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2021 Tajogaite eruption records infiltration of crustal fluids within the upper mantle beneath La Palma, Canary Islands

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The 2021 Tajogaite eruption at La Palma has represented a unique opportunity to investigate the characteristics of the mantle source feeding modern volcanism in the Canary Islands. With the aim of track the fingerprint of carbon in the local oceanic lithosphere-asthenosphere system, we report the isotopic composition of CO_2 ($\delta^{13}C$ values *versus* Vienna Pee Dee Belemnite) in olivine- and clinopyroxene-hosted fluid inclusions (FI) from the 2021 Tajogaite lavas and from lavas/ultramafic xenoliths (olivine-clinopyroxenites, clinopyroxenites, dunites and harzburgites) from the nearby 1677 San Antonio eruption cone/lavas, in an attempt to characterize the origin and evolution of carbon within the local mantle source. Our results indicate that the 2021 and 1677 lavas exhibit $\delta^{13}C$ values ranging from –4.94‰ to –2.71‰ and $CO_2/^3He$ ratios from 3.37 to 6.14×10^9. Ultramafic xenoliths fall in a comparable range of values despite showing higher CO_2 concentrations. Our $\delta^{13}C$ values fall within the range of carbon isotope results previously reported for the Dos Aguas cold spring located in the Taburiente Caldera (northern La Palma), suggesting an apparent carbon isotope homogeneity at the scale of the entire island. The (relatively narrow) $\delta^{13}C$ vs. $CO_2/^3He$ ratio range of La Palma samples is interpreted to reflect either i) variable extents of open-system degassing of a common mantle endmember having $\delta^{13}C$ of ~1.7‰, or ii) mixing between depleted mantle-like carbon ($-6‰ < \delta^{13}C < -4‰$) and crustal carbon ($\delta^{13}C = 0‰$) endmembers. Both models testify a crustal carbon component recycled in the local mantle. This component, also detected in mantle xenoliths from the neighboring island of El Hierro and the easternmost Lanzarote, indicates a regional characteristic of the mantle beneath the Canary Islands, interpreted as a result of infiltration of carbon-rich melts during past metasomatic events in the local mantle.

KEYWORDS

Canary Islands, La Palma, 2021 Tajogaite eruption, Ocean island volcanism, fluid inclusions, carbon isotopes, recycled carbon

1 Introduction

Volcanic eruptions open avenues to explore the composition and geodynamic evolution of the Earth's upper mantle. The eruptions of Ocean Island Basalt (OIB) volcanoes (such as in the Canary Islands, Samoa, Cook Islands, Azores, and Pitcairn; Anderson, 1912; Machado et al., 1962; Duncan et al., 1974; Rose and Koppers, 2019; Carracedo et al., 2022; exceptions are Hawaii, Iceland and the Piton de la Fournaise volcano at Reunion Islands), are especially attractive owing to their prevalent effusive nature and hence relatively easy access to eruption sites, relative to arc volcanoes which are characterized by more explosive activity. Moreover, OIB eruptions promote the investigation of deeper portions of the Earth's mantle when compared with Middle Oceanic Ridge Basalts, MORB (Herzberg et al., 2007; Hofmann, 2007; Dasgupta et al., 2010; Jackson, 2016), and eventually favors the exploration of the dynamics of mantle plumes (Dasgupta et al., 2010; Jackson, 2016).

The Canary Islands are among the most studied OIB localities. This is partly due to the relatively densely inhabited environment (and, hence, the considerable volcanic risk), and also the scientific controversies and debate within the Earth science community regarding the origin of volcanic activity in the archipelago, and the characteristics of the feeding mantle source (Carracedo et al., 1998; Anguita and Hernán, 2000; Troll and Carracedo, 2016). One of the biggest open questions regarding the origin of volcanism in the Canary Islands is how the local mantle source has evolved after the breakup of Pangea (Hoernle et al., 1995; Carracedo et al., 1998; Anguita and Hernán, 2000; Gurenko et al., 2009; Troll and Carracedo, 2016). It has been suggested that the mantle underneath the Canary Islands is compositionally heterogeneous due to the coexistence of different mantle components. The mantle end-members that have been proposed (Hoernle et al., 1991; Hoernle and Schmincke, 1993; Simonsen et al., 2000; Gurenko et al., 2006; 2009; 2010; Day et al., 2010; Day and Hilton, 2011; Sandoval-Velasquez et al., 2021b; Day and Hilton, 2021; Sandoval Velasquez et al., 2022a) to contribute (in variable proportions) to melting and volcanism include: i) an HIMU (high-μ = elevated $^{238}U/^{204}Pb$) mantle component; ii) a Depleted MORB mantle (DMM), where MORB stands for Middle Ocean Ridge Basalt; iii) an enriched mantle (EM) component; and iv) a high $^{3}He/^{4}He$ ratio (> 9Ra) mantle component (represented at La Palma), whose origin would be intimately connected with both old and recent geodynamic processes (e.g., paleo-subduction events, the opening of the Atlantic Ocean, and the influence of a mantle plume).

