continent (Broadley et al., 2016; Correale et al., 2019; Álvarez-Valero et al., 2020, 2022). However, active volcanoes in Antarctica are almost inaccessible for sampling fluids, and those that are collected are highly contaminated by atmospheric interactions that completely obscure the mantle component, such as those from Mt Erebus volcano (Ilanko et al., 2019) and Mt Melbourne (Lee et al., 2025).

We present the results of a geochemical exploration of volcanic fluids emitted at Deception Island (DI; Fig. 1) during the Spanish Antarctic campaign in 2022–2023. DI is an active volcano that erupted most recently in 1967, 1969 and 1970 (e.g., Smellie, 2001). It is located at the southwestern end of the Bransfield Strait, between the South Shetland arc and the Antarctic Peninsula (Fig. 1; section “Geological setting” in the Supplementary materials). Similar to seamounts in the Bransfield Strait, DI can be characterized as part of a back-arc basin, with mantle sources receiving materials from the devolatilization of the subducted Phoenix Plate (e.g., Anderson et al., 2023, 2024), and hence is located in a complex regional geodynamics setting controlled by both subduction and extensional tectonics (Li et al., 2021 and references therein; section “Geological setting” in the Supplementary materials).

During the austral summer of 2023 we collected volcanic gases along multiple subaerial vents and fumaroles characterized by temperature anomalies of the soil (from  $\sim 30^\circ\text{C}$  to  $\sim 104^\circ\text{C}$ ; Table 1, Fig. 1), and from some gas emanations in shallow seawater (Fig. 1, Table 1, Fig. S1). The results of our exploration at DI reveal volatiles outgassing in different points along the rim of the island's interior bay (Port Foster), from the fumaroles distributed in different areas of the island and from submarine emissions very close to the coast (Fig. 1, Fig. S1, Movie S1). Our analyses have demonstrated that large gas releases are still occurring at DI in numerous areas, even far from the eruptive vents of the most-recent eruptions (Fig. 1), revealing that these volcanic gases are suitable samples for investigating their mantle source. We also explored the possible role of the latitudinal variations of both C and N in shallow marine systems to the mantle heterogeneity via the subduction of sediment. This approach will help to fill the knowledge gap about how surface biology can impact the mantle C and N systematics.

## 2. Materials and methods

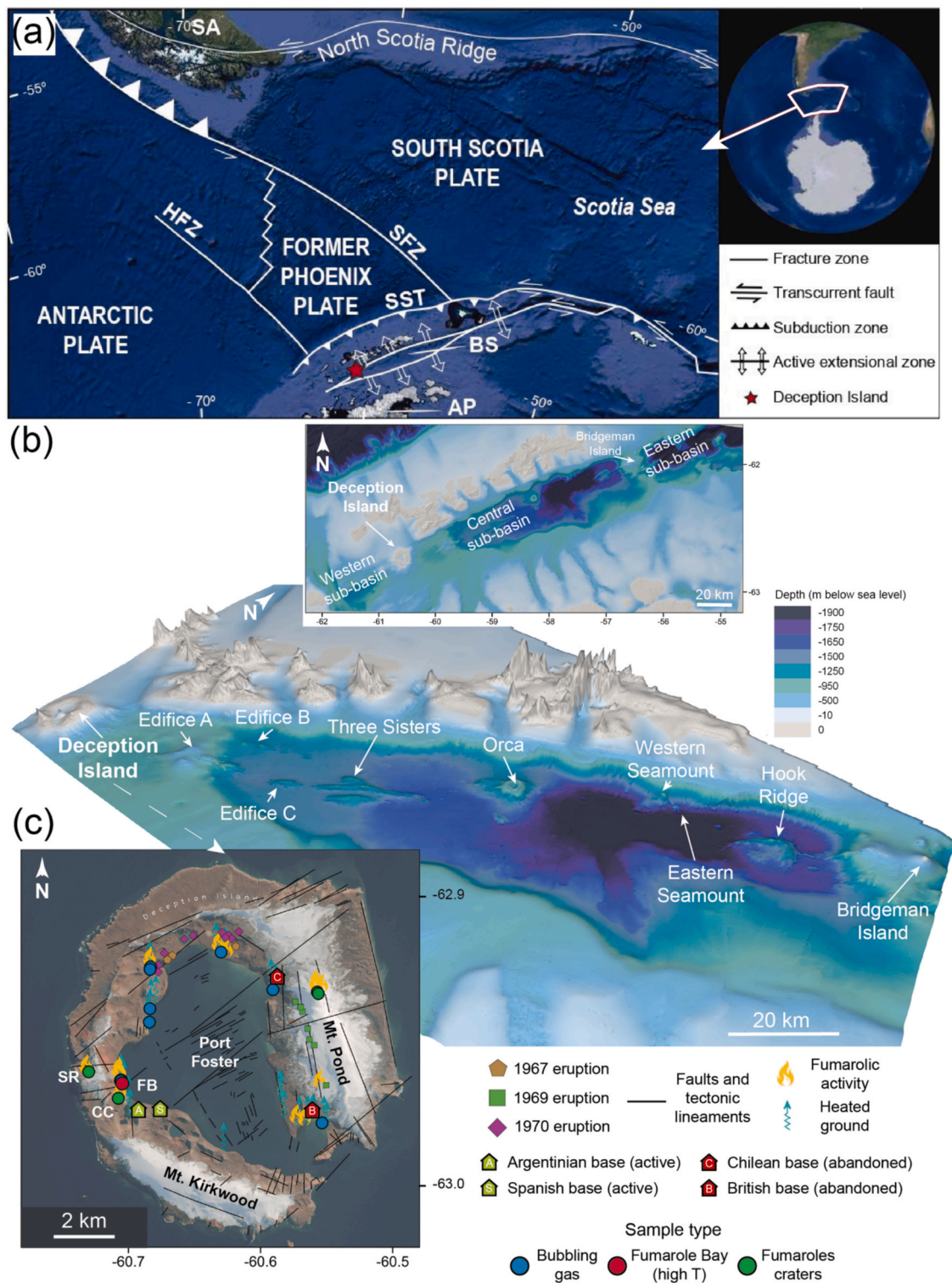
The discharged gases were collected using a stainless-steel funnel in the case of bubbling gases in the water and using a probe inserted 50 cm into the emission orifice for soil gases. Two-way Pyrex bottles with vacuum valves at both ends and two steel bottles equipped with were connected to the system and used as sample containers (more details in caption Fig. S1).

