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A carbon-rich lithospheric mantle as a source for the large CO_2 emissions of Etna volcano (Italy)

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ABSTRACT

Etna volcano in Italy releases an exceptional amount of CO_2 (9083 t/day) and contributes to 10% of global volcanic emission. The reasons for its extreme CO_2 degassing are not yet understood. Using high-precision high field strength element (HFSE) concentrations in magmas from volcanoes in southern Italy, we show that the high Nb/Ta of Etna (up to 26) reveals a mantle source affected by carbonatite metasomatism, which is likely responsible for the large CO_2 fluxes. As observed at Etna, carbon-rich mantle domains influence CO_2 degassing also outside of continental rifts and therefore play a fundamental role in explaining volcanic CO_2 fluxes in different geodynamic settings. Collectively, our study demonstrates that HFSE ratios in magmatic rocks are viable tracers for volcanic carbon degassing that can be used to study present-day settings and, possibly, past emissions.

INTRODUCTION

Over geological time, volcanism represents the main input for atmospheric CO_2. The highly heterogeneous CO_2 flux of present-day volcanoes testifies to the presence of multiple sources, which must be identified to infer long-term variations in CO_2 fluxes. The subcontinental lithospheric mantle (SCLM) is an important geochemical reservoir that can sequester large amounts of CO_2 due to the infiltration of fluids and melts during carbonatite-like metasomatism. Carbon-rich domains within the SCLM can release CO_2 along with other volatiles (i.e., H_2O, S, Cl, and Fl), when tapped by volcanism. This process is well known in continental rift settings and is responsible for the significant CO_2 emission in the East African Rift, which contributes ~30% of global volcanic emissions (Foley and Fischer, 2017; Aiuppa et al., 2019; Muirhead et al., 2020). However, outside of rift systems, the role of the SCLM in Earth's CO_2 cycle is poorly known.

After the Nyiragongo-Nyamuragira volcanic system (East African Rift), the largest emitters of volcanic CO_2 are Popocatepétl volcano in Mexico (9345 t/day) and Etna volcano in Italy (9083 t/day). As such, Etna contributes to 10% of global volcanic emissions (Aiuppa et al., 2019). The volume of CO_2 released by Etna largely exceeds the amount that can be dissolved in the erupted magma (D'Alessandro et al., 1997; Ferlito, 2018; Aiuppa et al., 2019), and it is three times that of Kīlauea (Hawaii), despite emplacing just a quarter of the magma volume.

Etna is located on the edge of a subduction zone and its volcanism is related to mantle upwelling due to the rollback of the Ionian slab (Gvirtzman and Nur, 1999). As such, subduction-derived fluids or assimilation of Mesozoic carbonates have been proposed as a source of the emitted CO_2 (e.g., Frezzotti et al., 2009; Heap et al., 2013). Yet, the magmas of Etna show an intraplate affinity with a limited influence from the Ionian subduction (Schiano et al., 2001, Tonarini et al., 2001), and there is no evidence of carbonate assimilation (Tonarini et al., 2001). Thus, the excessive degassing of CO_2 remains enigmatic and possibly requires a deep source (D'Alessandro et al., 1997; Ferlito, 2018). Because Etna is located between oceanic and continental lithosphere, it is plausible that carbon-rich SCLM metasomatism influences the CO_2 degassing of Etna. To evaluate this possibility, we report high-precision concentrations of high field strength elements (HFSE) that have been demonstrated to be sensitive to carbonatite metasomatism (e.g., Green, 1995; Pfänder et al., 2012). Magmas from Etna were analyzed along with samples from neighboring volcanoes from different geodynamic settings, namely (1) Stromboli (Tommasini et al., 2007), which is characterized by a clear subduction signature; (2) Pantelleria (Avanzinelli et al., 2014), with pure asthenospheric affinity (i.e., no SCLM contribution); and (3) Monte Vulture (Avanzinelli et al., 2008), a hybrid volcano emplaced on a geodynamic setting similar to that of Etna.