According to the historical record, a minimum of 13 eruptions in the last 500 years have occurred in the Canary Islands (Troll and Carracedo, 2016; Longpré, 2021). Most of the recent eruptions have been registered in La Palma, one of the youngest islands of the archipelago (<1.7 Ma; Guillou et al., 1998; Guillou et al., 2001; Carracedo et al., 2001; Klügel et al., 2017). On 19 September 2021, after 50 years of quiescence, the largest historical eruption of La Palma started with the formation of a fissure on the Cumbre Vieja ridge (southwestern flank of the island), a ~18 km long rift-like volcanic structure where the recent volcanism has concentrated since 150 ka (Guillou et al., 1998; Carracedo et al., 2001; Troll and Carracedo, 2016; Klügel et al., 2017). The fissural phase of the eruption rapidly evolved into a central eruption at the Tajogaite cone (Carracedo et al., 2022; Pankhurst et al., 2022; del Fresno et al., 2023) that released approximately 200 million m^3 of volcanic material (pyroclasts+lava, DRE; Carracedo et al., 2022) over almost 3 months of activity (the eruption ended on 13 December 2021). The petrological analysis revealed that the erupting magma was a high-temperature and low-viscosity primitive-basanitic melt derived from ~3% partial melting of a fertile asthenospheric mantle (Day et al., 2022; Pankhurst et al., 2022). According to Day et al. (2022), the mantle source that fed the 2021 eruption is a homogenous reservoir containing a pyroxenitic component inherited from the reaction between the peridotite and recycled crustal components, eventually determining the oxidized and HIMU-like signature of La Palma lavas.

Regarding the origin of La Palma volcanism, carbon isotope data can provide essential insights into the compositional properties of the mantle source, especially in order to test if the mantle has been modified during its history by any metasomatic agent transporting recycled carbon-rich crustal materials, and to what extent. This is because metasomatic melts/fluids in OIB context are systematically carbon-rich (e.g., Barry et al., 2014; Boudoire et al., 2018), and because carbon isotopes are powerful tracers of recycled crustal components in the mantle (Pineau and Mathez, 1990; Sano and Marty, 1995; Gennaro et al., 2017; Sandoval-Velasquez et al., 2021a; Sandoval-Velasquez et al., 2021b; Sandoval-Velasquez et al., 2022c). Indeed, the observations made by Day et al. (2022) are consistent with recent carbon isotopic studies in FI trapped in mantle xenoliths from the neighboring island of El Hierro, whose positive $\delta^{13}C$ signatures (from −2.38‰ to +0.96‰) relative to the upper mantle range (from −8‰ to −4‰; Sano and Marty, 1995) suggest mantle metasomatism caused by the infiltration of carbonated silicate melts, perhaps inherited from recycled crustal materials (Frezzotti et al., 2002a; Frezzotti et al., 2002b; Sandoval-Velasquez et al., 2021b). It has been also argued that such a recycled crustal carbon component may be a regional characteristic of the local mantle (as the HIMU endmember; Sandoval-Velasquez et al., 2022a), but the limited carbon isotope information existing for other islands (such as La Palma, Tenerife, Gran Canaria, La Gomera or Lanzarote) has so far impeded testing this hypothesis.

In this paper, we extend our knowledge of the carbon isotopic signature of the mantle source feeding the magmatism at La Palma, by presenting: the first carbon isotope data on FI entrapped in olivine and pyroxenes phenocrysts from the 2021 Tajogaite lavas and from the 1677 San Antonio lavas, as well as from representative ultramafic xenoliths (olivine-clinopyroxenites, clinopyroxenites, dunites and harzburgites) brought to the surface during the San Antonio eruption (see Figure 1). Our aim is to test our hypothesis about regional crustal carbon recycling in the mantle beneath the Canary Islands. We also take this opportunity to present new FI data from peridotite xenoliths collected from Lanzarote, considered as representative of the local lithospheric mantle (Siena et al., 1991). Our results contribute to deepening the understanding of the mantle source feeding recent volcanism at La Palma and contribute to the debate regarding the geodynamics of the Canary Islands.

FIGURE 1
Map of La Palma Island and location of the study areas. Seamount, Taburiente, Bejenado and Northern shield contours were designed after Troll and Carracedo (2016). 2021 Tajogaite lava field was designed using the topographical information published by COPERNICUS (https://emergency.copernicus.eu/mapping/list-of-components/EMSR546).

2 Volcanological evolution of La Palma

La Palma is located in the western part of the archipelago and is one of the youngest and most active islands of the Canary archipelago (Troll and Carracedo, 2016; Klügel et al., 2017). The oldest rocks found at La Palma are seamounts dated ca. 2–4 Ma ago that represent the submarine construction of the island (Figure 1; Troll and Carracedo, 2016; Klügel et al., 2017). The island presumably emerged 1.8–1.2 Ma ago, as recorded by an angular unconformity identified between the seamount edifice and the first volcanic deposits of the northern shield (Guillou et al., 1998; Guillou et al., 2001; Klügel et al., 2017). Today, the island consists of two major volcanic complexes: the northern shield (last eruption > 560 ka), which comprises the emerged seamounts, the Garafia, Cumbre Nueva, Taburiente and Bejenado volcanoes; and the southern Cumbre Vieja ridge, where recent (< 150 ka) volcanism has concentrated (Guillou et al., 1998; Guillou et al., 2001; Troll and Carracedo, 2016; Klügel et al., 2017) (Figure 1). Before 2021, the Cumbre Vieja had experienced 7 eruptions in the last 500 years, the most remembered being those that built the San Antonio, San Juan and Teneguía cones in 1677, 1949 and 1971, respectively (Carracedo et al., 2001; Troll and Carracedo, 2016). Erupted rocks at La Palma comprise basanites, alkali basalts, tephrites and phonolites with chemical signatures typical of OIB settings (Day et al., 2010; Day and Hilton, 2011; Klügel et al., 2017).