The chemical concentrations of helium (He), hydrogen ( $\text{H}_2$ ), neon (Ne), argon (Ar), nitrogen (N), oxygen ( $\text{O}_2$ ), carbon monoxide, methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ), and the isotope compositions of He, Ne and Ar were measured using standard analytical techniques. In detail, the gas chemical composition was determined using a PerkinElmer 8500 gas chromatograph equipped with a 4-m Carbosieve 5A column and double detector (flame-ionization detector and hot-wire detector). A thermal conductivity detector (TCD) was used to measure the concentrations of  $\text{H}_2$ ,  $\text{O}_2$ , N and  $\text{CO}_2$ , while a flame ionization detector (FID) was used for  $\text{CH}_4$ . Analytical errors of the measured concentrations are always within 5%.

He isotopes were analysed using a static vacuum mass spectrometer (GVI Helix SFT) with a double collector in order to detect  $^3\text{He}$  and  $^4\text{He}$  ion beams simultaneously (with a precision for the isotope ratio of within  $\pm 0.5\%$ ) after applying standard purification procedures to gas samples involving the elimination of reactive species from the examined samples using non-evaporating Getter pumps. The noble gas species were subsequently separated from each other using cryogenic techniques. We analysed the three noble gases (He, Ne and Ar) starting from the same aliquot of sample gas, which resulted in more-accurate determinations of the correlations present between the different noble gases measured. More details about the purification procedures are provided in Rizzo et al. (2018). The  $^3\text{He}/^4\text{He}$  ratio was determined by measuring  $^3\text{He}$  in an electron multiplier detector and  $^4\text{He}$  in an axial Faraday detector.  $^{20}\text{Ne}$  was measured using a multicollector Thermo-Helix MC Plus mass spectrometer, where He and Ne were separately admitted after cryogenic separation. The analytical errors for He and Ne were 0.1% and 0.3%, respectively. He-isotope compositions are expressed as R/Ra values, which normalize the  $^3\text{He}/^4\text{He}$  ratio of the sample (R) against the atmospheric  $^3\text{He}/^4\text{He}$  ratio ( $\text{Ra} = 1.386 \times 10^{-6}$ ; Ozima and Podosek, 2002). The Ar concentrations and its isotope compositions ( $^{40}\text{Ar}$  and  $^{36}\text{Ar}$ ) were analysed using a multicollector Helix MC-GVI mass spectrometer with an analytical uncertainty for single  $^{40}\text{Ar}/^{36}\text{Ar}$  measurements of  $< 0.1\%$ .

The C-isotope composition of  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2}$ ) was measured using a Delta Plus XP isotope ratio mass spectrometer equipped with a Thermo TRACE GC and a Thermo GC/C III interface (precision of  $\pm 0.1\%$ ). The  $^{13}\text{C}/^{12}\text{C}$  ratios of  $\text{CO}_2$  are reported in delta notation (‰) relative to VPDB (i.e.  $\delta^{13}\text{C}_{\text{CO}_2}$ ).

$\text{N}_2$  gases were purified by cryogenic separation followed by gas chromatography at the University of California, Los Angeles (UCLA). Nitrogen abundances were measured using manometry before mass-spectrometry analyses. The abundances of singly and doubly substituted isotopologues of N were determined from the ion currents for  $^{14}\text{N}^{14}\text{N}^+$ ,  $^{14}\text{N}^{15}\text{N}^+$  and  $^{15}\text{N}^{15}\text{N}^+$  with cardinal mass/charge ( $m/z$ ) ratios of 28, 29 and 30, respectively. These measurements were performed using the Nu Instruments Panorama mass spectrometer at UCLA. Ions with  $m/z$  ratios of  $\sim 30$  were quantified using a secondary electron multiplier, while the other ions were measured using Faraday cups with  $10^{11} \Omega$  amplifier resistors. A mass-resolving power of roughly 50,000 allowed  $^{15}\text{N}^{15}\text{N}^+$  to be resolved from the  $^{14}\text{N}^{16}\text{O}^+$  isobaric interference. See detailed methods in Young et al. (2016), Yeung et al. (2017), and Labidi et al. (2020). The sample quantities in the present study allowed measurement durations of between 1 and 4 h, yielding  $\Delta_{30}$  internal precisions of between 0.2‰ and 0.5‰ ( $1\sigma$ ).



**Fig. 1.** (a) Simplified regional map of the geodynamics setting (from Martos et al., 2014). AP: Antarctic Peninsula. BS: Bransfield Strait. HFZ: Hero Fracture zone. SA: South America. SFZ: Shackleton fracture zone. SST: South Shetland trench. (b) Locations of the Eastern Sub-basin, Central Sub-basin and Western Sub-basin, and the Deception Island (DI) and Central Bransfield Strait submarine volcanoes. Bathymetry is from the GMRT database (<https://www.gmrt.org/>) (Ryan et al., 2009), with fourfold vertical exaggeration. (c) DI orthophoto map showing the sampling sites along with the main faults and tectonic lineaments, the main vents of the 1967, 1969 and 1970 eruptions, the active and destroyed scientific bases, and the previously reported locations of heated ground and fumarole activity. CC: Cerro Caliente. FB: Fumarole Bay. SR: Stonethrow Ridge. Orthophoto is from European Union Copernicus Sentinel-2 imagery, taken on 17 March 2023. Faults and tectonic lineaments are from Maestro et al. (2025). Fumarole activity and heated ground are from López-Martínez et al. (2002) and Smellie and López-Martínez (2002).

