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Recycled crustal carbon in the depleted mantle source of El Hierro volcano, Canary Islands.

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Abstract:	The Canary Islands, in the eastern Atlantic, is among the most enigmatic Oceanic Island provinces on Earth, as the mantle source feeding its volcanism exhibits wide spatial heterogeneity and multiplicity of sources. Multi-isotope whole-rock studies have long revealed the presence of a recycled oceanic crust/lithosphere component in the mantle source. However, noble gas systematics have been more challenging to interpret, and carbon isotope constraints have to date remained unavailable to support/dismiss this interpretation. Here, we present the very first isotopic characterisation of CO 2 and noble gases (He-Ne-Ar) in fluid inclusions (FI) in minerals hosted in mantle xenoliths from El Hierro, the youngest and westernmost island of the Canary volcanic archipelago. Six fresh xenoliths from El Julan cliff valley were analysed (3 spinel lherzolites and 3 spinel harzburgites). We find carbon isotopic compositions of CO 2 in FI (δ 13 C) ranging from –2.38 to –1.23‰ in pyroxenes and from –0.19 to +0.96‰ in olivines. These unusually positive δ 13 C values, well above the typical mantle range (–8‰<δ 13 C<–4‰), prove, for the first time, the presence of a recycled crustal carbon component in the local source mantle. We interpret this 13 C-rich component as inherited from a mantle metasomatism event driven by fluids carrying carbon from C. In contrast, our El Hierro xenoliths identify a depleted mantle-like He signature, with an average Rc/Ra ratio (3 He/ 4 He normalised to air ratio and corrected for atmospheric contamination) of 7.45±0.26 Ra. The involvement of depleted mantle-like fluids, variably admixed with air-derived components (possibly recycled via paleo-subduction event(s)), is corroborated by Ne-Ar isotopic compositions. The depleted mantle-like He signature points against the involvement of a primordial He source in the local lithospheric mantle and proves a marginal role played by past subduction events in modifying the local mantle He budget. When put in the context of previous 3 He/ 4 He measurements in FI and surface gases along the Canary archipelago, our results confirm an overall west-to-east decrease of Rc/Ra ratios, which may be interpreted as due to increasing contributions from the African sub-continental mantle, the addition of radiogenic 4 He during magma migration in the oceanic crust (whose thickness increases eastward) and/or magma ageing.
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Cover letter

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We are pleased to submit the manuscript entitled "Recycled crustal carbon in the depleted mantle source of El Hierro volcano, Canary Islands." for consideration for publication in *Lithos*. This paper is the result of a collaborative effort between the University of Palermo, the Istituto Nazionale di Geofisica e Vulcanologia (INGV), the University of Milano-Bicocca, the Instituto Tecnológico y de Energías Renovables, S.A. (ITER, S.A.), (Tenerife, Canary Islands, Spain) and the Instituto Volcanológico de Canarias (INVOLCAN) (Tenerife, Canary Islands, Spain).

In this work, we report on the first isotopic results for CO_2 and noble gas in fluid inclusions trapped in mantle xenoliths collected from El Hierro, the youngest oceanic island in the Canary Islands. The CO_2 carbon isotopic compositions, the first-ever reported for El Hierro, prove the existence of a recycled crustal carbon component in the local source mantle. This component reflects the infiltration of metasomatic fluids, that we interpret as resulting from subducted altered oceanic crust (AOC) and/or oceanic lithosphere (OL), consistent with independent geochemical evidence (chemical and isotope tracers). Noble gas compositions in fluid inclusions constrain a MORB-like signature of the mantle beneath El Hierro, integrating the evidence of volcanic gases and erupted rocks. A careful review of $^{3}He/^{4}He$ data available for the Canary Islands is also undertaken that offers new insights to interpret the west-to-east isotopic variation over the archipelago. We propose that the $^{3}He/^{4}He$ depletion observed in the eastern islands may reflect a combination of an Enriched Mantle (EM) component in the mantle with magma ageing and/or assimilation of radiogenic He upon its ascent and ponding in the crust. Ultimately, our study provides new and valuable information on carbon and noble gas stored in/cycling through the Earth's mantle beneath the complex geodynamic setting of Canary magmatism.

We believe that this manuscript will be of interest to a wide range of scientists working in a variety of Earth Science topics, and we hope it can be considered for publication in *Lithos*.

Sincerely,

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ABSTRACT

The Canary Islands, in the eastern Atlantic, is among the most enigmatic Oceanic Island provinces on Earth, as the mantle source feeding its volcanism exhibits wide spatial heterogeneity and multiplicity of sources. Multi-isotope whole-rock studies have long revealed the presence of a recycled oceanic crust/lithosphere component in the mantle source. However, noble gas systematics have been more challenging to interpret, and carbon isotope constraints have to date remained unavailable to support/dismiss this interpretation. Here, we present the very first isotopic characterisation of CO_2 and noble gases (He-Ne-Ar) in fluid inclusions (FI) in minerals hosted in mantle xenoliths from El Hierro, the youngest and westernmost island of the Canary volcanic archipelago. Six fresh xenoliths from El Julan cliff valley were analysed (3 spinel lherzolites and 3 spinel harzburgites). We find carbon isotopic compositions of CO_2 in FI ($\delta^{13}C$) ranging from –2.38 to –1.23‰ in pyroxenes and from –0.19 to +0.96‰ in olivines. These unusually positive $\delta^{13}C$ values, well above the typical mantle range (–8‰<$\delta^{13}C$<–4‰), prove, for the first time, the presence of a recycled crustal carbon component in the local source mantle. We interpret this ^{13}C-rich component as inherited from a mantle metasomatism event driven by fluids carrying carbon from C. In contrast, our El Hierro xenoliths identify a depleted mantle-like He signature, with an average Rc/Ra ratio ($^3He/^4He$ normalised to air ratio and corrected for atmospheric contamination) of 7.45±0.26 Ra. The involvement of depleted mantle-like fluids, variably admixed with air-derived components (possibly recycled via paleo-subduction event(s)), is corroborated by Ne-Ar isotopic compositions. The depleted mantle-like He signature points against the involvement of a primordial He source in the local lithospheric mantle and proves a marginal role played by past subduction events in modifying the local mantle He budget. When put in the context of previous $^3He/^4He$ measurements in FI and surface gases along the Canary archipelago, our results confirm an overall west-to-east decrease of Rc/Ra ratios, which may be interpreted as due to increasing contributions from the African sub-continental mantle, the addition of radiogenic ^4He during magma migration in the oceanic crust (whose thickness increases eastward) and/or magma ageing.

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Highlights

- $\delta^{13}C$ of CO_2 in fluid inclusions tracks recycled crustal carbon in the El Hierro mantle source
- Crustal carbon may derive from subducted altered oceanic crust or lithosphere
- Noble gases indicate the MORB-like signature of the mantle beneath El Hierro
- Increasing crustal contribution concurs to the west-to-east $^3He/^4He$ decrease in the Canary

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Keywords: *Canary Islands, El Hierro, mantle xenoliths, fluid inclusions, recycled carbon, noble gases.*

1. INTRODUCTION

In Ocean Island and intra-plate settings, mantle heterogeneities have often been invoked to justify the variability of geochemical tracers (e.g., He, Sr, Nd, and Pb isotopes; Hofmann, 1997, 2003; Jackson and Dasgupta, 2008; Dasgupta et al., 2010; Day et al., 2010; Day and Hilton, 2011, 2020). These heterogeneities would derive from the long-term preservation of depleted and enriched components variably and locally mixing into the mantle (see Hofmann, 1997, 2003 for a review). Some of these components relate to recycling old subducted materials that lead to extreme isotopic signatures (e.g., Sobolev et al., 2007).

The study of the isotopic composition of fluids trapped in mantle xenoliths (e.g., Deines, 2002; Gautheron and Moreira, 2002; Pearson et al., 2014; Day et al., 2015) may help better-comprehending mantle features and evolution back in time, as they provide clues on the origin and cycling of volatiles in the Earth's interior. Noble gases in mantle xenoliths, in particular, are proven tools for constraining the relative mixing proportions among

different mantle reservoirs (e.g., Gurenko et al., 2006; Day and Hilton, 2011, 2020; Broadley et al., 2016; Rizzo et al., 2018; Kobayashi et al., 2019). In addition, carbon isotopes are key species for understanding the carbon recycling in the lithospheric and deeper mantle via subduction of crustal carbon components (e.g., organic matter and sedimentary carbonate) (Dasgupta and Hirschmann, 2010; Aiuppa et al., 2017; Duncan and Dasgupta, 2017; Li et al., 2019; Plank and Manning, 2019; Regier et al., 2020). Unfortunately, however, carbon isotope studies in mantle xenoliths are still limited to a relatively small number of localities (Deines, 2002; Demény et al., 2010; Correale et al., 2015; Gennaro et al., 2017; Boudoire et al., 2018; Rizzo et al., 2018).