3 Samples and methods

The carbon concentration and isotope data presented here stand on the results of initial FI screening and noble gas investigations (Sandoval Velasquez et al., 2022b; Sandoval-Velasquez et al., 2023). Based on these results, we selected the aliquots with the highest concentrations (> 1.0 × 10^{-7} mol/g) of CO_2 ($n = 14$) to determine the carbon isotopic composition of FI trapped in Tajogaite and San Antonio rocks. The isotopic determinations were conducted in the stable isotopes laboratory of INGV, Sezione di Palermo (Italy). The 2021 Tajogaite lavas were sampled between September 29th and 9 November 2021, with lava eruption dates recorded in the field by INVOLCAN staff and cross-checking with near-real-time satellite information reported by Copernicus (https://emergency.copernicus.eu/mapping/list-of-components/EMSR546). For this work, 4 lava samples were selected. We added to this set one lava sample and 9 xenoliths (3 pyroxenites, and 6 peridotite xenoliths) from the historical San Antonio volcano (Figure 1). Detailed information about sampling, petrology, FI composition and noble gas-Sr-Nd-W systematics of the samples are provided in a companion article (Sandoval-Velasquez et al., 2023). Finally, 4 representative peridotite xenoliths (spinel harzburgites) from Lanzarote, already characterized in terms of petrography and mineral chemistry (Siena et al., 1991), were also integrated in this study to determine the concentration and isotopic signature of C in olivine- and clinopyroxene-hosted FI. These samples were collected from Quaternary alkali basic lavas belonging to the cycles III and IV proposed by Fuster et al. (1968); the most recent volcanic deposits of the island.

After crushing, olivines and pyroxenes were hand-picked using a binocular microscope; aliquots of 0.1–3 g of crystals were thoroughly cleaned in an ultrasonic bath in 6.5% HNO_3 and HCl to remove possible carbonates attached to the crystal lattices, deionized water and high purity-acetone. Then, samples were precisely weighed and loaded into a crusher system consisting of a stainless-steel sample holder, a hydraulic crusher, and a glass sampler to trap and freeze CO_2. A Pfeiffer Hi-Cube turbo molecular pump was used to ensure the vacuum. The gas mixture trapped as FI (mainly CO_2) was released after crushing the crystals using a piston at a pressure of about 200 bar. The gas mixture was then purified in a Pyrex glass line composed of a 626B Baratron® Absolute Capacitance Manometer MKS (measuring range 10^{-3}–10 mbar) and two traps to quantify and cryogenically purify the gas mixture, respectively. The glass line was also connected to a pump to ensure low vacuum. After purification, the CO_2 was trapped in a glass sampler (adjusted to atmospheric pressure by adding pure helium). The sampler was then transferred to a Thermo (Finnigan) Delta Plus XP CF-IRMS [connected to a Trace GC gas chromatograph and a Thermo (Finnigan) GC/C III interface] to estimate the $^{13}C/^{12}C$ ratios. The analytical error (1σ) is ~0.3‰. As reported in Table 1, values are expressed in parts per mil (‰) relative to the Vienna Pee Dee Belemnite international standard using the delta notation

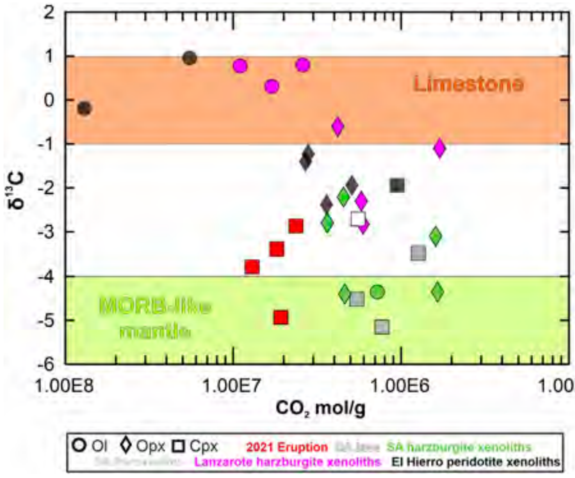

FIGURE 2
$\delta^{13}C$ ratio vs. CO_2 concentration (mol/g) of mineral-hosted FI in the studied samples from La Palma, which include the lava flow from the recent 2021 Tajogaite eruption, the 1677 lava flow from San Antonio (SA), as well as pyroxenitic and peridotitic xenoliths from San Antonio. The MORB-like mantle and crustal limestone ranges at $\delta^{13}C = -4$ to -7‰ and at $\delta^{13}C = -1$ to -1‰, respectively, are also reported for comparison after Sano and Marty (1995). El Hierro data is from Sandoval-Velasquez et al. (2021b).

($\delta^{13}C$). Further information about analytical procedures can be found in Gennaro et al. (2017).

4 Results

A petrographic description of the studied La Palma samples is provided as Supplementary Material. Regarding FI composition, in the 2021 Tajogaite lavas, the concentration of CO_2 varies in a narrow range from 1.28×10^{-7} to 2.34×10^{-7} mol/g, a value lower than that registered in the 1677 San Antonio lava FI (5.50×10^{-7} mol/g) (Table 1). The highest CO_2 concentrations are observed in the San Antonio pyroxenite and peridotite xenoliths, with values up to 1.64×10^{-6} mol/g (Figure 2). All La Palma samples show $CO_2/^3He$ ratios between 3.37×10^9 and 1.06×10^{10} that broadly correlate with increasingly positive $\delta^{13}C$ compositions (Figure 3). Most of the determined $\delta^{13}C$ values (from −5.16 to −2.21‰) are heavier than the MORB range (from −8 to −4‰; Sano and Marty, 1995) except for samples LP-21N (Opx), LP-58 (Ol), LP-12 (Opx), LP-202 (Opx), LP-SA-2.2 (Px) and LP-SA-2.3 (Px), which show an upper mantle-like signature (Figure 2). The C isotope compositions of lavas, pyroxenite, and peridotite xenoliths from La Palma are essentially overlapping (Figures 2, 3).