A HIGH Nb/Ta COMPONENT FOR ETNA AND MONTE VULTURE

Isotope dilution HFSE data along with radiogenic isotope data and trace element content are given in the Supplemental Material[1]. The most striking feature of Etna lavas is their high Nb/Ta ratio (up to 26), which is not observed in mid-oceanic ridge basalt (MORB) and ocean-island basalt (OIB) (average of 15.9 ± 0.6; Pfänder et al., 2007). Other volcanoes of the region, such as Pantelleria and Stromboli, display lower Nb/Ta values (17–20), while Monte Vulture also shows high Nb/Ta (up to 22). The geochemical twins Nb and Ta are incompatible elements that show little or no relative fractionation during magmatic processes but are sensitive to subduction processes and carbonatite metasomatism (e.g., Green, 1995). As such, high Nb/Ta may derive from fluids that are released by the Ionian

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[1]Supplemental Material. Figures S1 and S2, Tables S1 and S2, analytical methods, and references for the literature data reported in the figures. Please visit https://doi.org/10.1130/GEOL.S.17265194 to access the supplemental material, and contact editing@geosociety.org with any questions.

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subduction, where residual Ti-rich phases like rutile can cause Nb-Ta fractionation (e.g., Green, 1995; Münker et al., 2004). On the other hand, carbonatite-like metasomatism of the SCLM can result in magmas with high Nb/Ta (Pfänder et al., 2012) as evidenced by the extreme Nb/Ta observed in carbonatites (up to 1000; Hoernle et al., 2002; Bizimis et al., 2003).

The OIB-like Nb/Ta of Pantelleria indicates that the high Nb/Ta is not a common feature of the regional asthenosphere, but affects only Etna and Monte Vulture. These two volcanoes share a peculiar tectonic setting, being on the opposite edges of the subducting Ionian slab. Monte Vulture shows a geochemical affinity between intraplate and arc magmatism (Avanzinelli et al., 2008; Caracausi et al., 2013). Etna has a geochemical signature similar to OIB (Viccaro and Zuccarello, 2017; Casetta et al., 2019), although influence by the Ionian subduction has been proposed for the younger alkaline products (Schiano et al., 2001; Tonarini et al., 2001). Etna has Ba/Ce and Th/La ratios similar to those of Pantelleria, OIBs, and MORBs but significantly lower than arc magmas such as Stromboli (Fig. 1). When considered together, Etna, Monte Vulture, and Stromboli display a broadly negative correlation in Ba/Ce and Th/La versus Nb/Ta space (Fig. 1), which argues against a subduction influence on the Nb/Ta ratios. At Etna, such a possibility is also excluded because the highest Nb/Ta values are observed in tholeiites, which are the oldest products of the volcano and devoid of subduction influence (Schiano et al., 2001; Tonarini et al., 2001). Because tholeiites require a larger degree of partial melting than alkali basalts (as also evident from Ba/Ce and Th/La; Fig. 1), a role of residual phases in generating the anomalous Nb/Ta is also unlikely. In any case, olivine, pyroxene, amphibole, garnet, and phlogopite (i.e., the mineral phases expected in the mantle source of Etna; Viccaro and Zuccarello, 2017; Casetta et al., 2019), show negligible or similar partition coefficients for Nb and Ta (Adam and Green, 2006), which ultimately eliminates the possibility that partial melting could significantly fractionate Nb from Ta.

Interaction with the lithospheric mantle can strongly influence the composition of intraplate magmas (Halliday et al., 1995; Pfänder et al., 2012). The possible role of the SCLM at Etna and Monte Vulture is supported by the negative correlation between Nb/Ta and K/K*, which is an index for assessing lithospheric mantle contributions (Halliday et al., 1995). Relative to MORBs and OIBs, carbonatites display remarkably higher Nb/Ta and lower Zr/Nb (Fig. 2). Etna and Monte Vulture are clearly distinguished from OIBs and MORBs since both ratios point toward the field of carbonatites. The lowest Zr/Nb recorded in tholeiites from Etna is at odds with their expected high degree of partial melting but consistent with a larger contribution of a carbonatite-like component. Therefore, the high Nb/Ta is best explained by carbonatite metasomatism, which is a widespread process in the lithospheric mantle (Pfänder et al., 2012; Foley and Fischer, 2017). The SCLM carbonatite-like metasomatism is also consistent with other geochemical features of Etna, such as the strong depletion in Rb (e.g., low Rb/Th; Fig. S1 in the Supplemental Material). Carbonatite melts are characterized by low Rb (and Cs) contents, with respect to silicate melts, where Rb is one of the most incompatible elements.