The Canary Islands represent an ideal laboratory for studying heterogeneities in noble gas and carbon mantle signatures, as ultramafic xenoliths, volcanic rocks, and surface emissions associated with the active volcanism of the archipelago prove the involvement of multiple sources at play the mantle source (Gurenko et al., 2006; Day and Hilton, 2020). The origin of volcanism in the Canary Islands is still a matter of debate, given the area's geodynamic and tectonic complexity (Anguita and Hernán, 2000). There is consensus, however, that a mantle plume model fits most of the geophysical and geochemical evidence (Fig. 1; Hoernle and Schmincke, 1993; Pérez et al., 1994; Hoernle et al., 1995; Carracedo et al., 1998; Montelli, 2004; Day et al., 2010; Day and Hilton, 2020). However, in terms of noble gases, only the geothermal gases of the Taburiente caldera (La Palma island), with their $^{3}He/^{4}He$ of > 9Ra (where Ra is the $^{3}He/^{4}He$ atmospheric ratio), identify a primordial component in the Canary mantle source (Pérez et al., 1994, 1996; Hilton et al., 2000; Day and Hilton, 2020; Fig. 1). In contrast, volcanic rocks of the same island record a depleted mantle (MORB; Middle Oceanic Ridge Basalt) signature (e.g., Hilton et al., 2000), and other Islands ($^{3}He/^{4}He$ are available for El Hierro, Gran Canaria, Tenerife, La Gomera, Fuerteventura and Lanzarote) generally exhibit MORB-like, or even more radiogenic (lower $^{3}He/^{4}He$ ratios) signatures (see Fig.1 and Table S1 for isotopic values and references). These variations have been taken as evidence of mantle heterogeneities in the sources of magmas. In particular, steaming from multi-isotope (He-Nd-Sr-Pb-Os-O) results, an Enriched Mantle (EM) component has been proposed in the eastern portion of the archipelago (Hoernle et al., 1991; Carnevale et al., 2021), while a HIMU (High-μ= elevated $^{238}U/^{204}Pb$) mantle signature has been identified in its western edge (Gurenko et al., 2006; Day and Hilton, 2011, 2020). These results prove that recycled volatiles (e.g., derived from melting of old subducted oceanic crust/lithosphere in the case of the HIMU component) get admixed with depleted (MORB) and plume mantle sources underneath the archipelago (Day and Hilton, 2011, 2020).

One complication in these interpretations is that most $^{3}He/^{4}He$ measurements refer to volcanic gases and/or FI in lava phenocrysts (measured with different extraction techniques) that can be affected by secondary and shallow processes. For example, FI may be susceptible to the addition of cosmogenic ^{3}He and/or radiogenic ^{4}He, and to diffusive He loss from crystals, while volcanic gases can suffer from shallow contamination by crustal and atmospheric fluids. Therefore, noble gas results on mantle xenoliths are urgently needed to constrain the mantle signature beneath each island in the Canary archipelago.

The case is exacerbated even more for carbon, whose origin has mainly been inferred from the isotopic composition of CO_2 ($\delta^{13}C$) in volcanic gases and groundwaters from La Palma and Tenerife, and generically considered of magmatic or mantle origin (see supplementary Table S1 for isotopic values and references). Thus, whether or not a recycled carbon component exists in the Canary source mantle remains unanswered. As subduction of altered ocean crust/lithosphere is a crucial pathway for the return of shallow crustal carbon back into the mantle (Alt and Teagle, 1999; Alt et al., 2013; Hazen et al., 2013; Hammouda and Keshav, 2015; Martin and Hermann, 2018; Plank and Manning, 2019), the existence of recycled carbon underneath western Canary is expected (but yet unproven) given the HIMU affinity of the erupted magmas.

Here, we present the first isotopic measurements of noble gases and CO_2 in fluid inclusions (FI) in mantle xenoliths from El Hierro, the youngest oceanic island of the Canary (Carracedo et al., 1998) and where occurred the most recent eruption in 2011-2012 (Padrón et al., 2013). From this, we constrain the $^{3}He/^{4}He$ signature of the mantle beneath El Hierro that, combined with a careful review of existing data, offer new insights to interpret the west-to-east He variability along the archipelago. Our CO_2 isotope compositions, the first-ever reported for El Hierro, and the first FI results for the Canary archipelago, allow us recognising a recycled crustal carbon component in the local source mantle.

2. GEOLOGICAL AND VOLCANOLOGICAL SETTING

The Canary Islands are an archipelago composed of 7 main volcanic islands (from East to West: Lanzarote, Fuerteventura, Gran Canaria, Tenerife, La Gomera, La Palma and El Hierro) located in front of the western coast of North Africa and extended for almost 500 km (Fig. 1). The volcanic islands and seamounts formed on oceanic lithosphere of Jurassic age close to a passive continental margin (Schmincke, 1982; Carracedo et al.,

1998; Anguita and Hernán, 2000; Troll and Carracedo, 2016). Although the volcanism that formed the Canary started more than 20 Ma, ages between 47 and 142 Ma have been also reported for the old seamounts located NE and SW of the archipelago (Schmincke, 1982; Carracedo et al., 1998; van den Bogaard, 2013). Quaternary volcanic deposits have been reported along the Canary Islands (except for La Gomera) and most of them are considered volcanically active (Carracedo et al., 1998; Troll and Carracedo, 2016). The most recent eruption was registered in 2011-2012 in El Hierro (Padrón et al., 2013).

The Canary Islands exhibit an enormous spectrum of volcanic rocks, from carbonatites, nephelinites, basanites, tephrites, tholeiitic and alkali olivine basalts associated with shield-volcanism processes to rhyodacites, rhyolites, trachytes and phonolites related to a highly explosive felsic volcanism (Schmincke, 1982; Abratis et al., 2002; Carracedo et al., 1998; Troll and Carracedo, 2016). It is worth mentioning that this magmatic activity has brought to the surface important quantities of ultramafic xenoliths along the entire archipelago (e.g., Admunsen, 1987; Siena et al., 1991; Neumann and Wulff-Pedersen, 1997; Frezzotti et al., 2002b; Oglialoro et al., 2017).

Several hypotheses have been formulated about the origin of the Canary Islands: Anguita and Hernan (1975) proposed a connection between the Islands and the Atlas Mountains by a mega-shear that experienced a tensional phase causing decompression melting and volcanism. Araña and Ortiz (1991) suggested that compressive tectonics are the cause of the magmatism and the uplift of the archipelago; instead, Hoernle and Schmincke (1993) and Carracedo et al. (1998) described a mantle plume model where volcanism is generated by a thermal mantle anomaly (a hot-spot) which is supported by geochemical evidence, the progressive west-to-east age increase of the islands and the relative movement of the African plate (approximately 2 cm/year; Carracedo et al., 1998). Finally, Anguita and Hernán (2000) integrated these hypotheses and proposed a unified model to explain the complexity of the thermal and tectonic evolution of the Canary Islands.

El Hierro is the youngest (1.12 Ma) and westernmost island of the Canary and its history is summarized in three stages (Troll and Carracedo, 2016 and references therein): (i) the formation of the Triño Volcano (1.12 Ma to 1.03 Ma); (ii) the collapse of the latter and the emplacement of a new volcanic structure (the Golfo volcano; 545 – 176 ka), and (iii) the development of a triple rift system where most of the recent volcanism has focused. This volcanism is mainly dominated by high alkali silica-saturated rocks and Hawaiian-type

tholeiites (extruded during the Golfo volcano eruption), which may contain ultramafic xenoliths (Neumann, 1991; Oglialoro et al., 2017).

3. SAMPLES AND METHODS

The analysed suite of mantle xenoliths consists of 3 spinel lherzolites and 3 spinel harzburgites selected among over 35 peridotite samples from El Julan cliff valley, El Hierro (Canary Islands; Fig. 1), and erupted 30 – 40 ka ago (Oglialoro et al., 2017). Sampling details and petrographic characteristics of these rocks are already presented elsewhere (Oglialoro et al., 2017; Colombo, 2020). For the present study, sample selection was performed based on the type of fluid and melt inclusions present to sample metasomatic CO_2-rich fluids in the lithospheric mantle (Frezzotti et al., 2012b; Frezzotti and Touret, 2014), limiting the contribution of CO_2 in FI formed during degassing of host basanitic magmas during ascent. In selected peridotites, FI coexist with a complex network of glass microveins. Two types of FI are present: CO_2 ($\pm N_2$) and CO_2 ($\pm N_2$ traces) + daughter minerals (>70% in volume), including anhydrite, Mg-calcite, dolomite, hydrated Mg-sulphate; sulphohalite; apatite; spinel; magnesite, and talc (Oglialoro et al., 2017; Remigi et al., 2019). Microveins contain silicate glass and carbonate droplets and are present in olivine (Ol) grains, and along Ol and orthopyroxene (Opx) grain boundaries. Maximum calculated densities of CO_2-N_2 are extremely high, up to 1.19 g/cm^3, corresponding to fluid trapping at 1.8±0.02 GPa or about 65 km depth (at 950°C; Oglialoro et al., 2017).