In Lanzarote samples, CO_2 is also the predominant phase in FI [on average 5.09×10^{-7} mol/g ($n = 8$)]; pyroxenes exhibit the highest concentrations compared with olivine (Figure 2). Unlike La Palma peridotites, the isotopic composition of CO_2 ($\delta^{13}C$) reveals more positive values than the MORB range. Two groups of data were identified: pyroxenes with values that vary between −2.83 and −0.60‰ and olivines from +0.31 to +0.80‰.

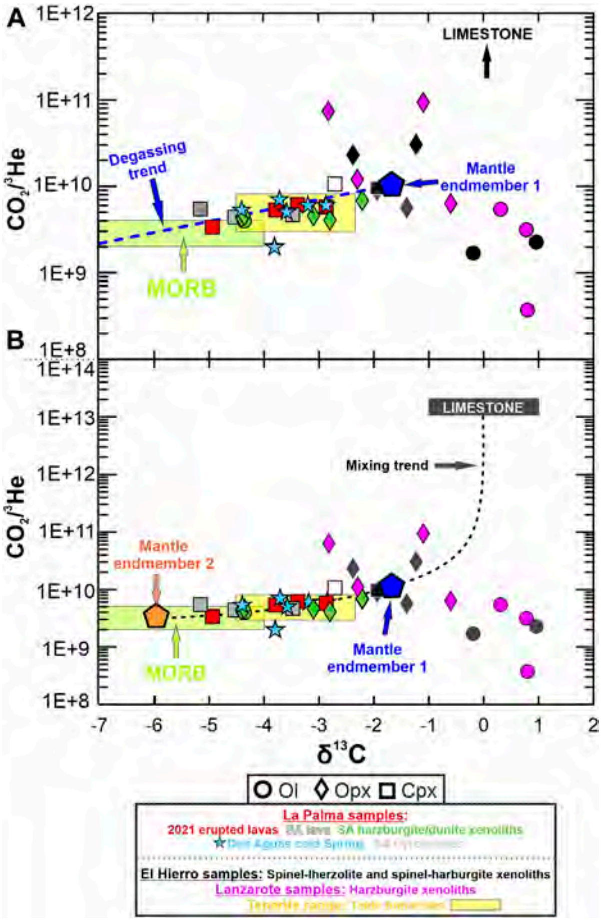

FIGURE 3
$\delta^{13}C$ vs. $CO_2/^3He$ ratios of the studied samples from La Palma compared to literature data from the entire Canary archipelago. In **(A,B)**, two alternative models to explain the origin of the carbon isotopic signature of the Canary Islands mantle source are proposed. **(A)** The blue polygon represents the proposed mantle endmember for La Palma in case of an open-degassing model. The mantle endmember was fixed at $\delta^{13}C = 1.7$‰ and $CO_2/^3He = 8.10 \times 10^9$. The open-system degassing trend was estimated after Hoefs (2015); a Δ melt-vapor distribution coefficient of 2.5 was considered. **(B)** A binary mixing model between two different endmembers: 1) a mantle endmember (orange polygon) at $\delta^{13}C = -6$‰ and a $CO_2/^3He = 3 \times 10^9$ and a limestone endmember at $\delta^{13}C = 0$‰ and a $CO_2/^3He = 1 \times 10^{13}$. $\delta^{13}C$ data from Dos Aguas Spring, Tenerife and El Hierro were taken from the literature (Melián et al., 2012; Padrón et al., 2015; Torres-González et al., 2020; Sandoval-Velasquez et al., 2021a; Day and Hilton, 2021; Padrón et al., 2022). MORB and Limestone ranges were designed after Sano and Marty (1995). SA, San Antonio.

5 Discussion

Sandoval Velasquez et al. (2022b), Sandoval-Velasquez et al. (2023) previously reported on the noble gas (He-Ar) signature of the same FI studied here, showing that Tajogaite lavas exhibit a uniform, temporally invariant MORB-like $^3He/^4He$ composition (7.38 ± 0.22 Ra) during the eruption, consistent with the He isotopic signature of San Antonio lavas. However, ultramafic xenoliths from San Antonio, which represent the local oceanic lithospheric mantle composition, are characterized by lower (< 7 Ra)

TABLE 1 CO_2 concentrations and isotopic ratios. List of the lavas and ultramafic xenoliths from La Palma and Lanzarote. $CO_2/^3He$ values were estimated using the information presented in Sandoval-Velasquez (2022), Sandoval-Velasquez et al. (2022a), Sandoval-Velasquez et al. (2022b), Sandoval-Velasquez et al. (2023).