**Table 1**

Geographical coordinates of the sampling points and temperature.

| Point ID                | X Longitude | Y Latitude | Location Name       | T °C  |
|-------------------------|-------------|------------|---------------------|-------|
| <b>Fumarole Beach</b>   |             |            |                     |       |
| DI-02                   | −60.710147  | −62.967436 | Fumarole Bay        | 103.1 |
| DI-03                   | −60.709030  | −62.968287 | Fumarole Bay        | n.a   |
| DI-10                   | −60.709136  | −62.968422 | Fumarole Bay        | 104.2 |
| <b>Gas Bubbling</b>     |             |            |                     |       |
| DI-05                   | −60.710145  | −62.967436 | Fumarole Bay        | n.a   |
| DI-04                   | −60.690266  | −62.946944 | Murature Point      | n.a   |
| DI-01                   | −60.690293  | −62.942328 | South of Cross Hill | 27.8  |
| DI-14                   | −60.690888  | −62.927891 | Telefon Bay         | 34    |
| DI-17                   | −60.638124  | −62.921992 | Crater 70           | n.a   |
| DI-07                   | −60.597894  | −62.93425  | Pendulum Cove       | n.a   |
| DI-06                   | −60.557000  | −62.979550 | Whalers Bay         | 46.0  |
| DI-09                   | −60.557000  | −62.979550 | Whalers Bay         | 45.0  |
| DI-11                   | −60.597894  | −62.93425  | Pendulum Cove       | 2.0   |
| <b>Fumaroles Flanks</b> |             |            |                     |       |
| DI-08                   | −60.711694  | −62.973647 | Cerro Caliente      | 94.4  |
| DI-12                   | −60.564297  | −62.934480 | Mt. Pond            | 96.0  |
| DI-13                   | −60.563525  | −62.935002 | Mt. Pond            | 100.5 |
| DI-16                   | −60.734775  | −62.964816 | Stonethrow Ridge    | 47.0  |

### 3. Results and discussion

#### 3.1. Characterization of volatiles: He isotopes and C-He systematics

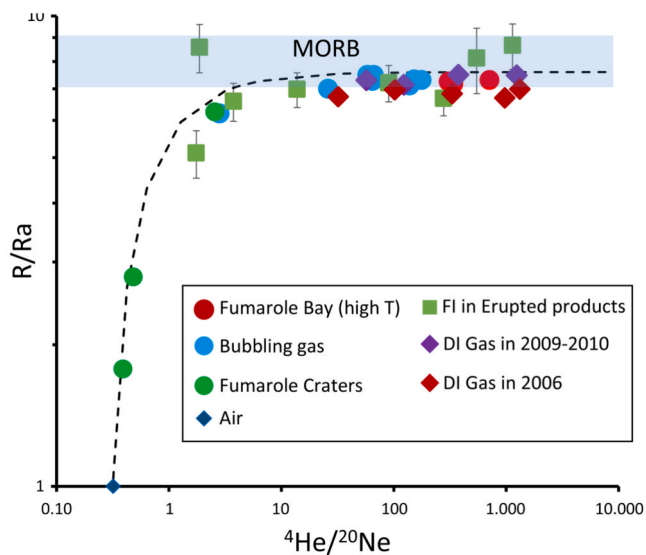
Samples from gas bubbling in the seawater close to the shoreline (<5 m deep) as well as from fumaroles reveal two main compositional sets: (i) a CO<sub>2</sub>-dominated set, with CO<sub>2</sub> > 96%, and (ii) an N-dominated group, with N<sub>2</sub> > 60%. In general, decreasing CO<sub>2</sub> amounts are balanced by a relative increase in N amounts (Table 2). The gases from the high-temperature emissions at Fumarole Bay and those emitted in the central-western side of Port Foster bay (Fig. 1) are CO<sub>2</sub>-rich gases, characterized by O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> concentrations lower than 1% (Table 2). This indicates low atmospheric contamination as well as low crustal contributions in the fluids (e.g. Caracausi et al., 2003; Martelli et al., 2008; Labidi et al., 2021). In contrast, the gases emitted along the shorelines on the eastern side of DI show elevated N<sub>2</sub> concentrations, sometimes even higher than in air, ranging from 0.5% to 96.3%. In those emanations the O<sub>2</sub> amounts range from 0.2% to 20.1%, indicating substantial contributions from air-derived fluids.

We also measured the He, Ne, Ar, C of CO<sub>2</sub> and N isotopes of the gases in order to constrain the sources of volatiles emitted from DI volcano. The <sup>4</sup>He/<sup>20</sup>Ne ratios of the DI gases are generally one order of magnitude higher than in air (i.e. 0.318; Ozima and Podosek, 2002), indicating that the air-derived He component is negligible in most of the collected gases (Fig. 2). The highest <sup>4</sup>He/<sup>20</sup>Ne values correspond to the two high-temperature fumaroles at Fumarole Bay (Fig. 2). In contrast, the gases from the Mt Pond fumaroles (96–100°C; Table 1) are characterized by a high air-component with <sup>4</sup>He/<sup>20</sup>Ne ratios of 0.4–0.5 (Table 2, Fig. 2). The diagram of R/Ra versus <sup>4</sup>He/<sup>20</sup>Ne in Fig. 2 indicates that all samples fit along a mixing line between the air and a mantle component showing an endmember with R/Ra values ranging from 7.1 to 7.6 Ra. This range of He-isotope ratios overlaps the values in the fluid inclusions in minerals from the main eruptive DI events and in gas emissions from previous investigations (Kusakabe et al., 2009; Padrón et al., 2015; Álvarez-Valero et al., 2022; Fig. 2), which indicates that a MORB-type mantle is the source of He at DI.