For noble gas and CO_2 analysis, xenoliths were crushed and sieved to handpick fresh and unaltered crystals of Ol, Opx, and Cpx with diameters generally ≥0.5 mm. The noble gas and CO_2 concentrations and isotopic ratios of FI were investigated at the noble gas and stable isotopes laboratories of INGV, Sezione di Palermo (Italy), following the preparation and analytical techniques described in Gennaro et al. (2017) and Rizzo et al. (2018). Before noble gas determinations, samples were cleaned in an ultrasonic bath in 6.5% HNO_3, in deionised water and high-purity acetone. After then, samples were weighed and loaded into an ultra-high-vacuum crusher for noble gas analyses, where the first estimate of the concentration of CO_2 in FI was performed. The estimation of CO_2 was performed by measuring the total pressure of gas (CO_2+N_2+O_2+noble gases) released during crushing (by an IONIVAC Transmitters ITR90) in a known volume of the system, then the residual pressure of N_2+O_2+noble gases was subtracted after removing CO_2 in a "cold finger" immersed in liquid nitrogen. FI

were released by single-step crushing at about 200 bar and room temperature (21°C) to prevent/limit the addition of cosmogenic and radiogenic helium accumulated in the crystal lattices (Kurz, 1986; Graham, 2002; Rizzo et al., 2018; Correale et al., 2019). After the manometric determination of the CO_2 concentration, the resulting gas mixture was purified in a stainless-steel ultra-high-vacuum preparation line to remove all gas species (N_2, H_2, H_2O, CO_2) except noble gases. Then, Ar was adsorbed in a charcoal trap submerged in liquid nitrogen. He and Ne were finally adsorbed in a cryogenic trap in which a charcoal trap is in contact with a cold head cooled down at about 10 °K by a helium compressor, and separately released at about 42 and 83 °K, respectively. Once desorbed, He and Ne were admitted in two distinct split-flight-tube mass spectrometers (Helix SFT, Thermo Scientific), while Ar in a multi-collector mass spectrometer (Argus, GVI). Analytical uncertainties (2σ) for $^{3}He/^{4}He$, $^{20}Ne/^{22}Ne$, $^{21}Ne/^{22}Ne$, $^{40}Ar/^{36}Ar$, and $^{38}Ar/^{36}Ar$ ratios are <0.94%, <0.07%, <0.328%, <0.0614%, and <0.0945%, respectively. Further details on the type and analytical uncertainty of adopted standards and their reproducibility over time and blank levels can be found in Rizzo et al. (2018) that followed analogous protocols.

Abundances of He (^{3}He, ^{4}He), Ne (^{20}Ne, ^{21}Ne, ^{22}Ne) and Ar (^{36}Ar, ^{40}Ar and $^{40}Ar^{*}$) isotopes are determined. $^{3}He/^{4}He$ ratios are reported as R/Ra (where R is the $^{3}He/^{4}He$ ratio of the sample and Ra the $^{3}He/^{4}He$ ratio of air = 1.384×10^{-6}; Clarke et al., 1976). Although most of the samples showed low atmospheric contamination (air has $^{4}He/^{20}Ne = 0.318$, $^{20}Ne/^{22}Ne = 9.8$, $^{21}Ne/^{22}Ne = 0.029$, and $^{40}Ar/^{36}Ar = 295.5$; Ozima and Podosek, 2001), $^{3}He/^{4}He$ was corrected for contamination based on the measured $^{4}He/^{20}Ne$ ratio as follows:

$$Rc/Ra = ((R_M/Ra)(He/Ne)_M - (He/Ne)_A)/((He/Ne)_M - (He/Ne)_A) \qquad \text{eq. 1}$$

where subscripts M and A refer to measured and atmospheric theoretical values, respectively. The corrected $^{3}He/^{4}He$ ratios are reported as Rc/Ra values. However, the correction was either small or negligible for most of the samples.

^{40}Ar was corrected for air contamination ($^{40}Ar^{*}$) assuming that the measured ^{36}Ar was entirely of atmospheric origin as follows:

$$^{40}Ar^{*} = {}^{40}Ar_{sample} - [{}^{36}Ar_{sample} \times (^{40}Ar/^{36}Ar)_{air}] \qquad \text{eq. 2}$$

189 $$^{40}Ar_{air} = {}^{40}Ar_{sample} - {}^{40}Ar \quad \text{eq. 3}$$

190

191 After noble gas analysis, seven aliquots with the highest concentrations of CO_2 (2 aliquots of Ol, 4 of Opx and
192 1 of Cpx) were selected to determine the carbon isotopic composition of FI ($^{13}C/^{12}C$) in the stable isotopes
193 laboratory of INGV-Palermo. Selected crystals were cleaned in an ultrasonic bath in 10% HCl, weighed and
194 loaded in a crusher system consisting of a stainless- steel sample holder, a hydraulic press (which exerts a
195 single-step pressure of approximately 200 bar), a glass sampler to freeze CO_2, and a pump to ensure the vacuum
196 (10^{-3} - 10^{-4} mbar) inside the system. During crystals crushing, a glass sampler submerged in liquid nitrogen
197 was maintained online to freeze CO_2, and eventually, those gaseous species condensing at a temperature ≥-
198 196°C. Subsequently, the sampler was connected to a glass line equipped with a 626B Baratron® Absolute
199 Capacitance Manometer MKS (measuring range 10^{-3}–10 mbar), for the purification procedure and
200 quantification of CO_2 concentration (mol/g). The purified CO_2 was condensed in the same glass sampler
201 (adjusted to atmospheric pressure by adding pure helium) and transferred to the laboratory of stable isotopes
202 for the following isotopic measurements. The measured $^{13}C/^{12}C$ ratios are expressed in parts per mil (‰;
203 relative to the V-PDB international standard) using the delta notation ($\delta^{13}C$). The analytical error estimated as
204 2σ was better than 0.6‰. Further details on the adopted analytical procedure can be found in Gennaro et al.
205 (2017) and Rizzo et al. (2018) that followed analogous protocols.

206

207 **4. RESULTS**

208 The elemental and isotopic compositions of noble gases and CO_2 in El Hierro mantle xenoliths are reported in
209 Table 1. FI composition is dominated by CO_2, as found previously (Oglialoro et al., 2017). CO_2 exhibits a
210 broad positive correlation with noble gas and nitrogen concentrations (Fig. S1). Both CO_2 estimates, during
211 noble gases analysis and CO_2 isotopic determinations (see Table 1), are similar and vary from $5.31x10^{-10}$ to
212 $2.17x10^{-6}$ mol/g. The highest CO_2 concentrations are observed in Cpx (from $7.70x10^{-8}$ to $2.17x10^{-6}$ mol/g),
213 followed by Opx (from $1.65x10^{-8}$ mol/g to $6.92x10^{-7}$ mol/g) and Ol (from $5.31x10^{-10}$ mol/g to $8.45x10^{-8}$ mol/g).
214 $^4He/^{20}Ne$ ratios vary between 5.9 and 776.1, with the lowest values measured in sample 1.1 (Opx and Cpx) and
215 sample 1.23 Cpx. These samples also have low Rc/Ra (<6) and $^4He/^{40}Ar^*$ (<0.07) values, indicating isotopic

fractionation during diffusive He loss from FI (see SM1 for details). These samples are thus disregarded in the further discussion below. The remaining sample aliquots exhibit Rc/Ra values in the 7 to 8 Ra range within the MORB range (Graham, 2002). The $^{40}Ar/^{36}Ar$, $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios values range from 805.0 to 5328.4, from 9.84 to 10.49, and from 0.0286 to 0.0330, respectively. The spread of Ar and Ne isotopic signatures is well reproduced by mixing between a depleted mantle (MORB) source and an atmospheric component (see SM2 for details). The isotopic composition of CO_2 (expressed as $\delta^{13}C = R_{Sample}/R_{Standard} - 1$, where $R = {}^{13}C/{}^{12}C$ and the standard is the Vienna Pee Dee Belemnite, VPDB) reveals the highest $\delta^{13}C$ values in Ol (-0.19‰ and +0.96‰), while Opx and Cpx exhibit somewhat more negative compositions, ranging from -2.38‰ to -1.23‰. These C isotope compositions are well above the typical depleted mantle (MORB) range (Sano and Marty, 1995).