Sample	Locality	Rock type	Phase	Eruption date	Latitude (N)	Longitude (W)	CO_2	$CO_2/^3He$	$\delta^{13}C$ (‰)
LP 21N	La Palma	Basanite	Cpx	09/11/21	28.62187	17.87381	1.90E-07	3.37E + 09	−4.94
LP21-ST1	La Palma	Basanite	Cpx	09/11/21	28.61101	17.89913	1.80E-07	6.14E + 09	−3.39
LP21-ST2	La Palma	Basanite	Cpx	09/11/21	28.61101	17.89913	1.28E-07	5.33E + 09	−3.79
LP21-ST3A	La Palma	Basanite	Cpx	09/11/21	28.61119	17.90225	2.34E-07	5.74E + 09	−2.87
LP-SA1 lava	La Palma	Basanite	Cpx	1677	28.48406	17.85271	5.50E-07	1.06E + 10	−2.71
LP-SA-2.1	La Palma	Amphibole bearing-clinopyroxenite	Cpx	-	28.48406	17.85271	1.26E-06	4.68E + 09	−3.48
LP-SA-2.2	La Palma	Clinopyroxenite	Cpx	-	28.48406	17.85271	7.63E-07	5.45E + 09	−5.16
LP-SA-2.3	La Palma	Clinoproxenite	Cpx	-	28.48406	17.85271	5.41E-07	4.39E + 09	−4.53
LP-58	La Palma	Dunite	Ol	-	28.48406	17.85271	7.16E-07	3.96E + 09	−4.36
LP-73	La Palma	Spinel Harzburgite	Opx	-	28.48406	17.85271	3.60E-07	4.07E + 09	−2.80
LP-61	La Palma	Spinel Harzburgite	Opx	-	28.48406	17.85271	1.60E-06	4.56E + 09	−3.10
LP-12	La Palma	Spinel Harzburgite	Opx	-	28.48406	17.85271	4.58E-07	4.40E + 09	−4.41
LP-201	La Palma	Spinel Harzburgite	Opx	-	28.48406	17.85271	1.64E-06	4.58E + 09	−4.36
LP-101	La Palma	Spinel Harzburgite	Opx	-	28.48406	17.85271	4.50E-07	6.83E + 09	−2.21
CL 54	Lanzarote	Spinel Harzburgite	Ol	-	-	-	1.74E-07	5.42E + 09	0.31
CL 27	Lanzarote	Spinel Harzburgite	Ol	-	-	-	1.14E-07	3.14E + 09	0.78
CL 32	Lanzarote	Spinel Harzburgite	Ol	-	-	-	2.58E-07	3.71E + 08	0.80
CL 54	Lanzarote	Spinel Harzburgite	Opx	-	-	-	1.66E-06	9.36E + 10	−1.10
CL 75	Lanzarote	Spinel Harzburgite	Opx	-	-	-	5.94E-07	6.31E + 10	−2.83
CL 33	Lanzarote	Spinel Harzburgite	Opx	-	-	-	4.20E-07	3.77E + 09	−0.60
CL 27	Lanzarote	Spinel Harzburgite	Opx	-	-	-	5.82E-07	1.11E + 10	−2.25

^{3}He/^{4}He compositions, suggesting the presence a more radiogenic component in the Cumbre Vieja local lithospheric mantle. Based on this information, Sandoval-Velasquez et al. (2023) proposed that the Cumbre Vieja magmatism is fed by a source homogeneous for He isotopes, whose uniform isotopic signature (7.37 ± 0.17 Ra) resulted from the prolonged and efficient mixing of three distinct mantle fluid components: a depleted mantle (MORB-like: 8 ± 1 Ra) He source, a radiogenic (< 7 Ra) He component, and a high ^{3}He/^{4}He component (Ra > 9; the latter contributing for only 6%–15%).

5.1 The δ^{13}C signature of the southern Cumbre Vieja ridge and the northern shield

The mineral-hosted FI in the 2021 Tajogaite lavas exhibit very homogeneous $CO_2/^3He$ (between 3.37×10^9 and 6.14×10^9) and δ^{13}C values (between −4.94‰ and −3.39‰) (Figure 3). Most of the FI δ^{13}C values plot above the upper mantle range (−8‰ to −4‰; Sano and Marty, 1995) (Figure 2), similarly to the San Antonio lava that shows the heaviest δ^{13}C composition (−2.71‰) among the magmatic samples (Figures 2, 3). The FI in lavas and ultramafic xenoliths exhibit overlapping δ^{13}C signatures (Figure 2), strongly suggesting that the heavy FI carbon isotope signature of the lavas is source-inherited and not affected by crustal contamination processes. In fact, petrographic observations showed that San Antonio peridotites trapped secondary FI whose origin would be related to mantle metasomatism (see Supplementary Material); in all peridotites (clinopyroxenites, harzburgites and dunite) FI trails typically originate from glass microveins permeating the rocks or are intimately associated with reaction rims (composed of secondary olivine, clinopyroxene and glass) around primary orthopyroxenes. When considering the consistency of δ^{13}C values in both lavas (basanites; Sandoval-Velasquez et al., 2023) and xenoliths, and the composition of the interstitial glass found in San Antonio peridotites, the above-mentioned metasomatism seems to be associated with the infiltration of the lithospheric mantle by basanitic/trachitic melts (see Sandoval-Velasquez et al., 2023), the latter probably generated in a deep mantle region (asthenosphere) similar to that feeding the recent volcanism of La Palma.