The high CO_2 degassing of Etna could derive from shallow level assimilation of crustal carbonates (e.g., Frezzotti et al., 2009; Heap et al., 2013), as suggested for other volcanoes such as Popocatépetl and Mount Merapi (Indonesia) (Schaaf et al., 2005; Deegan et al., 2010). These two volcanoes show clear evidence of carbonate assimilation such as carbonate xenoliths and shifts toward radiogenic $^{87}Sr/^{86}Sr$ (Schaaf et al., 2005; Deegan et al., 2010). At Etna, $^{87}Sr/^{86}Sr$ is significantly lower (0.7029–0.7036) than local Mesozoic carbonates (~0.707), and it correlates negatively with Nb/Ta (Fig. S2). Therefore, assimilation of crustal carbonate cannot explain the high Nb/Ta of Etna or, in general, its magma composition, as previously demonstrated by Tonarini et al. (2001). Thermally induced decarbonation of Mesozoic limestone may contribute to the CO_2 emission of Etna (Heap et al., 2013), but it would have no effect on the magma geochemistry. However, a major role for such a process was discarded on the basis of carbon and sulfur isotopes (D'Alessandro et al., 1997). Unlike crustal carbonates, mantle carbonatites are characterized by unradiogenic Sr (Hoernle et al., 2002; Bizimis et al., 2003). Thus, the high Nb/Ta (and low Zr/Nb and Rb/Th) of Etna and Monte Vulture reveals carbonatite-like metasomatism in the SCLM beneath southern Italy. Because mantle domains affected by carbonatite-like metasomatism can contain carbon on the order of few weight percent (Foley and Fischer, 2017), the SCLM represents a viable source for the anomalously high CO_2 fluxes recorded at Etna.

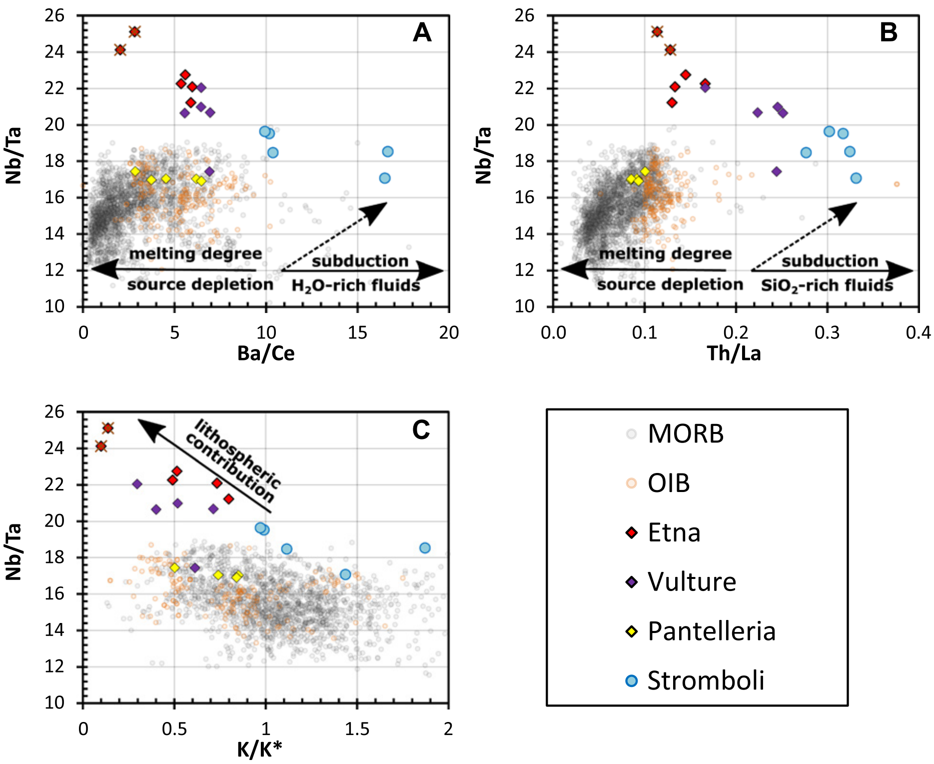

Figure 1. Effects of partial melting, subduction processes, and lithospheric contribution on Nb/Ta ratios. (A,B) Etna volcano and Monte Vulture (Italy) have Ba/Ce and Th/La values similar to those of ocean island basalts (OIBs) but higher Nb/Ta. Etna tholeiites (crossed symbols) show the highest Nb/Ta along with the lowest Ba/Ce and Th/La, which attests to no influence of the subduction, and a high degree of partial melting. (C) The negative correlation between Nb/Ta and K/K* (an index for assessing lithospheric mantle contributions) at Etna and Monte Vulture suggests an influence of the lithospheric mantle. K* is calculated from the geometrical mean of Nb and U concentrations normalized to the values of the primitive mantle. References for mid-oceanic ridge basalt (MORB) and OIB values are reported in the Supplemental Material (see footnote 1).

A CARBON-RICH SCLM BENEATH ETNA

The carbon content of the SCLM can increase due to carbonatite-like metasomatism associated with the infiltration of deep melts that are possibly related to mantle plumes or paleosubduction (e.g., Aulbach et al., 2017; Foley

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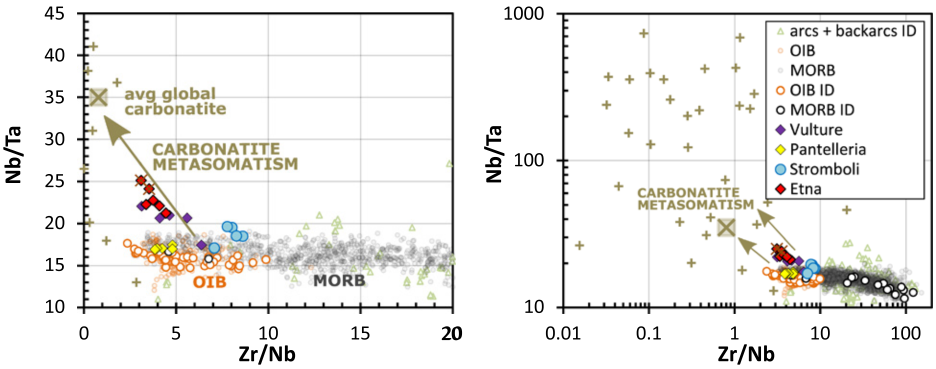

Figure 2. Evidence for a carbonatitic component in Etna volcano and Monte Vulture (Italy) from the high field strength element (HFSE) systematic. In Nb/Ta versus Zr/Nb space, Etna and Monte Vulture plot between the fields of ocean island basalt (OIB), mid-oceanic ridge basalt (MORB), and carbonatites, which demonstrates the presence of a carbonatite-like component, especially in Etna tholeiites (crossed symbols). Open symbols are isotope dilution (ID) literature data. References for MORB, OIB, arcs, and carbonatite are reported in the Supplemental Material (see footnote 1).

and Fischer, 2017). Carbonatite-like metasomatism in the SCLM has been suggested for the neighboring Hyblean plateau (Trua et al., 1998; Beccaluva et al., 1998) (a few tens of kilometers south of Etna), which taps a mantle source similar to that of Etna (Viccaro and Zuccarello, 2017; Casetta et al., 2019). Mantle xenoliths of the Hyblean plateau have $^3He/^4He$ ratios similar to those of Etna, which suggests a common origin of volatile elements (Frezzotti et al., 2009), and show evidence of carbonatite-like metasomatism as abundant CO_2 fluid inclusions (Sapienza and Scribano, 2000; Sapienza et al., 2005). Strikingly, magmas from the Hyblean plateau also have high Nb/Ta (Trua et al., 1998), which further stresses the connection between high Nb/Ta and carbonatite-like metasomatism. Notably, carbonatite metasomatism was also observed in mantle xenoliths from Vulture (Rosatelli et al., 2007)

Beyond their extreme Nb/Ta ratio, magmas from Etna and Monte Vulture display a peculiar tungsten signature, with W/U and W/Th lower than that of OIBs and MORBs (Fig. 3). As for Nb/Ta, Pantelleria and Stromboli have W/U and W/Th similar to typical mantle values (Fig. 3), which excludes fractionation of W from U and Th during mantle melting or subduction. The behavior of W during carbonatite metasomatism is unknown, but it is possible that the low W/U and W/Th of Etna originated in the SCLM. Indeed, Etna tholeiites have the lowest W/U and the highest Nb/Ta (Fig. 3B).

Fonseca et al. (2014) showed that a reduced mantle (fayalite-magnetite-quartz [FMQ] <-2) can contain higher amounts of W^{4+}, which is significantly more compatible than W^{6+}. Although carbonatites are relatively oxidized melts, most of the carbon in the SCLM is thought to be stored in reduced minerals, which include diamonds (Foley and Fischer, 2017). Therefore, reduced, carbon-rich SCLM domains may partially retain W during partial melting, which would result in melts with low W/U and W/Th. Mantle xenoliths from the Hyblean plateau support low oxygen fugacity (f_{O2}) conditions in the SCLM of Etna, as they contain reduced carbon mostly in the form of hydrocarbons but also as nanodiamonds (Simakov et al., 2015).

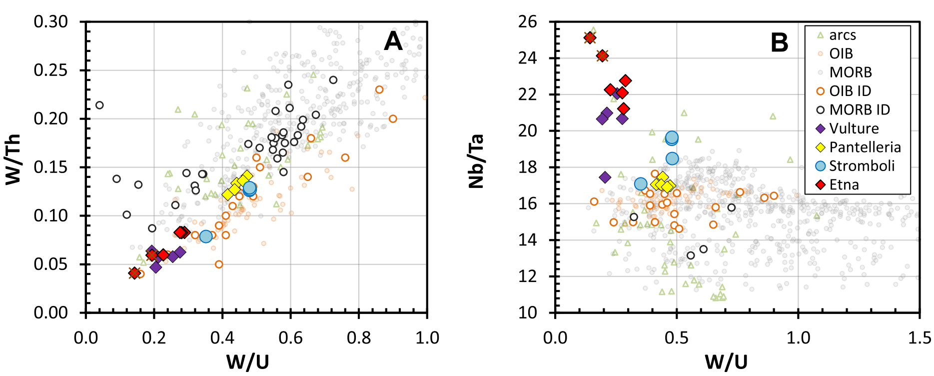

Figure 3. Tungsten signature of the studied magmas. (A) Etna and Monte Vulture (Italy) show W/U and W/Th ratios lower than those of Pantelleria, Stromboli, and most of the mid-oceanic ridge basalts (MORB), ocean island basalts (OIB), and arcs (see the Supplemental Material for references [see footnote 1]). (B) The lowest W/U ratios are observed in Etna tholeiites (crossed symbols), which have the highest Nb/Ta. Open symbols indicate literature data with Nb/Ta obtained by isotope dilution (ID).

GEODYNAMIC IMPLICATIONS

The previous observations can be combined with the peculiar tectonic setting of Etna and Monte Vulture to draw a coherent geodynamic model (Fig. 4). The roll back of the Ionian subducting plate (Gvirtzman and Nur, 1999) induces a corner flow of the mantle around the slab moving from the Hyblean domain toward Etna. This process may induce physical erosion of the bottom portion of the Hyblean continental lithosphere, which is the most susceptible to metasomatism (e.g., Foley and Fischer, 2017), bringing it beneath Etna. During partial melting, fragments of continental lithosphere, characterized by carbonatite-metasomatism and high Nb/Ta, can release large amounts of CO_2 and other volatiles (Fig. 4). A similar mechanism was proposed to explain the large CO_2 emission in the eastern rift of the East African Rift system, which involved advection of portions of the cratonic mantle roots toward thinner lithospheric domains (Muirhead et al., 2020).

Recently, Barreca et al. (2020) suggested the presence of a slab window in the subducting Ionian plate that allows portions of the shallow mantle wedge to flow in the opposite direction and toward Etna. Such a scenario could explain the presence of a slight subduction signature in the recent alkaline activity but not the high Nb/Ta of Etna magmas. In fact, the slab window opened after the tholeiitic activity of Etna (Barreca et al., 2020), which possibly explains the decreasing Nb/Ta in the younger alkaline basalts where the older carbonatite-like signature is partially overprinted. Accordingly, CO_2 and volatile fluxes at Etna during its tholeiitic phase were likely even higher than now, as suggested by the postulated increase in H_2O/CO_2 of the mantle source of Etna through time (Casetta et al., 2019). Indeed, relative to tholeiites, the more recent alkaline magmas are thought to derive from a mantle with higher H_2O/CO_2, as is expected from a contribution of water-rich subducting fluids that partially overprint the older carbonatite-like signature.

Monte Vulture also has elevated Nb/Ta (although not as high as at Etna) and has low Zr/Nb, W/Th, and W/U. Monte Vulture is located in a tectonic setting similar to that of Etna (on the eastern margin of the Ionian subduction; Fig. 4), and analogies linking the two volcanoes were suggested based on $CO_2/^3He$ ratios and He-Sr isotopes (Caracausi et al., 2013). Thus, mantle roots beneath the Apulia region may be also affected by carbonatite metasomatism.

CONCLUSIONS

HFSE concentrations reveal the involvement of a carbon-rich SCLM beneath Etna and Monte

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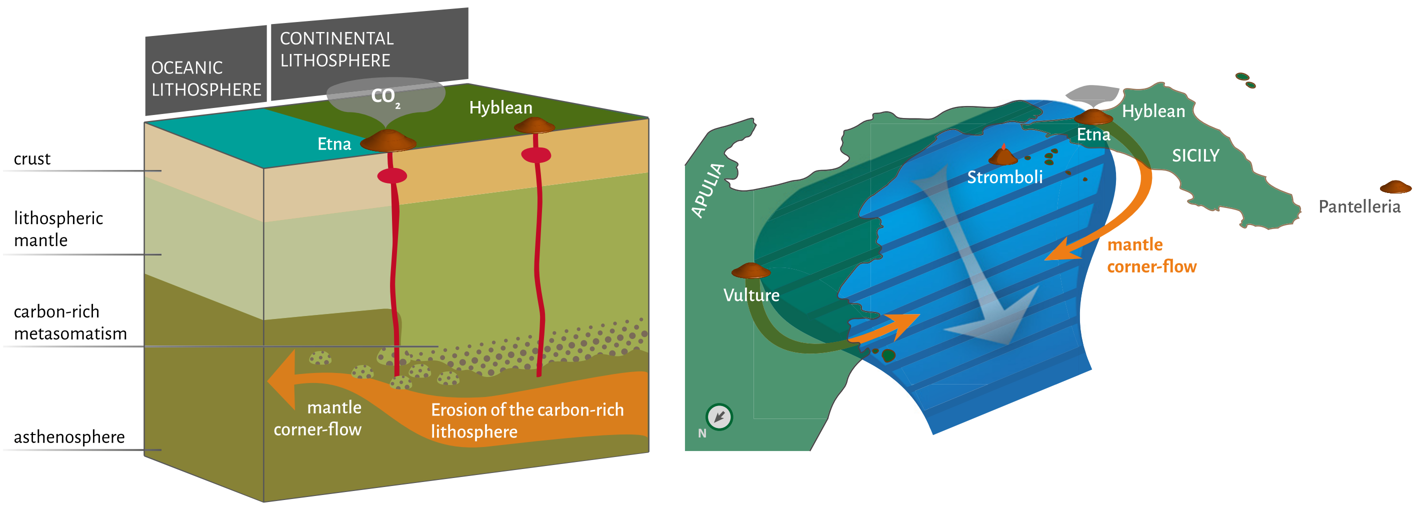

Figure 4. Proposed geodynamic model. Fragments of the bottom portions of the Hyblean (Italy) carbon-rich subcontinental lithospheric mantle are physically transported toward the region beneath Etna volcano through mantle corner flow, which is triggered by the roll back of the Ionian subduction plate (gray arrow). A symmetric mechanism is likely occurring on the other side of the Ionian plate beneath Monte Vulture.

Vulture that represents the most likely source for the large CO_2 degassed at Etna. As such, HFSE can be used to study the role of carbonatite metasomatism and its effect on CO_2 degassing. This approach could potentially be applied to every volcano, in particular when mantle xenoliths are not available. Moreover, it can be used to reveal the occurrence of carbonatite metasomatism in magmas that erupted in the past, which provides a unique tool for identifying eruptions that might have released large amounts of CO_2 into the atmosphere, contributing to major climatic changes on Earth.

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