5. DISCUSSION

5.1. A depleted mantle noble gas signature for the El Hierro mantle source beneath and the Canary archipelago

The average (mean±std deviation) Rc/Ra measured in El Hierro mantle xenoliths is 7.45±0.26 Ra (Fig. 2). This value is comparable to the $^{3}He/^{4}He$ values reported in lava phenocrysts and cumulates from the same island (7.66±0.35 Ra; Fig. 2A), and slightly below the maximum Rc/Ra value measured in groundwater samples during the 2011-2012 volcanic unrest (~8.2 Ra; Padrón et al., 2013). Averaging these results, we infer the mean $^{3}He/^{4}He$ signature for El Hierro at 7.58±0.34 Ra, which we consider representative of the source mantle. This signature is classically MORB-like, confirming previous indications of a dominant Depleted MORB Mantle (DMM) source (Day and Hilton, 2011, 2020). Therefore, as additionally implied by Ne and Ar isotopes (Fig. S2), we find no evidence of primordial noble gas contribution from the lower mantle, as found instead in the high (Rc/Ra >9) volcanic gases from La Palma (see Table S1). As discussed in Day and Hilton (2011), the MORB-like Rc/Ra values are evidence for the El Hierro source mantle having been scarcely impacted by any crustal He addition during past (ancient, 1-2 Ga) oceanic crust/lithosphere subduction events (implied by the HIMU magma affinity; Hofmann, 1997). It is well possible, instead, that Ne and Ar (being well more abundant in air and air-saturated seawater than He) are better records of paleo-subduction(s) events,

considering that the MORB-air mixing arrays (see SM2 and Fig. S2) may well reflect recycling of atmospheric gases in the slab. The stable $^{3}He/^{4}He$ ratios at El Hierro (Fig. 3B) point to a temporally invariant mantle source during the last million years (i.e., since the early Pleistocene).

5.2. Implications for isotopic variations along the Canary archipelago

We put our El Hierro results in a more general context by comparing them with a suitably revised catalogue of $^{3}He/^{4}He$ ratios measured along the Canary Islands (fumaroles, groundwater, bubbling gas and FI information from lavas, cumulates, carbonatites, and mantle xenoliths; Table S1, Figs. 2B, 3 and S3). This revised dataset is built together after filtering out samples affected by secondary processes (diffusive fractionation, cosmogenic and radiogenic ingrowth of helium) and whose pristine isotopic signature may thus have been compromised (see SM1 for details). Statistical treatment of the data (Fig. 3A) allows further refinement of this data filtering, based on the criteria described in SM3. The resulting (after data filtering) isotopic information is reported in Table S2 and Figs. 3B-3C and 4A-4B.

This comparison confirms (Day and Hilton, 2020 and references therein) the presence of a clear lower mantle component only in volcanic gases from La Palma (9.52±0.32Ra), whereas FI in phenocrysts from the same island show ratios (7.52±0.66 Ra) comparable to those from El Hierro and La Gomera (Fig. 3C). The different $^{3}He/^{4}He$ signatures of La Palma and El Hierro have been proposed to derive from mantle sources containing different proportions of (i) recycled oceanic crust and gabbroic lithosphere (ii) a deep mantle source with $^{3}He/^{4}He$ >9.7 Ra (for La Palma) and (iii) the DMM (dominant at El Hierro) (Day and Hilton, 2011, 2020). This interpretation is reasonably valid also for La Gomera that shows geochemical features similar to the westernmost islands. Further to the east, from Tenerife to Lanzarote, the $^{3}He/^{4}He$ ratios decrease at the lower end of the MORB range or even below (Fuerteventura and Lanzarote).

Based on Sr-Nd-Pb-Os isotopic systematics, the lower $^{3}He/^{4}He$ values in Tenerife and eastern Canary have been suggested to derive from increasing contributions from an enriched mantle (EM) derived from the incorporation of the continental lithospheric mantle from the West African margin (Hoernle et al., 1991; Simonsen et al., 2000; Gurenko et al., 2006); Sr-Nd-Pb isotopes in carbonatites from Fuerteventura also support the existence of such enriched mantle component (Carnevale et al., 2021). While not ruling out this

possibility, we also consider the possible role of ascending magma interactions with the oceanic crust, whose thickness progressively increases eastward (Fig. 3C). As evident in Fig. 3C, the progressive eastward decrease of the Rc/Ra values that starts in Tenerife (in both volcanic gases and FI) is paralleled by a corresponding marked increase in crustal thickness (Martinez-Arevalo et al., 2013). Based on this evidence, we argue that the $^{3}He/^{4}He$ signature presently observed in samples from Tenerife, Gran Canaria, Fuerteventura, and Lanzarote may also be controlled by the addition of crustal He during magma-crust interactions. This inference is plausible if we consider that ascending melts are more prone to be contaminated by the assimilation of crustal-derived radiogenic ^{4}He, lowering the original $^{3}He/^{4}He$ values. Accordingly, the high $^{3}He/^{4}He$ values observed mostly in El Hierro and La Palma, but also in La Gomera, would reflect a minimal contribution of crustal materials. Sr-Nd-Pb-O isotopic ratios indicate crustal assimilation is negligible in lavas erupted from El Hierro and La Palma (Gurenko et al., 2006; Day et al., 2010). Instead, volcanic rocks from Gran Canaria and carbonatites from Fuerteventura bring evidence of 5-8% and 10-20% of crustal assimilation, respectively (Thirlwall et al., 1997; Hoernle, 1998; Demény et al., 1998; Gurenko et al., 2006; Day et al., 2010), which could justify the lowering of their $^{3}He/^{4}He$ values.

Magma ageing also can change the abundance of helium isotopes and can be invoked to explain the low $^{3}He/^{4}He$ ratios observed in magmatic rocks from the eastern Canary Islands. As discussed by several authors, when magma ponds in the crust for a long time, the $^{3}He/^{4}He$ ratios eventually decrease due to the accumulation of radiogenic ^{4}He over time (Torgersen and Jenkins, 1982; Hilton et al., 1993; Burnard, 2013). In the case of Gran Canaria, it is possible to estimate the production of radiogenic ^{4}He in magmas based on the U and Th abundances reported in basaltic rocks (Ballentine and Burnard, 2002). Considering an average concentration of 0.8 ppm and 3.4 ppm for U and Th, respectively (Thirlwall et al., 1997), the quantity of ^{4}He produced in Gran Canaria magmas would be 8.93×10^{-18} mol/g*yr. Although no information about magma residence time has been reported in the literature, van den Bogaard et al. (1988) proposed an eruptive periodicity of 0.05 Ma, which is closely connected with periods of differentiation and recharge of magma reservoirs. Thus, assuming a starting Rc/Ra = 8, a ^{4}He concentration of 2.5×10^{-12} mol/g (the maximum concentration reported in volcanic rocks in Canary Islands, Fig. 2) and the above ^{4}He production rate, we conclude that a crustal residence time between 0.05 and 0.06 Ma is sufficient to lower the initial $^{3}He/^{4}He$ to 6.96 Ra, which agrees well with the values reported for Gran Canaria basalts (~6.69 $\pm$ 0.46 Ra).

298 We reiterate our interpretation is no alternative to and does not intend to dismiss earlier models (Hoernle et
299 al., 1991; Simonsen et al., 2000; Gurenko et al., 2006) that emphasise the role of mantle heterogeneity. Any
300 contribution of crustal He may, in fact, contribute to additionally lowering the $^{3}He/^{4}He$ values of lavas derive
301 from an already enriched (EM) mantle source. We argue that additional work on FI in mantle xenoliths is
302 needed (especially in La Palma, Tenerife, Gran Canaria, Lanzarote, and Fuerteventura) in order to quantify
303 better the relative roles played by crustal interactions and mantle heterogeneities (a continental lithospheric
304 component in the mantle source) in this portion of the Canary Islands. Mantle xenoliths are indeed much better
305 proxies of the source mantle than lavas, in which a role of shallow crustal processes is often more challenging
306 to dismiss.

307

308 ***5.3. Recycled CO_2 in the mantle source***

309 Our results thus bring no evidence of a recycled crustal He component in the El Hierro mantle source. This
310 contrasts with our El Hierro CO_2 isotopic measurements that, being the first FI results for Canary Islands,
311 points to a ^{13}C-enriched mantle source (Fig. 4). We find that both olivines and pyroxenes exhibit higher $\delta^{13}C$
312 values than the classical MORB range ($-8‰ < \delta^{13}C < -4‰$; Sano and Marty, 1995), and approaching those
313 of crustal carbonate reservoirs (Marty and Jambon, 1987; Sano and Marty, 1995). Our mantle xenolith results
314 are unique for the Canary Islands, as previous isotopic compositions of CO_2 ($\delta^{13}C$) have only been obtained
315 for volcanic gases and groundwaters (from La Palma and Tenerife) and for some carbonatites (from
316 Fuerteventura) (see Table S1 and Fig. 4). In the remaining Islands, no $\delta^{13}C$ information is available due to the
317 lack of surface gas emissions and the technical challenges in extracting CO_2 from (and measuring $\delta^{13}C$ in) FI
318 in lavas.