Prior to our study, the only available δ^{13}C information for the Cumbre Vieja Ridge refers to dissolved CO_2 in groundwater samples from a small well, periodically sampled during the October 2017 to February 2018 seismic-deformation unrest (Torres-González et al., 2020). This unrest has more recently been interpreted as an early sign of volcanic activity resumption that ultimately culminated in the 2021 eruption (Carracedo et al., 2022; Padrón et al., 2022; Pankhurst et al., 2022). As reported by Torres-González et al. (2020), the highest δ^{13}C value measured during the unrest was −7.1‰, while the lowest was −10.3‰, which is well below the δ^{13}C values reported here for the Tajogaite/San Antonio FI in our study. According to Torres-González et al. (2020), the δ^{13}C in La Palma groundwaters could plausibly have fractionated due to biological processes. Moreover, it should be considered that δ^{13}C of dissolved CO_2 and TDIC (Total Dissolved Inorganic Carbon) in thermal fluids often fractionates by multi-step CO_2 dissolution and carbonate precipitation/dissolution processes (Simmons and Christenson, 1994; Barry et al., 2014; Güleç and Hilton, 2016; Venturi et al., 2017). Such a fractionation may explain the discrepancy between the δ^{13}C in groundwaters and the δ^{13}C in FI data.

In the Northern Shield, δ^{13}C values are available for the Dos Aguas spring, a CO_2-rich bubbling cold spring located in the Taburiente Caldera (Figure 1). Before the 2021 Tajogaite eruption, the Dos Aguas spring was the only visible gas emission on La Palma (Pérez et al., 1994; Hilton et al., 2000; Padrón et al., 2012; Padrón et al., 2015; Torres-González et al., 2020; Day and Hilton, 2021; Padrón et al., 2022). This site is also especially important because it is the only locality where a high ^{3}He/^{4}He contribution, higher than the MORB-like range (8 ± 1 Ra) (Graham, 2002), has been detected in the Canary Islands. At the Dos Aguas spring, relatively constant high ^{3}He/^{4}He ratios (up to 10.24 Ra, where Ra is the atmospheric ^{3}He/^{4}He) have been reported through the last decades by different authors (i.e., Pérez et al., 1994; Padrón et al., 2012; Padrón et al., 2015; Padrón et al., 2022; Torres-González et al., 2020; Day and Hilton, 2021). The carbon isotopic composition of the Dos Aguas spring (measured during the last 30 years) has shown homogeneous δ^{13}C values between −3.6‰ and −2.9‰ and upper mantle-like $CO_2/^3He$ ratios, matching the range of the Tajogaite and San Antonio samples (Figures 3A, B) and providing further evidence of the existence of a heavy C isotopic reservoir beneath La Palma.

The fact that variable sample types (spring gases and mineral-hosted FI) from three localities >10 km apart from each other (Dos Aguas, Tajogaite and San Antonio) exhibit similar δ^{13}C compositions is relevant and suggests their feeding from a common, relatively homogeneous deep source. As mentioned above, the low δ^{13}C values reported from the Cumbre Vieja groundwaters are likely an underestimation of deep sources due to shallow depth fractionation processes; therefore these data will not be discussed further.

5.2 Inferences about the δ^{13}C signature of the Canary Islands

The overall similarity of δ^{13}C values in lavas and mantle xenoliths from La Palma (Figures 2, 3) suggests that the heavy C isotope signature recorded by the lavas comes from a^{13}C-enriched mantle source. Recent studies in FI trapped in mantle xenoliths have proved that the local upper mantle beneath the Canary Islands has been intensely metasomatized by silicate and carbonate-rich melts (Admunsen, 1987; Neumann, 1991; 2004; Neumann and Wulff-Pedersen, 1997; Frezzotti et al., 2002a; Frezzotti et al., 2002b; Oglialoro et al., 2017). Admunsen (1987) and Neumann and Wulff-Pedersen (1997) first observed the presence of interstitial silicate glasses in mantle xenoliths from La Palma, El Hierro, Tenerife and Lanzarote. These authors suggested that interstitial glasses reflect metasomatic reactions between silicate melts and the surrounding peridotites at mantle conditions. Subsequently, Frezzotti et al (2002a), Frezzotti et al. (2002b) recognized the presence of carbonates (Mg-calcite and dolomite) inside FI trapped in ultramafic xenoliths from Tenerife and La Gomera, confirming the infiltration of volatile-rich carbonate melts in the western portion of the local upper mantle. Similarly, petrological studies performed in mantle xenoliths from

El Hierro, which together with La Palma define the westernmost and most youthful extent of the archipelago indicated the formation of interstitial microveins composed of carbonate droplets (calcite and Mg-calcite) inherited from deep infiltration of volatile-rich, carbonate-silicate melts (Oglialoro et al., 2017; Remigi et al., 2019; Colombo, 2020).

Accordingly, Sandoval-Velasquez et al. (2021b) reported heavy $\delta^{13}C$ (> −2.38‰) CO_2 isotopic compositions in FI from the same suite of mantle xenoliths from El Hierro. These data proved the crustal affinity of the fluids that have interacted with the local mantle. They likely are derived from either recycled sediments, altered oceanic crust, or oceanic lithosphere materials.

Our results show that CO_2 contents in FI in Lanzarote peridotite xenoliths are within the same range of El Hierro measurements (Figure 2), which indicates that the fluids were trapped under mantle conditions and supports the existence of a comparable C-rich fluid pervading the mantle beneath the eastern islands. This is corroborated by the variability of $\delta^{13}C$ values (−2.83‰ < $\delta^{13}C$ < +0.80‰), which fall in the same range of El Hierro mantle xenoliths displaying also a similar systematic distribution between olivine and pyroxene crystals (Figures 3A, B). The analogous $\delta^{13}C$ signature of FI in mantle xenoliths from both Lanzarote (easternmost island) and El Hierro (westernmost island of the archipelago) would suggest a regional permeation of the mantle beneath the archipelago with C-rich fluids that exhibit a heavy isotope signature ($\delta^{13}C$ > −3‰). As pyroxene is more sensitive than olivine to metasomatism in the Canary mantle, it can be used as a more trustable proxy for unveiling the composition of metasomatic fluids (Frezzotti and Touret, 2014); by averaging the composition of FI entrapped in pyroxenes from El Hierro and Lanzarote xenoliths we infer the averaged “regional” (Canary archipelago) source mantle characteristics at $\delta^{13}C$ of −1.71‰ and $CO_2/^3He$ of 8.10 × 10^9 (“Mantle endmember 1” in Figures 3A, B).