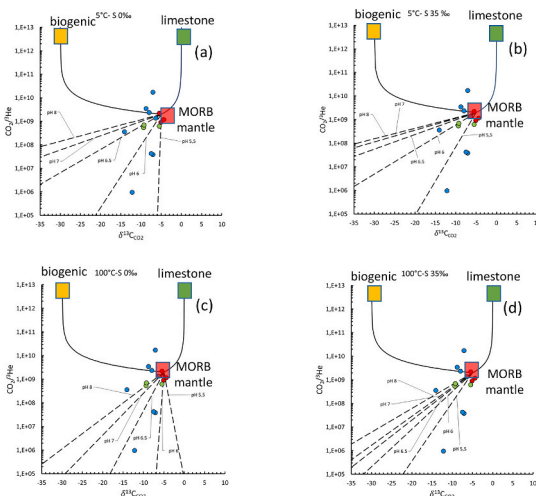
δ<sup>13</sup>CO<sub>2</sub> shows a wide range of values between −4.4‰ and −14.1‰ (Table 2, Fig. 3). Like with He, the C-isotope composition of the gases includes MORB-like values (−5 ± 1‰; e.g. Pineau and Javoy, 1983; Marty and Zimmermann, 1999) but extends to lower δ<sup>13</sup>CO<sub>2</sub> values. This could reflect the contribution of <sup>13</sup>C-depleted components in the mantle source, akin to the recycling of subducted organic C (e.g. Hu et al., 2023; Aitchison et al., 2025). Alternatively, magma degassing or water–gas interactions in the subsurface could modify a once MORB-like <sup>13</sup>C/<sup>12</sup>C ratio of degassed CO<sub>2</sub> (e.g. Deines, 2002; Aubaud, 2012; Paonita

**Table 2**  
Chemical and isotopic data (n.a. = not available; b.d.l. = below detection limit).

| Point ID                | <sup>4</sup> He | <sup>20</sup> Ne | <sup>40</sup> Ar | H <sub>2</sub> | O <sub>2</sub> | N <sub>2</sub> | CH <sub>4</sub> | CO <sub>2</sub> | δ <sup>13</sup> CO <sub>2</sub> | R/Ra | Err +/- | R/Ra <sub>c</sub> | <sup>40</sup> Ar/ <sup>36</sup> Ar | Err +/- | δ <sup>15</sup> N | D <sub>30</sub> | 2 se Δ <sub>30</sub> |
|-------------------------|-----------------|------------------|------------------|----------------|----------------|----------------|-----------------|-----------------|---------------------------------|------|---------|-------------------|------------------------------------|---------|-------------------|-----------------|----------------------|
| <b>Fumarole Beach</b>   |                 |                  |                  |                |                |                |                 |                 |                                 |      |         |                   |                                    |         |                   |                 |                      |
| DI-02                   | 43.80           | 0.06             | 73.46            | 2028           | 0.09           | 0.97           | 1.48            | 99.49           | −5.5                            | 7.31 | 0.05    | 7.31              | 308.25                             | 0.45    | −1.7              | 18.6            | 0.3                  |
| DI-03                   | 103.43          | 0.34             | 721.43           | 5              | 0.50           | 3.30           | 274             | 96.47           | −5.1                            | 7.25 | 0.05    | 7.26              | 298.25                             | 0.09    | 0.5               | 12.0            | 0.3                  |
| DI-10                   | 81.58           | 0.24             | 381.99           | 4426           | 0.25           | 2.46           | 218             | 96.86           | −4.4                            | 7.18 | 0.05    | 7.19              | 300.80                             | 0.11    | −0.2              | 13.9            | 0.4                  |
| <b>Gas Bubbling</b>     |                 |                  |                  |                |                |                |                 |                 |                                 |      |         |                   |                                    |         |                   |                 |                      |
| DI-05                   | 69.85           | 0.40             | 617.22           | 66             | 0.11           | 2.03           | 132             | 97.32           | −6.4                            | 7.31 | 0.05    | 7.32              | 297.11                             | 0.11    | n.a.              | n.a.            | n.a.                 |
| DI-04                   | 5.53            | 0.09             | 322.01           | b.d.l.         | 0.16           | 0.50           | 0.7             | 97.96           | −7.1                            | 7.28 | 0.06    | 7.31              | 296.28                             | 0.16    | −0.7              | 16.8            | 0.3                  |
| DI-01                   | 40.05           | 0.26             | 389.39           | b.d.l.         | 0.35           | 2.18           | 0.7             | 97.34           | −8                              | 7.33 | 0.05    | 7.34              | 297.51                             | 0.12    | 0.8               | 14.7            | 0.2                  |
| DI-14                   | 28.11           | 0.20             | 671.11           | b.d.l.         | 0.18           | 1.48           | 12              | 97.76           | −8.8                            | 7.12 | 0.05    | 7.13              | 301.74                             | 0.19    | 0.2               | 16.1            | 0.3                  |
| DI-17                   | 407.86          | 15.69            | 9473.21          | b.d.l.         | 2.00           | 96.30          | 0.4             | 0.39            | −12.2                           | 7.00 | 0.04    | 7.08              | 298.09                             | 0.08    | n.a.              | n.a.            | n.a.                 |
| DI-07                   | 40.94           | 14.56            | 9741.23          | b.d.l.         | 9.16           | 86.02          | 8               | 1.51            | −7.1                            | 6.21 | 0.05    | 6.87              | 296.52                             | 0.08    | −0.6              | 17.0            | 0.3                  |
| DI-06                   | 494.52          | 8.49             | 7572.13          | b.d.l.         | 0.31           | 76.00          | 4471            | 22.25           | −7.5                            | 7.49 | 0.05    | 7.53              | 296.31                             | 0.12    | n.a.              | n.a.            | n.a.                 |
| DI-09                   | 479.28          | 7.25             | 7981.30          | 5              | 0.24           | 74.51          | 4477            | 22.91           | n.a.                            | 7.50 | 0.05    | 7.53              | 296.86                             | 0.10    | 0.5               | 18.2            | 0.5                  |
| DI-11                   | 5.53            | 13.09            | 8667.24          | b.d.l.         | 19.41          | 77.08          | 4.3             | 0.91            | −14.1                           | 1.56 | 0.03    | 3.24              | 297.64                             | 0.10    | n.a.              | n.a.            | n.a.                 |
| <b>Fumaroles Flanks</b> |                 |                  |                  |                |                |                |                 |                 |                                 |      |         |                   |                                    |         |                   |                 |                      |
| DI-08                   | 31.65           | 12.39            | 7353.50          | 290            | 15.76          | 62.13          | 11              | 19.27           | −5.5                            | 6.25 | 0.06    | 7.00              | 296.45                             | 0.08    | −1.5              | 18.9            | 0.3                  |
| DI-12                   | 6.16            | 15.83            | 9125.36          | 518            | 18.75          | 77.53          | 31              | 2.46            | −9.4                            | 1.78 | 0.04    | 5.24              | 296.61                             | 0.14    | n.a.              | n.a.            | n.a.                 |
| DI-13                   | 8.05            | 16.74            | 9920.58          | 1826           | 18.08          | 74.80          | 73              | 5               | −9.3                            | 2.79 | 0.05    | 6.28              | 296.59                             | 0.08    | n.a.              | n.a.            | n.a.                 |
| DI-16                   | n.a.            | n.a.             | n.a.             | 34             | 20.11          | 76.87          | 0.4             | 0.74            | −14.1                           | n.a. | n.a.    | n.a.              | n.a.                               | n.a.    | n.a.              | n.a.            | n.a.                 |



**Fig. 2.** He isotopic ratios (as R/Ra) vs the  $^4\text{He}/^{20}\text{Ne}$  ratios in the analysed samples showing the gases emitted from the fumaroles far from the rim of the bay have the highest air-derived He contributions and the samples of the campaign 2023–24 show a mixing trend (dashed line) between air and a deep sources with an He isotopic signature of  $7.4 \pm 0.1$  Ra. All the error bars for the He isotopic signature of free gases are within the symbols. For comparison the He isotopic signature in minerals of the most representative activities of the volcano and in gas emissions collected in previous investigations (Kusakabe et al., 2009; Padrón et al., 2015; Álvarez-Valero et al., 2022). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Plots of carbon dioxide ( $\text{CO}_2/{}^3\text{He}$ ) versus the carbon-isotope composition of  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2}$ ). Dashed lines show the predicted model for Rayleigh-type gas dissolution at temperatures of 5°C and 100°C and salinities (S) of 0‰ and 35‰. The model curves (dashed lines) were obtained over a range of pH values for increasing extents of gas dissolution and calculated using the Rayleigh fractionation equation; see Supplementary materials and Randazzo et al. (2021, 2022) for more details. Solid lines show mixing trends between a mantle endmember ( $\text{CO}_2/{}^3\text{He} = 10^{13}$ ,  $\delta^{13}\text{C} = 0\text{‰}$ ), limestone ( $\text{CO}_2/{}^3\text{He} = 10^{13}$ ,  $\delta^{13}\text{C} = 0\text{‰}$ ), biogenic endmembers ( $\text{CO}_2/{}^3\text{He} = 1 \times 10^{13}$ ,  $\delta^{13}\text{C} = -26\text{‰}$ ) (Sano and Marty, 1995). The choice of any point (different from a mantle endmember) as the starting endmember resulting from the mixing between crustal (limestone plus biogenic) and the mantle one would lead to similar, but shifted, dissolution lines.

et al., 2012; Paonita et al., 2021; Randazzo et al., 2021; Buttitta et al.,

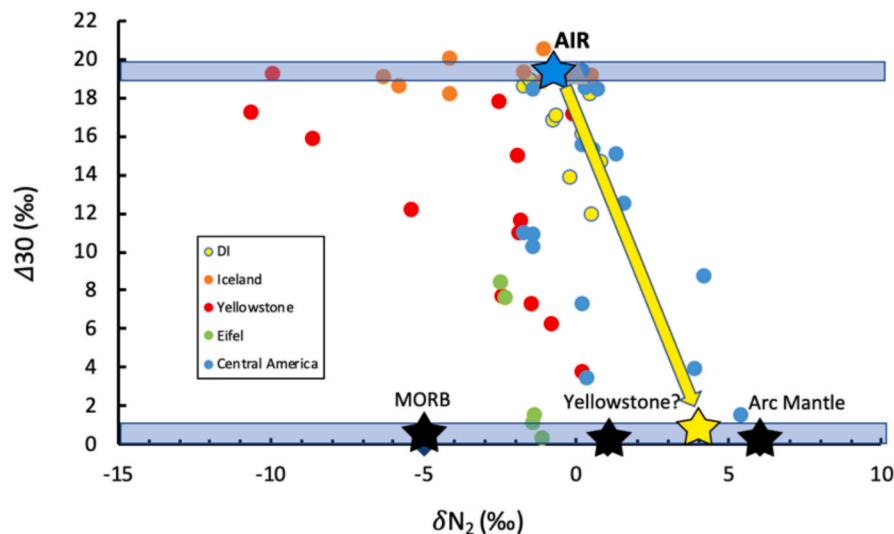
2023). Comparing  $\text{CO}_2/{}^3\text{He}$  ratios with  $\delta^{13}\text{C}_{\text{CO}_2}$  values is useful for evaluating the potential influences of mixing and isotopic fractionation (e.g. Randazzo et al., 2021; Buttitta et al., 2023). We take  ${}^3\text{He}$  to be mainly of primordial origin, as opposed to subducted species in the Earth's mantle, with a MORB-like  $\text{CO}_2/{}^3\text{He}$  ratio of  $2\text{--}3 \times 10^9$  (Marty et al., 2020 and references therein). An elevated  $\text{CO}_2/{}^3\text{He}$  ratio would be indicative of the addition of non-MORB-like  $\text{CO}_2$  in gas mixtures, possibly from crustal components in mantle sources (e.g. Sano and Marty, 1995). Instead, the  $\text{CO}_2/{}^3\text{He}$  ratios were low in most of the samples studied here (Fig. 3, Fig. S2), being down to  $\sim 3$  orders of magnitude lower than the mantle component and 6 orders of magnitude lower than crustal components (Fig. 3, Fig. S2). This excludes any mixing scenario involving the addition of crustal C to a MORB-type mantle. In addition, the  $\text{CO}_2/{}^3\text{He}$  ratios are extremely variable, even for those collected from nearby sampling sites, and these ratios combined with  $\delta^{13}\text{C}_{\text{CO}_2}$  values are not aligned with the magma degassing trends (Fig. S2), indicating that this was not the main process influencing these data. We therefore explain the data by considering a volcanic gas moving through a water column in the subsurface, and modelling this as a partial dissolution of gases in water (e.g. Gilfillan et al., 2009). The volcanic gas tends to be stripped of its  $\text{CO}_2$ —owing to the solubility of  $\text{CO}_2$  in water—as it undergoes  ${}^{13}\text{C}/{}^{12}\text{C}$  isotope fractionation (more details about the calculations are provided in the Supplementary materials). This results in both  $\delta^{13}\text{C}_{\text{CO}_2}$  values and  $\text{CO}_2/{}^3\text{He}$  ratios decreasing (e.g. Gilfillan et al., 2009; Randazzo et al., 2021). The water–gas interactions result in the  $\text{CO}_2/{}^3\text{He}$  ratios progressive decreasing in the residual gases (Fig. 3, Fig. S2) and in a large variability in the  $\delta^{13}\text{C}_{\text{CO}_2}$  values as a function of (i) the water temperature (up to 100°C, representative of the  $T_{\text{MAX}}$  at the DI fumaroles; Supplementary materials), (ii) salinity (S) ranging from 0‰ in meteoric waters to 35‰ in seawater, and (iii) pH ranging from 5 to 8 (Fig. 3, Fig. S2).

Our model combining partial gas dissolution ( $>90\%$ ) fits well with the data of the bubbling gases and those from the fumarole areas (Fig. 3, Fig. S2). This indicates that all gases outgassing at DI are coming from the same mantle source, with the C-isotope composition and  $\text{CO}_2/{}^3\text{He}$  ratio matching a MORB-type mantle; the data support MORB-like signatures modified mainly by water–gas processes in the subsurface (Fig. 3, Fig. S2).

### 3.2. Nitrogen isotopes: A N-bearing mantle

Nitrogen concentrations in DI samples of 60% or higher are observed in the fumarole areas sampled subaerially, away from the rim of Port Foster bay (Table 2). The N could be fully air-derived or may include a magmatic contribution. The  $\delta^{15}\text{N}$  values of the DI gases are between  $-1.7\text{‰}$  and  $0.8\text{‰}$ , which is similar to the range for air. The  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratios are lower than 310, also similar to the values for air (298.6; Lee et al., 2006). The isotope data could indicate both Ar and  $\text{N}_2$  being sourced from air, but the  ${}^{15}\text{N}/{}^{14}\text{N}$  measurements show otherwise. Those clumping measurements may unambiguously quantify air contributions in samples where the provenance of N is unknown. At temperatures  $> 200^\circ\text{C}$ , equilibrium among  $\text{N}_2$  isotopologues results in  $\Delta_{30}$  values of  $< 0.5\text{‰}$ , which is above a purely stochastic reference (Yeung et al., 2017). This means that any volcanic or crustal N—either mantle-derived and inherited from the slab, or with contributions from shallow crustal reservoirs—has a  $\Delta_{30}$  value of  $\sim 0\text{‰}$  (Labidi et al., 2020). In contrast, air has a pronounced disequilibrium between isotopologues, leading to an atmospheric  $\Delta_{30}$  value of  $19.1 \pm 0.3$  (2 $\sigma$ ) (Yeung et al., 2017). This means measuring the  $\Delta_{30}$  values of a natural sample can easily provide an unambiguous quantification of high-temperature  $\text{N}_2$ , versus air-derived components.

While  $\delta^{15}\text{N}$  data are dominated by values similar to those in air, this is not the case for  $\Delta_{30}$ . Those data are variable, ranging from 12‰ to 18‰ (Fig. 4, Table 2), which implies that while air is dominated by  $\text{N}_2$  in those samples, a high-temperature component with a  $\Delta_{30}$  value of 0‰ contributes to the mixed gases, with up to 40% of N. The data show that



**Fig. 4.** Nitrogen gas-isotope composition of volcanic discharges at DI. The differing  $\Delta_{30}$  values indicate that our samples included variable amounts of atmospheric N. Gases collected at Fumarole Bay have the lowest  $\Delta_{30}$  values, down to  $12.0 \pm 0.3\text{‰}$ , indicating they have the smallest air-derived  $\text{N}_2$  contributions. Note that the same gases have  $\text{CO}_2/{}^3\text{He}$  ratios within the range of MORB-like values (Fig. 3). Variable  $\delta^{15}\text{N}$  values are also observed, between  $-1.7\text{‰}$  and  $0.8\text{‰}$ . N-isotope data of volcanic discharges from Iceland, Eifel, Yellowstone, and Central America are from Labidi et al. (2020, 2021). According to previous approaches using of the same diagram (Labidi et al., 2020, 2021; Labidi and Young, 2022), the high-temperature component in the DI mantle is identified by extrapolating the isotope trend between  $\delta^{15}\text{N}$  and  $\Delta_{30}$  values. At  $\Delta_{30} \sim 0\text{‰}$ , the  $\delta^{15}\text{N}$  value of the genuine high-temperature component at DI is  $2\text{--}3\text{‰}$  (yellow star). The black stars are from Labidi et al. (2020) and Labidi and Young (2022) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Source .

the samples with the highest N contents ( $>60\%$ ) are dominated by air-derived N, thus reflecting the circulation of the air component in the subsurface. In contrast, the samples with the lowest N concentrations correspond to the lowest  $\Delta_{30}$ , suggesting the influence of high-temperature N. The diagram of  $\delta^{15}\text{N}$  versus  $\Delta_{30}$  in Fig. 4 displays a trend allowing extrapolation to a component with  $\Delta_{30} \sim 0\text{‰}$ . Based on the data, the high-temperature N has a  $\delta^{15}\text{N}$  value between  $2\text{‰}$  and  $3\text{‰}$  (Fig. 4), which is close to typical arc compositions with  $\delta^{15}\text{N}$  at  $0\text{--}5\text{‰}$  (Labidi et al., 2021), and different from the MORB endmember with a value of  $-5\text{‰}$ . Given that mantle  ${}^3\text{He}$  is not recycled in origin (Porcelli et al., 2002),  $\text{N}_2/{}^3\text{He}$  ratios are expected to increase due to the addition of N in enriched mantle sources. The plot of  $\Delta_{30}$  versus  $\text{N}_2/{}^3\text{He}$  in Fig. S3 shows binary mixing relationships that yield the composition of the high-temperature component (Labidi and Young, 2022). The high-temperature component was required to have an  $\text{N}_2/{}^3\text{He}$  ratio of  $7.0 \times 10^6$  to  $1.6 \times 10^7$  to fit the data in Fig. S3, which is about three times higher than estimates for the MORB-type mantle (Javoy and Pineau, 1991; Marty and Zimmermann, 1999; Labidi, 2022). This requires that the high-temperature volatiles derive from a mantle source that underwent N addition relative to the average MORB-type mantle.

### 3.3. Recycled component with a low C/N ratio below northern Antarctica

Elevated  $\delta^{15}\text{N}$  and  $\text{N}_2/{}^3\text{He}$  are consistent with the contribution of recycled N in the mantle source of DI, but C does not follow the same pattern of being recycled; instead, the C-He systematics indicate a strictly unmodified MORB-like signature (Fig. 3, Fig. S2). A subduction-related processes must have increased the N content of the mantle source below DI, but with this having a negligible or only minor effect on the C budget. Inevitably, the recycling of a slab-derived component with an unusually low C/N ratio is required to explain the data.

The C/N ratio for mantle value is roughly in the range 250–500 in the MORB mantle reservoirs (Marty et al., 2020). Furthermore, in the MORB mantle, evidence for recycled components with C/N ratios much higher than Earth's mantle, likely higher than 3,000, have been shown (Marty and Zimmermann, 1999). This is in stark contrast with our observations at the DI volcano, where the mantle source seems to show a contribution

of a subducted component with anomalously low C/N ratio. Sediments found immediately across the subduction trench on the *Phoenix* Plate (sediment core GC05-DP02, IODP; Kim et al., 2023) are a good candidate for understanding this observation, having an average C/N ratio of  $\sim 6$  (Kim et al., 2023) and a bulk N content of  $\sim 300$  ppm. This differs markedly from average MORB-type sources, which typically have an N content of  $\sim 0.3$  ppm and a C/N ratio of up to 500 (Marty et al., 2020 and references therein). Little contribution from those sediments would have a tremendous effect on the N budget of the mantle source without affecting C. Assuming they were unmodified by subduction, only 0.3% of those sediments with a low C/N ratio in a 99.7% MORB-type mantle would explain the MORB-like  $\text{CO}_2/{}^3\text{He}$  and the elevated  $\text{N}_2/{}^3\text{He}$  ratio observed here. It is however unlikely that pristine subducted sediment would be added to the mantle source, since devolatilization, fluid losses and sediment melting are to be expected in a subduction system. Devolatilization in forearc and arc settings would generate fluids containing N at concentrations that vary with the exact pressure, temperature, and oxidation conditions of slab devolatilization (Jackson et al., 2021). Most dehydration scenarios investigated in by Jackson and colleagues suggest that N would be highly incompatible during fluid losses; that is, it would be near-quantitatively partitioned in fluids during slab devolatilization. Depending on the C behavior during devolatilization, the C/N ratio of the fluids would be similar to or even lower than that of the protolith. In other words, subduction fluids originating from sediments produced in marine ecosystems observed near the Antarctica trench would almost certainly have a C/N ratio of about 6 (Tanioka et al., 2022; Kim et al., 2023), which would readily explain the peculiar enrichment of N measured at DI.