319

320 The El Hierro FI results demonstrate a crustal C component in the source mantle, previously un-identified in
321 volcanic gases/groundwater studies in the region (Fig. 4). When comparing our $\delta^{13}C$ values with either Rc/Ra
322 (Fig 4A) and $CO_2/^{3}He$ (Fig. 4B), the pyroxene-hosted FI fall along a MORB-Limestone mixing line, pointing
323 to a carbonate component in the local mantle. For comparison, volcanic gases from La Palma and Tenerife
324 exhibit $CO_2/^{3}He$ and $\delta^{13}C$ values that, although consistent with a mixing MORB-Limestone (Fig. 4B), have

less extreme compositions, in which thus the crustal C contribution is much less manifest. Besides, in the case of groundwaters from Tenerife and La Palma, the low Rc/Ra and more negative $\delta^{13}C$ values suggest the addition of crustal-derived radiogenic ^{4}He and organic carbon, as well the fractionation of carbon during CO_2 dissolution in water (Fig. 4A).

The olivine-hosted El Hierro FI exhibit even more extreme ^{13}C-rich compositions ($\delta^{13}C$ values of -0.19‰ and +0.96‰) (Fig. 4). Unlike pyroxenes from El Hierro and volcanic gases from Tenerife and La Palma, these unusually positive olivine results cannot result from a classical MORB-limestone mixing (Fig. 4A). In line with the HIMU affinity of the El Hierro mantle source (Day et al., 2010; Day and Hilton, 2011), we propose, instead, that this positive $\delta^{13}C$ signature derives from the addition to the local mantle of recycled crustal carbon transported by old subducted altered oceanic crust (AOC) and/or oceanic lithosphere (OL) (Fig. 4). Recycled AOC and OL components are essential carriers of crustal carbon into the mantle during subduction (Li et al., 2019; Plank and Manning, 2019). This is because AOC and OL precipitate carbonates during hydrothermal alteration at mid-ocean ridges (Alt and Teagle, 1999; Alt et al., 2013). Li et al. (2019) and references therein report the existence of carbonates in AOC and OL with $\delta^{13}C$ values as low as -24‰ and as high as +10.3‰, where the extremely positive $\delta^{13}C$ values result from the inorganic reduction of CO_2 to methane by either abiotic or biotic processes (Alt and Shanks, 2003) or microbial methanogenesis (Kenward et al., 2009). We show in Fig. 4 model binary mixing lines between MORB and AOC/OL, drawn by considering the range of $\delta^{13}C$ carbonate signatures observed in Li et al., (2019). In particular, from the dataset reported by Li et al., (2019), we select the isotopic compositions of two carbonates contained in AOC and two carbonates contained in OL, being characterised by different ages. Carbonates in AOC and OL older than 85 Ma exhibit $\delta^{13}C$ values as high as +3.5‰ and +2.1‰, respectively, while carbonates in AOC and OL younger than 85 Ma exhibit $\delta^{13}C$ as high as +4.7‰ and +10.9‰, respectively (Li et al., 2019). The Rc/Ra and $CO_2/^{3}He$ compositions of the AOC/OL end-member are unfortunately undetermined. For the sake of illustration, these AOC/OL components are here assumed (Fig. 4) to have Rc/Ra and $CO_2/^{3}He$ ratios corresponding to those of crustal limestones (0.01 Ra and 1.0×10^{13}, respectively), which is likely to be very rough assumption as, for example, CO_2 and He can undergo fractionation during eclogite formation and melting in the slab. Ultimately, the calculated mixing curves fit the $\delta^{13}C$ values measured in olivines well, supporting the presence of C-rich fluids derived from

353 recycled AOC and/or OL in the mantle beneath El Hierro (Fig. 4). We caution, however, that the AOC / OL
354 end-member can in fact sit in any position along the depicted mixing curve(s), so that (in the most extreme
355 case) the olivines may have recorded the eclogitic component fully (e.g., with no dilution from the MORB).
356
357 The existence of a C-rich component underneath El Hierro is strongly supported by petrological and FI
358 evidence on the same suite of mantle xenoliths (Oglialoro et al., 2017; Remigi et al., 2019; Colombo, 2020).
359 According to these authors, the presence of high-density CO_2-N_2 FI and interstitial microveins composed of
360 silicate glass (andesitic-trachytic in composition) and carbonate droplets (calcite and Mg-calcite) are evidence
361 of mantle metasomatism caused by deep infiltration of volatile-rich, carbonate-silicate melts, likely derived
362 from carbonated-eclogite melting at high pressure (Remigi et al., 2019). Mantle metasomatism by C-rich
363 (either carbonatitic or carbonate-silicate) melts underneath the Canary Islands has recurrently been described
364 earlier at El Hierro (Neumann, 1991) and in nearby islands (Frezzotti et al., 2002a, 2002b; Neumann, 2004).
365 The timing of the paleo-subduction event(s) of AOC-OL recycling is difficult to determine. However, it may
366 coincide with fossil subduction(s) (1-2 Ga old) responsible for the recycling of old oceanic crust and
367 lithosphere, invoked to support the HIMU mantle signature underneath El Hierro and La Palma (e.g., Hoernle
368 et al., 1991; Gurenko et al., 2006; Day et al., 2010; Day and Hilton, 2011, 2020).
369

370 **6. CONCLUDING REMARKS**

371 We have reported on the first FI-based $\delta^{13}C$ evidence for a recycled carbon component in the source mantle
372 feeding El Hierro volcanism. To the best of our knowledge, this is the first direct isotopic evidence for C-rich
373 metasomatic melts having modified the composition of the local mantle, perhaps in response to the past (old,
374 1-2 Ga old) oceanic subduction events that are implicated by the HIMU affinity of the mantle/magmas.

375 Pyroxene- and olivine-hosted FI record such infiltration of crustal C-rich melts in the mantle but exhibit
376 different extents of ^{13}C enrichment. The cause of this isotopic dissimilarity in the El Hierro xenolith mineral
377 suite is unknown. Some C isotopic fractionation may occur during mineral-melt-exsolved fluid interaction
378 deep in the mantle.

He, Ar and Ne systematics in our xenoliths confirm a depleted mantle (DMM-type) signature for the lithospheric mantle beneath El Hierro, in agreement with $^{3}He/^{4}He$ signatures previously reported for groundwater and lava-hosted FI. This helium isotopic signature of El Hierro persists in time, suggesting a homogeneity in the local mantle composition at least over the last million years. This MORB-like signature argues against a primordial He source affecting the local lithospheric mantle and suggests a marginal He slab transport during past subduction events. The more radiogenic He signature in the eastern Canary Islands may reflect a combination of an EM source, magma ageing and/or assimilation of radiogenic He upon magma ascent in the crust.

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Figure Captions

Figure 1. The Canary Islands archipelago and sampling locality in El Julan Cliff Valley at El Hierro. Modified from Anguita and Hernán (2000), Oglialoro et al. (2017) and Day and Hilton (2020). $^{3}He/^{4}He$ and $\delta^{13}C$ values are from Tables 1 and S3. Ages in Ma represent the maximum ages reported in lavas for each Island (see Day et al., 2010). The path of the Canary hotspot was traced based on Holik et al. (1991) and Carracedo et al. (1998).

Figure 2. ^{4}He vs Rc/Ra ratios ($^{3}He/^{4}He$ ratio corrected for atmospheric contamination) measured in FI. MORB range is reported at Rc/Ra = 8 ± 1 (Graham, 2002). White symbols are lava phenocrysts, the outline colours represent the island where the sample comes from (see legend). Purple asterisks represent the bulk ^{4}He concentrations and Rc/Ra values measured in ultramafic xenoliths from Lanzarote (see Table S1). A) The dotted blue line represents the maximum $^{3}He/^{4}He$ ratio reported in groundwater samples during the volcanic unrest of 2012 at El Hierro (Padrón et al., 2013). B) An arbitrary cut-off value is proposed at 9.0×10^{-14} mol/g (see section SM3).

Figure 3. A) Histogram of filtered data, the resulting Rc/Ra values were classified in 11 different clasess. An arbitrary cut-off value is proposed at 5 samples per class. Detailed description of data filtering is presented in SM3. **B)** Age vs Rc/Ra ratios ($^{3}He/^{4}He$ corrected for atmospheric contamination) after data filtering. We plotted the year in which surface gases were sampled (bubbling gas, fumaroles and groundwater) and the age of the outcrop in the case of FI. **C)** Variability of Rc/Ra ratios along the Canarian archipelago. In the upper part of the graph, we designed the thickness of the oceanic crust beneath the Canary Islands based on the seismic information presented by Martinez-Arevalo et al. (2013). EH: El Hierro, LP: La Palma, LG: La Gomera, T: Tenerife, Ft: Fuerteventura, La: Lanzarote.

Figure 4. **A)** $\delta^{13}C$ vs Rc/Ra ($^{3}He/^{4}He$ corrected for atmospheric contamination). Dotted black lines are binary mixing curves between two endmembers: 1) Limestone at $\delta^{13}C$ =-1‰ and 1‰ and Rc/Ra= 0.01 and 2) MORB-like upper mantle at $\delta^{13}C$ = -4‰ and Rc/Ra = 7.45. The yellow square represents the variability of fumarolic samples from El Teide (Tenerife). **B)** $\delta^{13}C$ vs $CO_2/^{3}He$. Dotted black lines are binary mixing between two endmembers: 1) Limestone at $\delta^{13}C$ =-1‰ and +1‰ and $CO_2/^{3}He = 10^{-13}$ and 2) MORB-like upper mantle at $\delta^{13}C$ = -4‰ and $CO_2/^{3}He$ = 1.00 x 10^{-9} and 2.00 x 10^{-9}. Detailed description of MORB-AOC and MORB-OL binary mixing curves is presented in section 5.3. The histogram shows the number of samples (AOC-OL) reported for each $\delta^{13}C$ class; $\delta^{13}C$ values measured in AOC and OL were obtained from Li et al. (2019).