Our results for lavas, pyroxenites and mantle xenoliths from La Palma plot between this inferred Canary Mantle endmember 1 and the MORB range (Figures 3A, B). Interestingly, the Teide fumaroles on Tenerife Island exhibit similarly intermediate compositions (see yellow band in Figures 3A, B). Therefore, we envisage two distinct mechanisms/processes that can explain the positive $\delta^{13}C$ vs $CO_2/^3He$ tendency and (more broadly) the more ^{13}C-depleted compositions at La Palma relative to El Hierro and Lanzarote.

In the first scenario (model A), we ascribe the $\delta^{13}C$ and $CO_2/^3He$ compositions of La Palma lavas, xenoliths and Teide fumaroles to degassing processes starting from a regionally homogeneous Canary mantle (corresponding to the Canary “Mantle endmember 1” above) (Figure 3A). Several authors have demonstrated that, upon increasing extents of degassing (e.g., during volatile exsolution into a separate fluid phase), the original $\delta^{13}C$ composition of a system (a melt, or even the mantle) evolves toward progressively more negative (^{13}C-depleted) compositions (Javoy et al., 1978; Mattey, 1991; Boudoire et al., 2018). This occurs because, during degassing, ^{13}C is preferentially partitioned into a CO_2-rich fluid phase relative to the coexisting melt of basaltic composition, leaving this latter (or a degassed, residual mantle reservoir) enriched in ^{12}C instead (Javoy et al., 1978; Mattey, 1991; Porcelli et al., 1992; Deines et al., 2002; Aubaud et al., 2005; Aubaud, 2022).

To quantitatively test this hypothesis (Figure 3A), we model an open-system degassing process starting from the composition of the Mantle endmember 1 at $\delta^{13}C$ = −1.71‰ and $CO_2/^3He$ = 8.10 × 10^9 (which are the estimated averages for the pyroxenes from El Hierro and Lanzarote xenoliths), and using the mathematical expression of Hoefs (2015), Eq. 1:

$$\frac{Rv}{R_{lo}} = f^{\left(\frac{1}{\alpha}-1\right)} \tag{1}$$

where Rv/R_{lo} is the instantaneous isotope ratio of the vapor leaving the liquid and the remaining liquid, α is the fractionation factor and f is the fraction of the residual liquid. As observed in Figure 3A, all samples from La Palma and the Tenerife range fit the modeled degassing curve, indicating the likelihood of the process. These model calculations imply that a common ^{13}C-enriched, homogeneous mantle source (enriched in a recycled crustal carbon component) may exist beneath the Canary Islands, with all the inter- and intra-island variability caused by degassing processes. If this hypothesis is true, then the fluids trapped in the La Palma ultramafic xenoliths would not have a primary origin, but would represent secondary FI formed after the interaction with the transporting melt (here represented by the SA lava: sample LP-SA1 lava). Petrographic observations on the mantle xenoliths seem to support the secondary origin of trapped fluids (see Supplementary Material). Thus, trapping melt-derived fluids would explain why ultramafic xenoliths fit the same degassing trend.

In the second scenario (model B; Figure 3B) the intermediate $\delta^{13}C$ vs. $CO_2/^3He$ compositions of La Palma FI can be interpreted as reflecting binary mixing between two distinct reservoirs, i.e., a crustal limestone component (at $\delta^{13}C$ = 0‰ and $CO_2/^3He$ = 1 × 10^{13}, Sano and Marty, 1995) and a depleted (MORB-like) Canary “Mantle endmember 2” (at $\delta^{13}C$ between −6‰ and −4‰ and $CO_2/^3He$ = 3 × 10^9; the latter representing the lowest $CO_2/^3He$ observed in our dataset). In this interpretation, the Canary mantle source would be regionally heterogeneous, and modelled by a depleted (MORB-like) mantle endmember that was variably refertilized and enriched in carbon via interaction with a recycled crustal carbon component (illustrated by a limestone at $\delta^{13}C$ = 0‰ and $CO_2/^3He$ = 1.0 × 10^{13}). The Canary “Mantle endmember 2”-limestone mixing curve also explains the compositional variability of both FI and surface fluids. In this scenario, the maximum estimated contribution of the crustal limestone component at La Palma would be <10%.