### 3.4. Mantle response to local biogeochemistry of the shallow marine system

While oceanic sediments represent a substantial C source in subduction zones that deliver both inorganic and organic components into the subduction system (e.g. Kurokawa et al., 2022; Hu et al., 2023; Aitchison et al., 2025), recent studies based on the C-He systematics of volcanic fluids from the Aleutian-Alaska Arc (i.e. high latitudes in the

North Pacific) have indicated that less C returns to the deep mantle than previously thought. This also implies that subducting organic C is not a reliable atmospheric C sink over subduction timescales (Lopez et al., 2023). Our unique He-N-C isotope database from mantle-derived volatiles in a polar region reveals that biologically derived N dominated C in the recycling of these components within the high-latitude subduction system allowing to an N-rich mantle. This may reflect a latitude effect in sediment formation and successively of their influence on the chemistry of the fluids recycled in the Earth's interior via subduction. Shallow marine systems at high latitudes have elevated C/N ratios, reflecting variabilities in the temperature and nutrient availability that control the latitudinal variability in carbon: nitrogen: phosphorous (C:N:P) stoichiometry. Genomic data have revealed that biological nutrient stress resulting from the rate of nutrient supply and the balance of the different components (e.g. N versus P) are predictive of hemispheric and regional differences in this stoichiometry (Tanioka et al., 2022). Therefore, the sediments deposited in high-latitude regions such as those near Antarctica do not respond to the same biogeochemistry as at low latitudes, and it should reflect the low C/N ratios in the correspondent marine ecosystems (Tanioka et al., 2022). Those have a distinct impact on mantle with latitude, once recycled, to explain the low C/N in the mantle below DI. This illustrates a unique link between surface biogeochemistry and mantle composition that occurs via plate tectonics.

This study supports the observed latitude dependence of the redox state of the arc mantle because of latitudinal variations in the primary production of phytoplankton and the related characteristics of the subducted sediment (Hu et al., 2024). Therefore, the subduction that occurs at different latitudes indicates the impact of surface processes on the interior composition of the Earth.

It should be noted that the high-CO<sub>2</sub> degassing volcanoes are clustered in tropical to subtropical regions (Aiuppa et al., 2019). In contrast, lower volcanic CO<sub>2</sub> fluxes are observed in higher latitude regions (e.g. Aleutian-Kamchatka-Kuriles region) where no or low-carbonate-containing lithologies are recycled in trenches (Aiuppa et al., 2019). The C-poor arc volcanoes are thought to be sourced by a mantle wedge source contaminated by C-poor slab fluids, suggesting that more-efficient recycling of C still occurs via subduction at low latitudes.

#### 4. Conclusion

Our work highlights the role of shallow ecosystems in creating some implications on Earth's mantle modern heterogeneity. It also emphasizes a previously unrecognized aspect of the global variability of C and N with latitude in marine ecosystems, underscoring that the geographical location of subduction zones plays a crucial role in how C and N are recycled into the Earth's mantle so as to contribute to the mantle heterogeneity. Both whether subduction occurs and also where it occurs dictate the efficiency and characteristics of this process in the Earth's deep reservoirs.

The present findings will lead to new perspectives into how to assess Earth's volatiles budget and understand the long-term impact of plate tectonics on the redistribution of volatiles within Earth's interior that consequently shapes the mantle heterogeneity.

#### CRedit authorship contribution statement

**Antonio Caracausi:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Methodology, Data acquisition, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Antonio Polo-Sánchez:** Writing – review & editing, Writing – original draft, Samples collection, Investigation, Data curation, Conceptualization, Visualization, Funding acquisition. **Antonio M. Álvarez-Valero:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Investigation, Funding acquisition, Data curation, Conceptualization. **Jabrane Labidi:** Writing – review & editing, Writing – original draft,

Conceptualization, Methodology, Data acquisition, Formal analysis, Data curation. **Edward D. Young:** Writing – review & editing, Methodology, Data acquisition. **Hirochika Sumino:** Writing – review & editing, Conceptualization. **Conxita Àvila:** Writing – review & editing, Samples collection, Methodology, Investigation. **Dario Buttitta:** Writing – review & editing, Writing – original draft, Visualization, Formal analysis, Data curation. **Adelina Geyer:** Writing – review & editing, Conceptualization. **Paolo Randazzo:** Writing – review & editing, Writing – original draft, Visualization, Formal analysis, Data curation.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This research was supported by the Spanish project EruptING (PID2021-127189OB-I00) MCIN/AEI/<https://doi.org/10.13039/501100011033> to A.M.A-V. Antonio Caracausi appreciates support by the “Ramón y Cajal” research program (RYC2021-033270-I; MCIN/AEI/10.13039/501100011033 - EU“NextGenerationEU/PRTR”). Antonio Polo-Sánchez acknowledges his PhD grant ‘Programa Propio III USAL 2021 co-funded with Banco de Santander’ and his joint COMNAP-IAATO Antarctic Fellowship 2022. We especially thank all the military staff of the Spanish Antarctic Base “Gabriel de Castilla” for their constant help and logistic support, without which this research would not have been possible. All the equipments for the gas sampling were provided by INGV Palermo. The analysis were carried out at INGV (Palermo) and UCLA. We are grateful to M. Tantiño, Y Oliveri and F. Salerno for the measurements in the laboratories of INGV of the gas composition, isotope composition of light noble gases and stable isotopes respectively. We are grateful to Sami Mikhail and an anonymous reviewer that contributed to improve the final manuscript. Discussions with Marie Edmonds provided thoughtful and helpful comments to construct our manuscript. The English Science Editing company provided language-editing support in the production of this manuscript.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gr.2026.03.018>.

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