Table 1. Noble gas and CO_2 compositions of FI hosted in El Hierro mantle xenoliths. Concentrations of noble gases isotopes, CO_2 and N_2 are reported in mol/g. [A] First estimation of CO_2 contents in FI during noble gas analysis; [B] CO_2 contents and $CO_2/^3He$ ratios measured from the glass line after CO_2 isotopic determinations. Reported errors are 2σ uncertainties.

Sample	Mineral	Rock type	ID (Oglialoro et al., 2017; Colombo, 2020)	Weight (g)	^3He	^4He	^{20}Ne	^{21}Ne	^{22}Ne	CO_2[A]	N_2*[C]	^{40}Ar	^{36}Ar	^{40}Ar*[D]	$^4He/^{20}Ne$	$^4He/^{40}Ar$*	$^4He/CO_2$
1.1	Ol	Sp Lherzolite	XML3	0.52644	1.28E-17	1.28E-12	5.67E-15	1.70E-17	5.65E-16	2.68E-08	4.73E-10	9.72E-12	2.35E-15	9.03E-12	225.9	0.14	4.78E-05
1.1	Opx	Sp Lherzolite	XML3	0.12869	2.48E-18	4.03E-13	6.74E-15	2.14E-17	6.82E-16	1.65E-08	3.29E-09	7.26E-12	2.66E-15	6.48E-12	59.8	0.06	2.45E-05
1.1	Cpx	Sp Lherzolite	XML3	0.08996	1.29E-18	1.58E-13	8.39E-15	2.56E-17	8.53E-16	7.70E-08	9.66E-09	6.27E-11	1.18E-14	5.92E-11	18.9	0.003	2.06E-06
1.15	Ol	Sp Harzburgite	XML11	0.51344	3.73E-17	3.60E-12	1.13E-14	3.35E-17	1.13E-15	8.45E-08	4.11E-10	6.09E-12	2.33E-15	5.41E-12	317.9	0.67	4.26E-05
1.15	Opx	Sp Harzburgite	XML11	0.11766	1.38E-17	1.42E-12	2.25E-14	6.73E-17	2.28E-15	4.20E-07	5.08E-09	1.37E-11	1.13E-14	1.03E-11	62.8	0.14	3.37E-06
1.15	Cpx	Sp Harzburgite	XML11	0.05385	3.62E-17	3.55E-12	2.73E-14	7.92E-17	2.79E-15	3.33E-07	4.70E-09	1.76E-11	2.18E-14	1.11E-11	129.9	0.32	1.07E-05
1.2	Ol	Sp Lherzolite	XML6	0.52471	4.80E-17	4.32E-12	7.10E-15	2.19E-17	7.06E-16	6.73E-09	8.79E-11	6.89E-12	6.24E-15	5.04E-12	608.5	0.86	6.42E-04
1.2	Opx	Sp Lherzolite	XML6	0.10331	4.72E-17	4.39E-12	1.06E-14	3.30E-17	1.05E-15	1.37E-07	4.42E-09	2.25E-11	4.98E-15	2.10E-11	415.8	0.21	3.21E-05
1.2	Cpx	Sp Lherzolite	XML6	0.04105	8.66E-17	8.21E-12	1.45E-14	4.49E-17	1.42E-15	8.12E-07	1.18E-08	1.33E-10	3.35E-14	1.24E-10	565.4	0.07	1.01E-05
1.22	Ol	Sp Lherzolite	XML8	0.50752	7.62E-18	7.66E-13	9.87E-16	3.10E-18	9.38E-17	5.31E-10	4.89E-11	1.31E-12	8.91E-16	1.04E-12	776.1	0.73	1.44E-03
1.22	Opx	Sp Lherzolite	XML8	0.31254	3.26E-17	3.29E-12	6.44E-15	1.91E-17	6.48E-16	5.59E-08	1.95E-09	3.91E-12	3.74E-15	2.81E-12	511.8	1.17	5.89E-05
1.23	Ol	Sp Harzburgite	XML5	0.50783	2.58E-17	2.49E-12	1.24E-14	3.74E-17	1.24E-15	4.38E-08	6.77E-10	4.92E-11	9.48E-15	4.64E-11	200.7	0.05	5.69E-05
1.23	Opx	Sp Harzburgite	XML5	0.10976	1.80E-17	1.71E-12	2.59E-14	7.87E-17	2.61E-15	4.13E-07	5.74E-09	3.55E-11	1.13E-14	3.22E-11	66.0	0.05	4.14E-06
1.23	Cpx	Sp Harzburgite	XML5	0.058	3.64E-18	4.93E-13	8.37E-14	2.50E-16	8.53E-15	5.19E-07	4.57E-09	4.47E-11	5.41E-14	2.87E-11	5.9	0.02	9.50E-07
1.3	Ol	Sp Harzburgite	-	0.52935	3.76E-17	3.57E-12	6.05E-15	1.82E-17	6.03E-16	5.75E-09	n.a	6.39E-12	6.12E-15	4.58E-12	589.8	0.78	6.20E-04
1.3	Opx	Sp Harzburgite	-	0.10888	7.71E-17	7.27E-12	3.62E-14	1.07E-16	3.63E-15	6.92E-07	8.23E-09	2.83E-11	1.43E-14	2.40E-11	200.7	0.30	1.05E-05
1.3	Cpx	Sp Harzburgite	-	0.05363	2.26E-16	2.13E-11	3.37E-14	1.06E-16	3.33E-15	2.17E-06	4.02E-08	5.81E-11	3.26E-14	4.85E-11	631.8	0.44	9.78E-06

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Table 1. Continued.

Sample	Mineral	R/Ra	Rc/Ra [E]	Error (+/-)	$^{40}Ar/^{36}Ar$	Error (+/-)	$^{38}Ar/^{36}Ar$	Error (+/-)	$^{20}Ne/^{22}Ne$	Error (+/-)	$^{21}Ne/^{22}Ne$	Error (+/-)	$CO_2/^3He$	$^3He/^{36}Ar$	CO_2 [B]	$CO_2/^3He$ [B]	$\delta^{13}C$ (‰)
1.1	Ol	7.20	7.21	0.16	4141.0	0.0	0.1880	0.0007	10.11	0.07	0.0304	0.00106	2.09E+09	5.47E-03	n.a	n.a	n.a
1.1	Opx	4.41	4.43	0.25	2734.4	97.7	0.1880	0.0007	10.04	0.16	0.0319	0.00249	6.64E+09	9.33E-04	n.a	n.a	n.a
1.1	Cpx	5.76	5.85	0.57	5328.4	76.0	0.1946	0.0008	9.87	0.14	0.0302	0.00161	5.98E+10	1.09E-04	n.a	n.a	n.a
1.15	Ol	7.44	7.45	0.15	2620.4	0.0	0.1831	0.0007	9.99	0.04	0.0296	0.00081	2.26E+09	1.60E-02	5.53E-08	1.48E+09	0.96
1.15	Opx	6.98	7.01	0.21	1210.0	11.8	0.1864	0.0007	9.94	0.06	0.0297	0.00120	3.04E+10	1.22E-03	2.75E-07	1.99E+10	-1.23
1.15	Cpx	7.33	7.34	0.21	805.0	6.4	0.1908	0.0007	9.84	0.11	0.0286	0.00121	9.19E+09	1.66E-03	n.a	n.a	n.a
1.2	Ol	7.99	7.99	0.15	1103.1	0.0	0.1848	0.0007	10.12	0.05	0.0312	0.00095	1.40E+08	7.69E-03	n.a	n.a	n.a
1.2	Opx	7.72	7.73	0.18	4516.6	76.2	0.2005	0.0008	10.40	0.13	0.0325	0.00230	2.90E+09	9.48E-03	2.67E-07	5.65E+09	-1.43
1.2	Cpx	7.59	7.59	0.20	3979.1	39.8	0.1654	0.0005	10.43	0.24	0.0323	0.00245	9.38E+09	2.58E-03	n.a	n.a	n.a
1.22	Ol	7.16	7.16	0.17	1465.4	0.0	0.1764	0.0006	10.49	0.24	0.0330	0.00390	6.96E+07	8.55E-03	n.a	n.a	n.a
1.22	Opx	7.11	7.11	0.16	1044.6	12.7	0.1861	0.0007	9.98	0.09	0.0296	0.00143	1.72E+09	8.70E-03	n.a	n.a	n.a
1.23	Ol	7.46	7.47	0.15	5187.2	0.0	0.2002	0.0008	10.09	0.04	0.0304	0.00081	1.69E+09	2.73E-03	1.28E-08	4.95E+08	-0.19
1.23	Opx	7.52	7.55	0.19	3137.1	37.6	0.1957	0.0008	10.01	0.07	0.0304	0.00136	2.30E+10	1.59E-03	3.64E-07	2.03E+10	-2.38
1.23	Cpx	5.07	5.32	0.40	826.7	2.9	0.1877	0.0007	9.84	0.06	0.0295	0.00076	1.42E+11	6.74E-05	n.a	n.a	n.a
1.3	Ol	7.58	7.59	0.15	1043.7	0.0	0.1846	0.0007	10.05	0.07	0.0303	0.00118	1.53E+08	6.15E-03	n.a	n.a	n.a
1.3	Opx	7.62	7.63	0.17	1975.5	12.8	0.1887	0.0007	10.04	0.06	0.0297	0.00109	8.98E+09	5.39E-03	5.09E-07	6.60E+09	-1.94
1.3	Cpx	7.65	7.66	0.16	1780.7	10.5	0.1888	0.0007	10.18	0.09	0.0321	0.00161	9.60E+09	6.94E-03	9.47E-07	4.19E+09	-1.94