Unfortunately, the currently available information makes it challenging to discriminate between the two models above (degassing vs mixing). We caution that additional $\delta^{13}C$ data, coupled to barometric determinations (in both lavas and ultramafic xenoliths) and more detailed petrographic and FI observations are required to prove a robust relationship exists between the extent of magma ascent and depressurization, the secondary origin of FI in mantle xenoliths and increasingly negative $\delta^{13}C$ signature. In addition to the evidences reported in support of scenario 1,

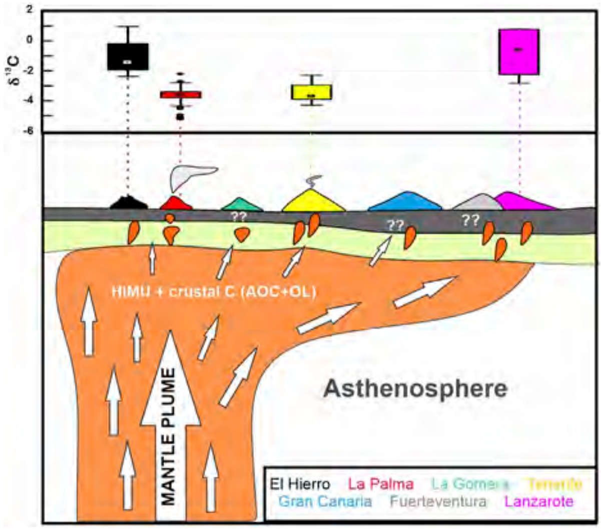

FIGURE 4
Diagram showing the origin of the crustal carbon identified in free gas and FI trapped in lavas and ultramafic xenoliths from La Palma, El Hierro, Tenerife and Lanzarote islands. $\delta^{13}C$ boxplots were designed using the data presented in this work and from the literature, please see Figure 3 for references. Modified from Hoernle and Schmincke (1993), Anguita and Hernán (2000), Troll and Carracedo (2016).

we note that our FI $\delta^{13}C$ results overlap with those obtained from the Dos Aguas Spring, a fact that more likely reflects a variability due to magma degassing. Alternatively, the variability of $\delta^{13}C$ values in spring gases should reflect the degassing of melts having distinct carbon isotopic signatures, implying a local and spatially-narrow mantle heterogeneity, which seems unlikely considering that the same $\delta^{13}C$ signature of Mantle endmember 1 was measured in mantle xenoliths from the easternmost island of Canary (i.e., Lanzarote). In any case, both models suggest the existence of a recycled crustal component in the mantle source beneath La Palma. As previously stated, this mantle component could also be present in the eastern portions of the archipelago (as suggested by $\delta^{13}C$ of Lanzarote samples and the petrologic studies performed in mantle xenoliths from La Gomera and Tenerife; Admunsen, 1987; Neumann, 1991; Neumann, 2004; Neumann and Wulff-Pedersen, 1997; Frezzotti et al., 2002a; Frezzotti et al., 2002b; Sandoval-Velasquez et al., 2022b), supporting a regional pattern. Further studies of FI in ultramafic xenoliths from islands such as La Gomera, Tenerife, Gran Canaria and Fuerteventura, coupled with a detailed comprehension of the FI composition and a comprehensive geodynamic framework, will clarify the extent of the recycled crustal component.

The hypothesis that the recycled crustal carbon is a regional characteristic of the upper mantle beneath the Canary Islands agrees well with the classic "Blob model" (Hoernle and Schmincke, 1993) and the more recent "edge-driven mantle convection model" (Gurenko et al., 2010). These theories would explain how a crustal component is brought to the surface by a HIMU-like mantle plume (which spreads beneath the archipelago), being the most plausible scenario to explain the $\delta^{13}C$ variability observed along the archipelago (Figure 4).

6 Conclusion

In this paper, we reported the first carbon isotopic data from FI of the Tajogaite lavas erupted in 2021 at La Palma. We also included new $\delta^{13}C$ information obtained from lavas and ultramafic xenoliths collected in the San Antonio volcano and reviewed previously published analytical $\delta^{13}C$ data on volcanic springs/fumaroles (particularly from La Palma and Tenerife) and FI (from El Hierro and La Palma) with the aim of better characterizing the isotopic signature of the local mantle source. The first $\delta^{13}C$ data of FI trapped in peridotite xenoliths from Lanzarote are also reported.

Our findings show that the $\delta^{13}C$ of La Palma fluids, including free gases and mineral-hosted FI, range between −5.16‰ and −2.21‰. Conversely, $\delta^{13}C$ from Lanzarote xenoliths are more positive (from −2.83 to +0.80‰) and very similar to isotopic data previously reported in mantle xenoliths from El Hierro, pointing to a regional infiltration of the mantle beneath the Canary Islands by crustal C-rich fluids with heavy isotope signature ($\delta^{13}C > -3$‰). With these new data we can propose that the variability of $\delta^{13}C$ at La Palma can be explained either by an open-degassing process starting from a mantle endmember with $\delta^{13}C = -1.70$‰ or by a binary mixing between a mantle reservoir ($\delta^{13}C = -6.0$‰) and a crustal carbon reservoir with a $\delta^{13}C$–0‰. In both cases, our data prove the presence of a crustal carbon reservoir in the local mantle under La Palma.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

AS-V: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Software, Visualization, Writing–original draft. FC: Data curation, Formal Analysis, Investigation, Writing–review and editing. TN: Conceptualization, Investigation, Supervision, Writing–review and editing. AA: Conceptualization, Formal Analysis, Funding acquisition, Investigation, Supervision, Validation, Visualization, Writing–review and editing. MC: Conceptualization, Investigation, Methodology, Resources, Supervision, Visualization, Writing–review and editing. MF: Investigation, Supervision, Validation, Visualization, Writing–review and editing. MA: Investigation, Resources, Visualization, Writing–review and editing. EP: Investigation, Resources, Visualization, Writing–review and editing. Matthew MP: Writing–review and editing, Investigation, Resources, Visualization. NP: Writing–review and editing, Investigation, Resources, Visualization. AR: Conceptualization, Formal Analysis, Investigation, Methodology, Supervision, Validation, Visualization, Writing–review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2024.1303872/full#supplementary-material

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