C. N_2*: N_2 values corrected for atmospheric contamination during the simultaneous extraction of CO_2 and noble gases.

D. ^{40}Ar*:^{40}Ar values corrected for atmospheric contamination. $^{40}Ar^* = {}^{40}Ar_{sample} - ({}^{36}Ar_{sample} \cdot ({}^{40}Ar/{}^{36}Ar)_{air})$. Where $^{40}Ar/^{36}Ar_{air} = 295.5$

E. Rc/Ra: R/Ra ratio corrected for atmospheric contamination. $Rc/Ra = ((R/Ra)_{sample} * ({}^4He/{}^{20}Ne)_{sample} - ({}^4He/{}^{20}Ne)_{air})/(({}^4He/{}^{20}Ne)_{sample} - ({}^4He/{}^{20}Ne)_{air})$. Where $^4He/^{20}Ne_{air} = 0.318$

670

Figure 1

Click here to access/download;Figure;Figure 1.tif

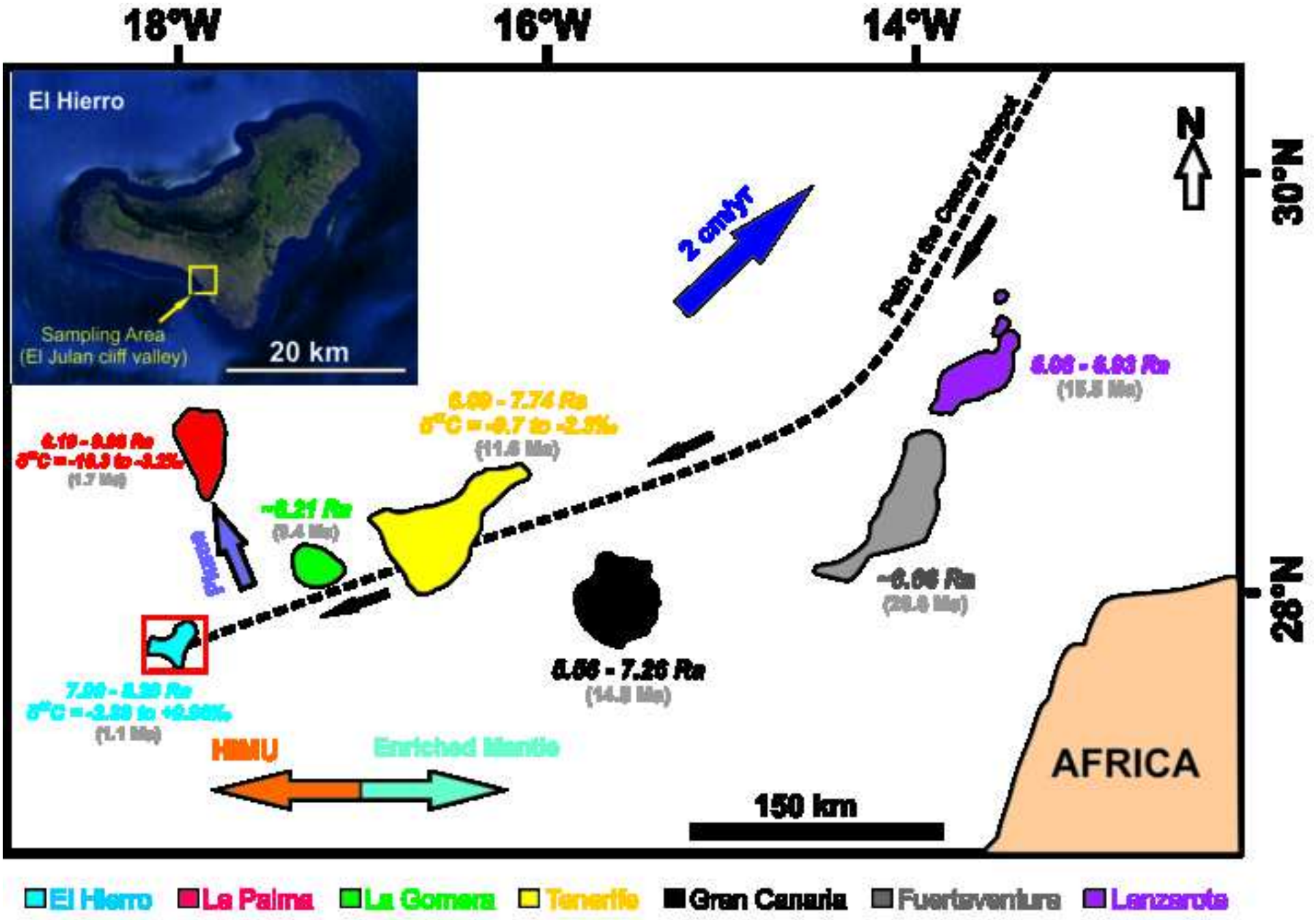

Figure 2

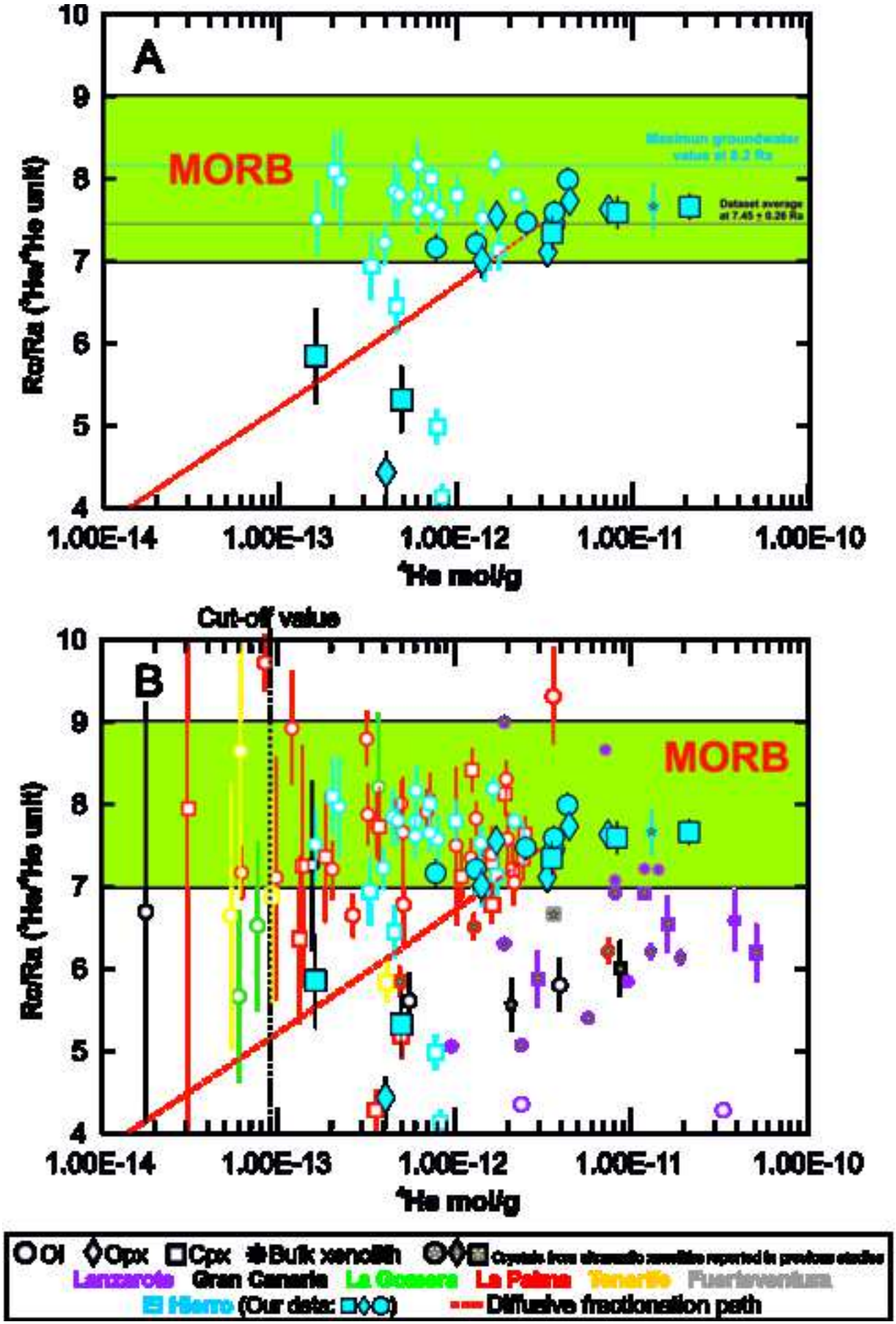

Figure 3

Click here to access/download;Figure;Figure 3.tif

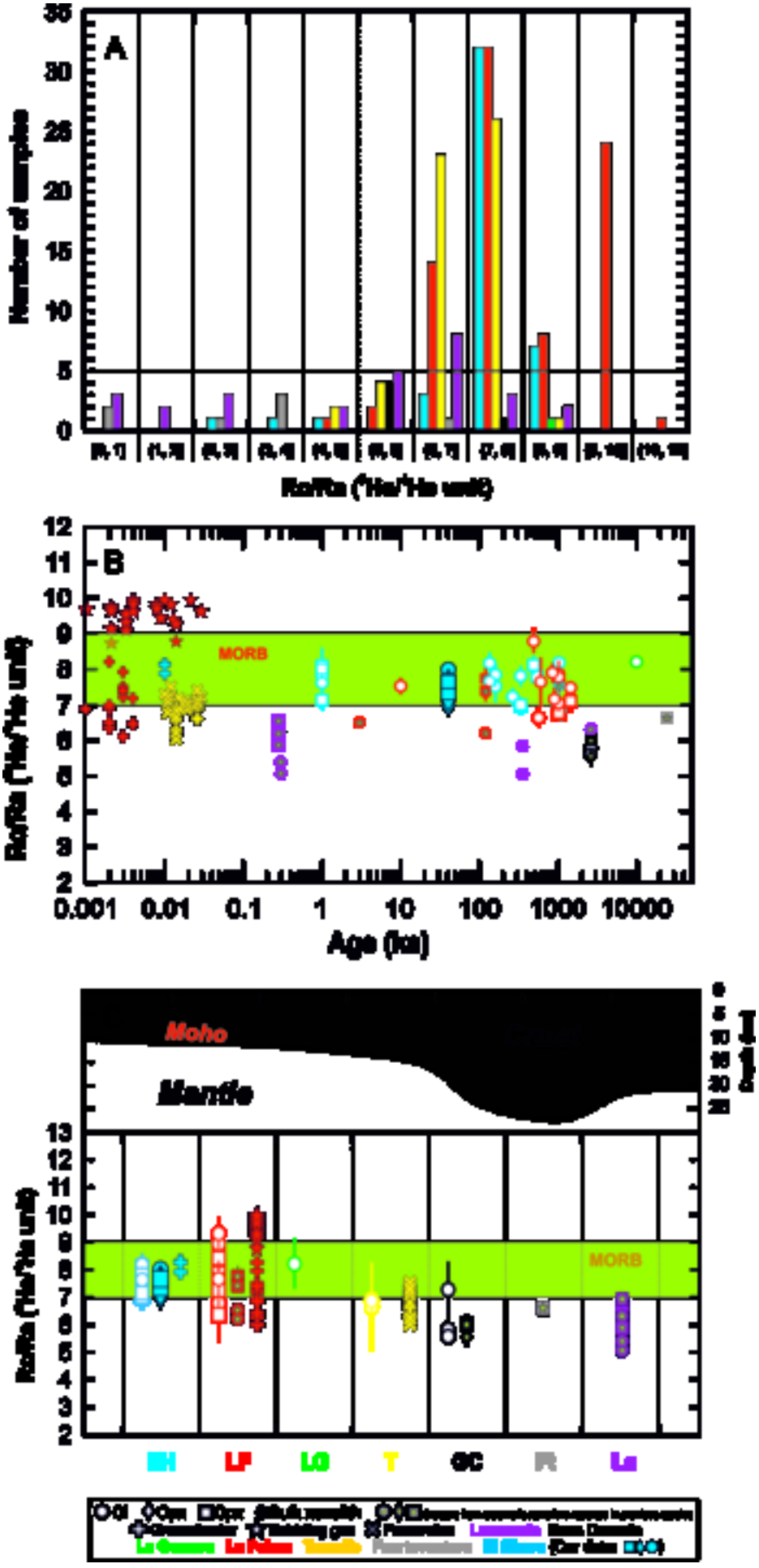

Figure 4

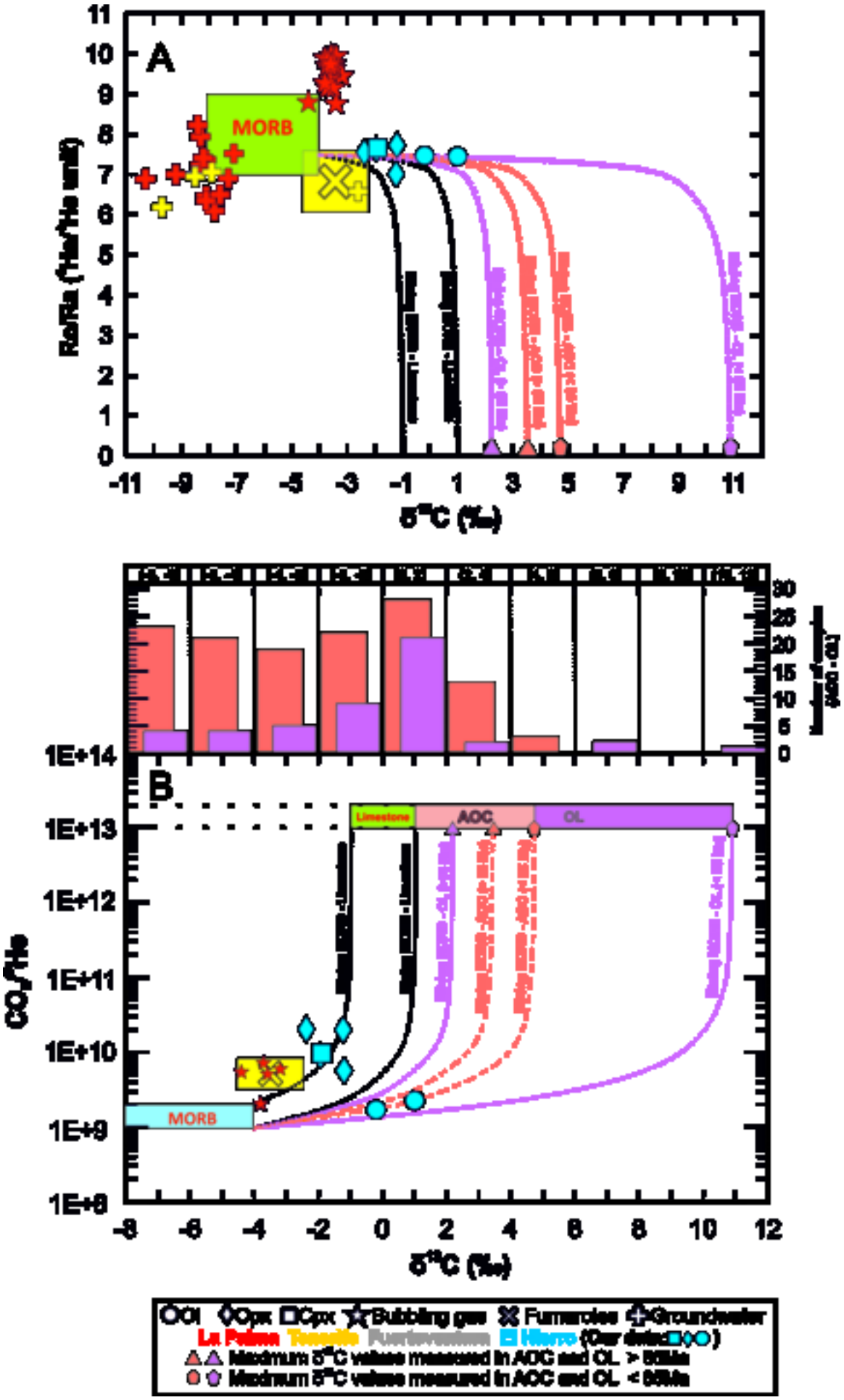

Table S1

Supplementary material/Appendix (Files for online publication only)

Table S1.xlsx

Table S2

Supplementary material/Appendix (Files for online publication only)

Table S2.xlsx

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: