Chemical Geology

THE COMPOSITION OF FLUIDS STORED IN THE CENTRAL MEXICAN LITHOSPHERIC MANTLE: INFERENCES FROM NOBLE GASES AND CO2 IN MANTLE XENOLITHS
--Manuscript Draft--

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Abstract:	We present the first isotopic (noble gases and CO2) characterization of fluid inclusions coupled to Raman microspectroscopy analyses in mantle xenoliths from Central Mexico, a geodynamically complex area where the Basin and Range extension was superimposed on the Farallon subduction (terminated at 28 Ma). To characterize the isotopic signature of the Central Mexican lithospheric mantle, we focus on fluid inclusions entrapped in mantle xenoliths found in deposits of the Joya Honda maar (JH), a Quaternary monogenetic volcano belonging to the Ventura Espiritu Santo Volcanic Field (VESVF) in the state of San Luis Potosí (central Mexico). Thirteen ultramafic plagioclase-free xenoliths were selected, all exhibiting a paragenesis Ol> Opx> Cpx >> Sp, and being classified as spinel-lherzolites and harzburgites. All xenoliths bring textural evidence of interstitial glass veins bearing dendritic trails of secondary melt and fluid inclusions (composed of silicate glass ± CO2 ± Mg-Ca carbonates ± pyrite). These are related to pervasive mantle metasomatism driven by carbonate-rich silicate melt. The Ar and Ne systematics reflect mixing between MORB-like upper mantle and atmospheric fluids, the latter interpreted as reflecting a recycled air component possibly inherited from the Farallon plate subduction. The 3He/4He ratios vary between 7.13 and 7.68 Ra, within the MORB range (7-9 Ra), and the 4He/40Ar* ratios (0.4 - 3.11) are similarly close to the expected range of the fertile mantle (1-5). Taken together, these pieces of evidence suggest that (i) either the mantle He budget was scarcely modified by the Farallon plate subduction, and/or (ii) that any (large) crustal contribution was masked by a later metasomatism/refertilization episode, possibly during the subsequent Basin and Range extension. A silicate melt-driven metasomatism/refertilization (revealed by the association between glass veins and fluid inclusions) is consistent with calculated helium residence time for the Mexican lithospheric mantle (20 to 60Ma) that overlaps the timing of the above geodynamic events. We propose that, after the refertilization event (e.g., over the last ~20Ma), the lithospheric mantle has evolved in a steady-state, becoming slightly more radiogenic. We also estimated 3He fluxes (0.027 - 0.080 mol/g), 4He production rates (340 - 1000 mol/yr), and mantle CO2 fluxes (3.93 x 107 mol/yr to 1.18x108 mol/yr) using the helium isotopic values measured in JH mantle xenoliths. Finally, the JH xenoliths exhibit CO2/3He ratios comparable to those of the upper mantle (from 3.38 x 108 to 3.82x109) but more positive δ13C values (between -1.0 and -2.7‰), supporting the involvement of a crustal carbonate component. We propose that the metasomatic silicate melts recycled a crustal carbonate component, inherited by the Farallon plate subduction.

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Saemundur Ari Halldórsson,
Special issue - Guest editor
Chemical Geology

VSI Barry(Hilton)>>>Submission Deadline mss 1 April 2021: Earth's Volatile Cycles within the Crust-Mantle System: A volume in memory of Dave Hilton; Peter Barry (WHOI, USA), Saemi Halldorson (University of Iceland), Evelyn Furi (CRPG, France), Justin Kulongoski (USGS, USA), Gray Bebout (Lehigh, USA)

Palermo, 25 March 2021

Dears,

We wish to submit the revised manuscript (CHEMGE13694) entitled "THE COMPOSITION OF FLUIDS STORED IN THE CENTRAL MEXICAN LITHOSPHERIC MANTLE: INFERENCES FROM NOBLE GASES AND CO_2 IN MANTLE XENOLITHS" for consideration by *Chemical Geology*. Our paper will be a contribution to the special issue in memory of Dave Hilton ("Earth's Volatile Cycles within the Crust-Mantle System"). This 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 and the *Universidad Autonoma de San Luis Potosí* (Mexico).

The manuscript was modified and improved following the valuable suggestions and comments of the Reviewers. Please find attached the corresponding files.

Thank you for your consideration of this manuscript.

Sincerely,

Corresponding author.

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THE COMPOSITION OF FLUIDS STORED IN THE CENTRAL MEXICAN LITHOSPHERIC MANTLE: INFERENCES FROM NOBLE GASES AND CO_2 IN MANTLE XENOLITHS

Manuscript number: CHEMGE13694

Guest Editor (Saemundur Ari Halldórsson):

First, I thank you for submitting this interesting manuscript to this special issue of Chemical Geology honoring the memory of David Hilton. Two reviewers have now returned their evaluation of your manuscript and both provide detailed review comments. You will see that while they are overall supportive of your work, they have also raised a number of critical comments that you will need to address.

For example, one reviewer (R1) points out that some available literature on this subject is left uncited, including several key references. This same reviewer also points out that fluid-melt partitioning is not discussed as means of explaining the range of values 4/40* observed in your xenoliths.

The other reviewer (R2) expresses concern related to the structure of the manuscript and suggests some condensing of the text. Further, he suggests some rewriting of a section addressing the presence of atmospheric components as he fails to see how the dataset presented support the story presented.

We are grateful for the valuable comments and suggestions of the Reviewers. In general, we have included several key references dealing with the study of noble gases in mantle xenoliths, eg., Matsumoto et al. (1998, 2000), Hopp et al. (2004, 2007a, 2007b), Buikin et al. (2005), and Czuppon et al. (2009). We have included a discussion on the possible influence of fluid-melt partitioning on the He/Ar* measured in the mantle xenoliths.

We also revised the section "*Evidence for a recycled air component: Ne and Ar*", here we included key diagrams such as ^3He vs ^{36}Ar and $^{20}Ne/^{22}Ne$ vs $^{40}Ar/^{36}Ar$ that support the existence of a recycled atmospheric component in the Mexican lithospheric mantle, likely inherited from subduction events. We also revised the subsection "No mantle plume component in the JH mantle source" since $(^{21}Ne/^{22}Ne)_{Ext}$ suggests a contribution of plume-derived Neon (<10%).

Finally, analytical uncertainties were added and the structure of the discussion was improved, by moving in the supplementary information part of the secondary processes previously discussed and additional elaboration following the Reviewers suggestions. This allowed to condense the content of the manuscript, as recommended by Rev. 2.

Point-to-point reply to Reviewers' comments

Reviewer #1:

General remarks:

This contribution reports new and actually the first, noble gas compositions and carbon isotope compositions, of mantle xenoliths from Joya Honda, Mexico. These data are complemented by petrologic information and Raman analyses.

Basically, the presented data are of good quality, the sample descriptions are excellent and the authors also explain the geological background in a sound way. Nothing to complain about that part.

I have mainly issues with their discussion of the noble gas results, whereas all other parts are fine. There are several points that deserve a significant change. Since these changes surely will affect the discussion, and maybe the conclusions, I need to recommend a major revision, unfortunately. Otherwise, the topic and quality of data is worth of publication in Chemical Geology.

Major issues:

1) The referencing of the authors seems strange. Besides the citation of Broadley et al. 2020, which deals with extraterrestrial material (ureilites) and hardly with lithospheric mantle, the authors neglect a large body of existing literature. This would be no problem if the cited papers are i) fitting their discussed point and ii) are the "best available on the market". In case of i), for example, it is not clear what the authors want to support with their references: If you discuss infiltration of fluids from a slab into the lithosphere above, it makes not much sense to cite papers that are related to potentially plume-induced rifting processes. And if you want to check for interaction with plume-related fluids it makes no sense to use papers dealing majorily with subduction or closed-system evolution… In case of ii): The authors cite Gautheron et al. 2005 ChemGeol to use their data of European Volcanics. Note, that in the same year Buikin et al. 2005 EPSL also presented stepwise crushing data of the Eifel and the Pannonian Basin with higher precision and higher gas amounts (not surprising, because our lab, which measured these data, performed a preselection with Ar of many more xenoliths to find the most gas-rich ones). Other high quality data of samples from lithospheric mantle are presented in Matsumoto et al. 1998 (Australia); 2000 (Australia); Hopp et al. 2004 EPSL (Saudi-Arabia); 2007a ChemGeol (Saudi-Arabia); 2007b EPSL (Kenya); Czuppon et al. 2009 (Australia).

R: We agree that the reference Broadley et al. (2020) is not appropriate for this paper, therefore this was removed from the main text.

2) The impact of subduction-related atmospheric noble gases in samples of the continental lithosphere was also discussed by Matsumoto et al. 2001, who reported a correlation between 3He and 36Ar in samples of the Horoman ophiolite. Maybe you can check this for your samples with highest 40Ar/36Ar as well. This was interpreted as a co-variation of mantle gases and (subduction-related) atmospheric gases. Hopp et al. (2007a ChemGeol) also discussed a potential subduction-related contribution of atmospheric fluids to the subcontinental mantle lithosphere on the basis of observed element-fractionated atmospheric compositions (i.e. elevated 36Ar/22Ne-ratios of the atmospheric endmember). The existence of such elevated subduction-related 36Ar/22Ne-ratios was demonstrated for mantle xenoliths from the Kamchatkan mantle wedge, with nearly atmospheric Ar and Ne, but MORB-like He compositions (Hopp and Ionov, 2011 EPSL). This point is also mentioned in below in 3) in more detail.

R: A fully reply to this comment is provided in the specific point below, in which we address the issue of atmospheric gas interactions more fully. As suggested by the reviewer, we examined a possible correlation between ^{36}Ar and ^{3}He contents to properly evaluate the impact of subduction-related atmospheric fluids in our mantle xenoliths. We identified a positive correlation between ^{3}He and ^{36}Ar (samples with ^{40}Ar/^{36}Ar > 500), which supports the existence of an atmospheric component recycled in the local lithospheric mantle (see new Figure 9)

3) Subsection 6.1.1 Atmospheric contamination:

First, I would not speak of "contamination", but "interaction with atmospheric fluids".

Secondly, your remark in L.369 "We find that most of the samples exhibit low air contamination…" is misleading (I assume, you mean interaction with atmospheric gases, not "air"). Looking at your Ne-isotopes most of your data have 20Ne/22Ne < 10.5 (28 out of 33), and 10 out 33 even below a 20Ne/22Ne of 10. A 20Ne/22Ne of 10.5 would correspond to about 74% atmospheric Ne, which is not my impression of "low"… Judging from your 36Ar/22Ne-ratios most of your samples fall in a range below the air-value (18.7) with values down to 1.7, only few are higher, with maximum values of up to 64. Low Ar/Ne were reported in clays, but most studies do not show these ratios.

So, there are two explanations for it: First, your sample suite is unique and an unknown fractionation process affected your xenoliths, or secondly, your calibration gas amounts are slightly offset. No matter what's the reason, commonly subduction-related atmospheric fluids would tend to show elevated 36Ar/22Ne-ratios relative to air, simply because Ne is more prone to early loss during the subduction process. I observed in fact high atmospheric 36Ar/22Ne in Kamchatkan xenoliths (Hopp and Ionov, 2011 EPSL). In another study we detected an elevated atmospheric 36Ar/22Ne ratio admixed with mantle fluids prior to interaction with late-stage local atmospheric gases in mantle xenoliths from Saudi-Arabia and peridotites from Zabargad Island, Red Sea, that evidence subduction-related admixing of atmospheric gases (Hopp et al., 2007 ChemGeol). This is mainly based on isotope ratio considerations 40Ar/36Ar vs 20Ne/22Ne. I would recommend to include the latter diagram.

R: We thank the reviewer for his insightful comments. This part of the manuscript was extensively restructured following his suggestions:
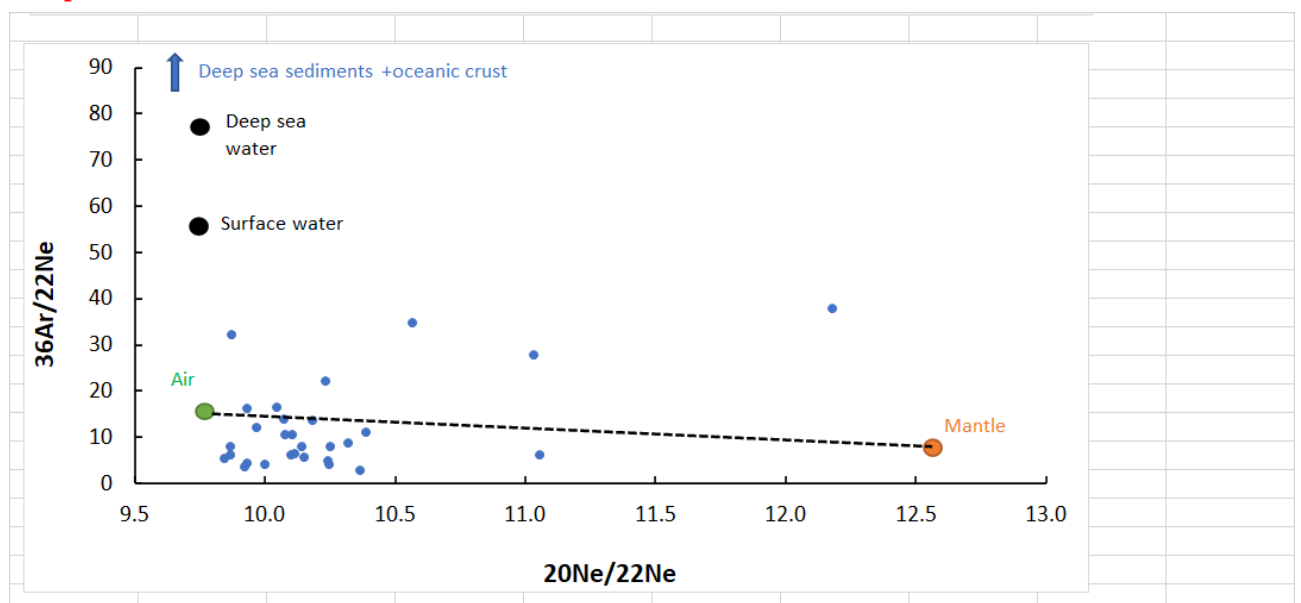
1) The title of section 6.1.1 was modified as follows: "*Interaction with atmospheric fluids and evidence for a recycled atmospheric component*"

2) We agree that the statement "*low atmospheric contamination*" was misleading since most samples exhibit $^{20}Ne/^{22}Ne$ and $^{36}Ar/^{22}Ne$ ratios close to the air values; therefore, this sentence was removed, and the text was edited as follows (see L. 362-377 of the revised manuscript):

"He, Ne and Ar systematics suggest the existence of an atmospheric component in our samples (especially in nodule V-I). In general, the measured R/Ra and $^4He/^{20}Ne$ values fall along an air-MORB mixing curve, and overlap with those measured in mantle xenoliths from the European SCLM, the West Antarctic Rift System (WARS), Eastern Australia, Red sea region and N/S Kenya rifts (Figure 7A). The existence of such an atmospheric component is corroborated by $^{40}Ar/^{36}Ar$ and $^{20}Ne/^{22}Ne$ ratios significantly below the expected MORB values (44,000 and 12.5, respectively; Burnard, 1997; Moreira, 1998; Sarda, 2004). As shown in Figure 7B, $^{40}Ar/^{36}Ar$ and $^3He/^{36}Ar$ values also fall along a two-component mixing between a MORB-like upper mantle and atmosphere (He/Ar ratios of 0.14 to 3.5 explain the whole data variability; see also Figure 9B). Likewise, samples fit the binary mixing air-MORB when using the three-isotope neon plot (Figure 7C), confirming the existence of atmospheric fluids in our inclusions. The atmospheric component is especially notable in nodule V-I that exhibits an isotopic signature close to that of air with $^4He/^{20}Ne$ ratios below 10 (for Opx and Cpx) and $^{40}Ar/^{36}Ar$ values below 392. These compositions confirm that this nodule likely suffered secondary processes that modified its pristine mantle signature. This sample is therefore not considered representative of the local SCLM (and omitted from the following discussion)."*

3) As suggested by the reviewer, we examined a possible correlation between ^{36}Ar and ^{3}He contents to properly evaluate the impact of subduction-related atmospheric fluids in our mantle xenoliths. We identified a positive correlation between ^{3}He and ^{36}Ar (samples with $^{40}Ar/^{36}Ar > 500$), which supports the existence of an atmospheric component recycled in the local lithospheric mantle (see new Figure 9).

Likewise, as the reviewer suggests, we included in the paper the diagram $^{20}Ne/^{22}Ne$ vs $^{40}Ar/^{36}Ar$ (new Figure 9B). Following Langmuir et al. (1978) and Hopp et al. (2007a), and considering the variability of He, Ne and Ar in our dataset, we calculated a $^{40}Ar/^{36}Ar$ signature of about 10,500 for the local upper mantle (see Figure 9B and Table 3). This further supports our interpretation that the Mexican lithospheric mantle has been contaminated by atmospheric fluids (likely derived from the mentioned subduction). We highlight that the conditions assumed for the above calculation are the same assumed for the mixing curves plotted in Figure 7. Accordingly, in Figures 7A and 7B we now report the corresponding values of $^{4}He/^{20}Ne$ (11,000) and $^{40}Ar/^{36}Ar$ (10,500) expected for the local mantle.

4) Regarding the $^{36}Ar/^{22}Ne$, when $^{36}Ar/^{22}Ne$ is plotted vs $^{20}Ne/^{22}Ne$, as proposed by e.g. Hopp et al. (2007), only a few samples have $^{36}Ar/^{22}Ne$ above air ratio (see below). So we find little evidence of Ar/Ne fractionation due to the fact that Ne is more prone to early loss during the subduction process. Instead, the majority of the samples fall along or slightly below the AIR-mantle line, suggesting that an unfractionated behaviour (see plot below). We thus feel information coming from the $^{20}Ne/^{22}Ne$ vs $^{40}Ar/^{36}Ar$ plot (suggested by the Reviewer as well) more useful and straightforward, also considerig we are able to calculate a $^{40}Ar/^{36}Ar$ value of the local mantle lower than MORB, supporting our inference of a recycled atmospheric component.

In summary, the diagrams ^{36}Ar vs ^{3}He and $^{20}Ne/^{22}Ne$ vs $^{40}Ar/^{36}Ar$ were added to the text as Figure 9; the corresponding table (Table 3) was also included. This information is presented in subsection 6.1.1: *"6.1.1 Interaction with atmospheric fluids and evidence for a recycled atmospheric component"*.

4) Diffusive fractionation and 4He/40Ar*-ratios:

If you state that the "4He diffusion coefficient is considerably higher than that of 40Ar (Dhe/Dar = 3.16 in solid mantle…)" you should be aware - and actually mention it in the manuscript - that this value is a calculated value assuming only atomic mass is governing the difference in diffusion coefficients. Burnard itself stated in his text "…assuming Eq 1 is true…" (Eq 1 is the relation between D and m). I have doubt, that this the case, because He is small enough to allow for interlattice diffusion, which is not likely for Ar. No matter, you should at least specify basic assumptions in your text.

R: We point out that our statement concerning the higher diffusion of He relative to Ar is based on previous studies (opportunely cited in the same sentence). Therefore, any assumption behind (i.e., the atomic mass is governing the difference in diffusion coefficients) is not ours. However, we agree with the reviewer that this aspect must be explicit. The text was edited as follows (See lines 56 – 61, in supplementary material):

"Previous studies suggest that the ^{4}He diffusion coefficient is considerably higher than that of ^{40}Ar (D_{4He}/D_{40Ar} = 3.16 in solid mantle; Burnard, 2004; Yamamoto et al., 2009); this is fundamentally based on the assumption that the difference in the atomic masses of the two elements are the key controls of their different diffusion coefficients. Likewise, the difference in mass between ^{3}He and ^{4}He implies important differences in their diffusivities (D_{3He}/D_{4He} = 1.15; Trull and Kurz, 1993; Burnard, 2004; Yamamoto et al., 2009).

5) Subsection 6.2 The effect of partial melting:

Nobody really knows precisely any partition coefficients, in spite of many efforts. For example, if you look at Heber et al. 2007 (which you cite), the error bars in distribution coefficients are large and mostly 100%. We only know that noble gases are incompatible, though even this was questioned in a study about Ar partitioning coefficients by Thomas et al 2008. Hence, I would not rely on those values. I also would not rely on the assumption that He is more incompatible than Ne, Ar. The studies which you cite do not support this unequivocally, due to the large uncertainties. I may also cite a paper that reported results for He suggestive of a more compatible behaviour as U,Th and, nominally, also as Ne,Ar (Parman et al. 2005). Therefore, you should not write (L. 445ff) "…it has been verified that He is more incompatible than Ar…" You may assume that, but that's not proven…

My major issue here is, that you ignore the far more important process of fluid-melt partitioning, which is nicely displayed in your xenoliths: You talk about the association of glass veins (= former melt) and fluid inclusions. Note, that this not means formation from host magma, because the melt veins and fluid inclusions probably formed earlier (as you also state, I agree with that). In this case, one would expect element fractionation according to the solubilities of the noble gases. Common fractionation factors are 2-4 (He/Ne) and 7-10 (He/Ar) (Lux, 1986; Jambon et al. 1986/87). In case that you observe $4He/40Ar* = 1$ in your fluids means, that your melt composition must already had about 7-10 times higher $4He/40Ar*$-ratios… (in case of equilibrium fractionation). Though we may argue about details, the large picture is, that your higher $4He/40Ar*$-ratios do not represent "unfractionated" mantle ratios but are already the most processed one… Quite the opposite, isn't it. From a rough estimate we would expect $4He/40Ar*$-ratios of about 0.1-0.5 in the xenoliths to be derived from a ca. unfractionated initial melt composition.

Even worse, as I found in my stepwise crushing experiments, not all xenoliths show one element composition. Both the air-corrected $3He/22Ne$ and $4He/40Ar*$ ratios may systematically vary during crushing, that means different generations of fluid inclusions seem present, incorporated at different times.

Regarding the lithophile tracers (L. 451ff): If the noble gases form by dissolution from a melt, and if this melt is progressively (by and large) losing fluids on its way through the mantle or crust, we would not expect any correlation with lithophile elements.

R: We understand the point of view of the Reviewer and appreciate his suggestions to consider the melt/fluid partitioning process. Regarding the partition coefficients, we disagree on the fact that we cannot rely on the crystal/melt partition coefficients proposed by Heber et al. (2007), as this study is published in a top geochemistry journal and is widely cited by a number of following studies (142 citations). Although it is true that Heber et al. (2007) report error bars of almost 100% for the partition coefficients, it must be also considered that the Authors suggest that argon has a partition coefficient of about one order of magnitude higher than that of helium (DHe = 0.00017 and DAr = 0.0011), being well outside the respective error bars. Furthermore, we point out that $^4He /^{40}Ar*$ ratios systematically much lower (at least one order of magnitude) than the typical mantle production ratio (1-5) have been measured in mantle xenoliths from several localities that, based on a careful petrological observation, have been inferred to be representative of very refractory mantle lithologies (e.g., Lower Silesia, Europe, Rizzo et al., 2018; Greene Point, Antarctica, Correale et al., 2019; Eifel and Siebengebirge, Europe, Rizzo et al., 2019, 2020; Yangtze craton, China, Correale et al., 2016). However, we agree with the Reviewer that the history of fluid inclusions trapped in our mantle xenoliths may have been ultimately influenced by the fluid/melt partitioning of metasomatizing melt(s), as we do not have evidence from mineral chemistry to constrain our

6) Subsection 6.3.1 Evidences for a recycled air component: Ne and Ar

L. 470: "Instead…" I can't follow you here: A ratio cannot be enriched… Do you mean "elevated" ? As a note, "…a primordial component in the local mantle…" is rather pointless. Most Ne in Earths mantle is primordial, no matter which mantle reservoir you look at. Only 21Ne is significantly affected by ingrowth of nucleogenic 21Ne with time (about 50% in MORB mantle). By the way, atmospheric neon is nearly purely primordial… You need to specify what you mean. Probably you

mean "solar" in the widest sense (there is still a debate about the true mantle 20Ne/22Ne). Furthermore, the EAR represents no uniform reservoir. You will find "hotspot" sources with elevated 3He/4He and lower 21Ne/22Ne, MORB-like signatures (e.g. Turkana depression) and finally compositions characteristic of subcontinental lithosphere. Though the latter is difficult for neon to distinguish, because of admixing of plume-type neon (in my Kenyan samples, Hopp et al. 2007 EPSL, I could identify a plume-contribution which we would now ascribe to the Rungwe hotspot detected shortly after). Nonetheless, He is not affected demonstrating a lithospheric dominance in southern Kenya. To summarize this, you should not use EAR as an acronym for one mantle region. It is diverse.

R: In order to avoid misunderstandings, the phrase *"Instead, samples from EAR exhibit an enrichment in $^{20}Ne/^{22}Ne$ relatively to $^{21}Ne/^{22}Ne$, due to the presence of a primordial component in the local mantle (Halldorson et al., 2014)"* was removed from the main text.

We agree that the EAR is not a uniform reservoir, therefore we subdivided the noble gas data in three different regions: the Ethiopia (Afar) region, where relatively high $^{3}He/^{4}He$ ratios ($>10Ra$) have been reported in ultramafic xenoliths (Halldorson et al., 2014), the Red Sea region (Hopp et al., 2004; Hopp et al., 2007a; Halldorson et al., 2014) and the N/S Kenya rifts (Hopp et al., 2007b and Halldorson et al., 2014). Figures 6, 7, 8 and 10 were updated accordingly.

L. 479: As mentioned above, there exist more references showing the influence of metasomatizing slab fluids that contain atmospheric gases.

R: As discussed above, diagrams ^{36}Ar vs ^{3}He and $^{20}Ne/^{22}Ne$ vs $^{40}Ar/^{36}Ar$ were included to discuss the existence of subduction-related atmospheric fluids in our samples. The references Matsumoto et al. (2001) and Hopp et al. (2007a) were added in the main text. See L. 386 and L. 388 of the revised manuscript.

L. 489-491: Again, nothing new under the Sun… Add references.

R: As mentioned above, references were added. However, the phrase *"Moreover, since Ne isotopes of JH overlap the fields of data from WARS and European SCLM mantle xenoliths, the recycling of an atmospheric component in the lithospheric mantle may be common to many other geodynamic contexts"* was deleted. Further details are provided in the comment: section 6.3.1 (Reviewer #2)

7) Subsection 6.3.2: No mantle plume component in the JH mantle source

Regarding the 21Ne/22Ne(Mantle) values: You need the error bars first, in order to make sense out of your data. You may also apply an error cut, i.e. <10% error is used for display (or < 20% if not

otherwise possible). I would also recommend to calculate an average air-corrected 21Ne/22Ne-value for your samples (error weighted) and check, if this value is significantly offset from MORB or not (you may use 20Ne/22Ne = 12.5 for calculation purposes). Your statement, that these air-corrected ratios do not favor a plume-contribution is not correct, if I look at your given values in the Table: Only one sample has a higher than MORB value (V-F opx, 0.0629 compared with MORB = 0.0595). However, since no errors are reported, a statistical relevance is difficult to judge, and perhaps all your data agree with MORB-values within error.

Again regarding the EAR: To my knowledge, the high 3He/4He-values are from basalts, not xenoliths. But again, the EAR is not an entity. You have hotspots (Rungwe, Afar) and MORB-type signatures (Turkana) and SCLM (many others), and mixtures… The diagram 21Ne/22Ne vs 4He/3He gives an overview of the various possible endmembers, and in it's form presented as Fig 9D was the first time shown by Hopp et al. 2004 (with SCLM endmember). A plume-contribution would be visible as a shift along a mixing trajectory towards (e.g.) the Loihi-composition representing deep-mantle. Your data seem to show exactly this behaviour, but not significant regarding the error, I presume. I agree, that your radiogenic mantle endmember is more MORB-like. But the change along the mixing trajectory with a plume component (if significant) is at odds with your section title.

To summarize this: You probably need to change the whole discussion here, but this depends on your error bars…

R: Error bars were added in Figures 7C and 10A. In the latter figure, we reported data by using an error cut <10% (2σ uncertainties). We agree that it is not possible to discard the contribution of deep-mantle Neon in our samples; even with error bars, some samples fall along the MORB-Plume mixing line ($^{21}Ne/^{22}Ne$ ext <0.05). Using the binary mixing trend, we have calculated a plume contribution <10% in our samples. On the other hand, the homogeneity of $^4He/^3He$ ratios and the fact that the samples less contaminated by the atmospheric component fall along the AIR-MORB line (Figure 7C), leads us to propend for a dominating MORB-like composition of the upper mantle. However, a new title for this section is proposed ("*6.1.2 Noble gas signature of the JH mantle source*") and the text was improved accordingly (see L. 426 – 440 of the revised manuscript).

Regarding the high $^3He/^4He$ values reported in the EAR, these are from both lavas and xenoliths (see Table S1 in Halldorson et al., 2014). In our study we only plotted values from xenoliths.

In subsection 6.4, L. 587ff it sounds as if you have detected for the first time 3He/4He-ratios > 7Ra for SCLM samples… This was already found by Matsumoto et al. 1998… Please, rewrite.

R: In order to avoid misunderstandings, the text was modified as follows (see L. 508 – 510 of the revised manuscript):

"However, some studies on noble gas systematics (including our results) support a more fertile signature ($^3He/^4He > 7.0$ Ra) for some portions of the SCLM on Earth (e.g., Southern Australia and West Antarctic Rift; Matsumoto et al., 1998; Broadley et al., 2016; Correale et al., 2019)"

Figure 8: Your arrow designated with "radiogenic 4He addition" is wrong. Both axes are affected by such addition. Please, correct.

R: The arrow and the phrase *"radiogenic ^4He addition"* were removed from the figure 8 to avoid misunderstandings.

Figures 6-9: Please, extend the literature fields, i.e. include the data of Buikin et al. (2005) for the European SCLM, and Hopp et al. (2007) EPSL for the EAR (Kenya data). If you are really want to give a thorough overview you also need to add data from Hopp et al. (2004) and Hopp et al. (2007) (ChemGeol) for Saudi-Arabia / Zabargad Island, and Matsumoto et al. 1998; 2000; as well as Czuppon et al. 2009 ChemGeol, for the Australian SCLM. But this I leave to the authors.

R: As suggested by the Reviewer, data from Matsumoto et al. (1998, 2000), Hopp et al. (2004, 2007a, 2007b), Buikin et al. (2005), and Czuppon et al. (2009), are now included in Figs. 6, 7, 8 and 10.

References:

There is one duplicate reference given (Rizzo et al 2018a and b, but it's the same…). But in the manuscript it is only 2018, seems correct there…

R: Rizzo et al. (2018a) and Rizzo et al. (2018b) are the same. The right reference is Rizzo et al. (2018). The text was fixed accordingly.

The reference of Broadley et al 2020 "Noble gas variations in ureilites…" is not fitting the topic. Please, remove (or correct, if erroneously cited).

R: The Broadley et al. (2020) reference was deleted from the main text. We agree that this reference is not appropriate.

Table 2:

Please, check your concentrations of sample V-I. 3He is wrong for Opx, 36Ar is wrong for cpx. And I also doubt the Ne in cpx.

R: You are right. Concentrations of sample V-I were accordingly changed since table cells were displaced.

Furthermore, be consistent in formatting (use either exponential or number style, but not both, in isotope data). Use absolute values instead % errors for all. Now, Ar isotope errors are given as % errors, the others as is (but % is shown in header). Add 21Ne/22Ne (ex to 12.5) in table header in order to make clear what you did. And add if errors are 1sigma or 2sigma uncertainties!

R: In order to be consistent in formatting, isotopic ratios are now reported using a number style except for $CO_2/^3He$ ratios due to the large number of decimal places.

Errors are now presented as absolute values. Errors are 1σ uncertainties except for the $^{21}Ne/^{22}Ne$ (ext to 12.5) ratio whose errors are 2σ uncertainties. See Table 2.

The $^{21}Ne/^{22}Ne$ (EX to 12.5) was added in the table header.

Minor points (typos etc.):

L. 57: Insert "of" after "north…"

R: The text has been modified accordingly.

L. 84: Delete the Broadley et al. 2020 reference. It deals with ureilites, not really appropriate here. Maybe you meant a different reference (see also my issue 1 above).

R: The Broadley et al. (2020) reference was deleted from the main text. We agree that this work is not appropriate for this paper.

L. 140: Should be "phlogopite".

R: Corrected

L. 141: Abbreviation of spinel is "sp".

R: Corrected.

L. 213: Delete the closing bracket after "performed". There is no opener.

R: The closing bracket was deleted.

L. 216ff: The air correction of He by application of Ne requires knowledge of the atmospheric He/Ne ratio in your samples. This might not be warranted, because you can fractionate air He and Ne from another by e.g. differences in low temperature solubility in water or simply by preferred loss of He, if introduced by weathering or adsorption.

R: We respectfully consider that the above consideration made by the reviewer does not apply to our study. $^3He/^4He$ ratios were corrected using the $^4He/^{20}Ne$ ratio as well as in many other noble

gas studies of fluid inclusions. Of course, this correction is valid assuming that there is no fractionation between He and Ne, which is true for most of the dataset except for the samples V-I Opx, V-I Cpx, V-H Opx and V-A Opx (see Figure 7A). Nevertheless, the cases of helium loss above reported probably do not affect the correction of their ^{3}He/^{4}He ratios, since ^{4}He/^{20}Ne ratios are relatively high. Anyway, samples V-I Opx, V-I Cpx, V-H Opx and V-A Opx were excluded from the discussion. In conclusion, we do not understand why the Reviewer is mentioning a fractionation of air He and Ne invoking differences of solubility in water, since we are dealing with mantle xenoliths in which fluid inclusions are dominated by CO_2.

L. 222: You may add a reference to your air value (Steiger and Jäger 1977). More recently, most workers rely on the air ratio of Lee et al. 2006, but that won't change much here.

R: Two references for air values were added: Steiger and Jäger (1977) and Ozima and Podosek (2002). See L. 216 of the revised manuscript.

L. 235: In my copy the delta-sign disappeared. Probably only a display problem, but check your article carefully later on.

R: Delta-sign was added.

L. 256: What do you mean with "areas" ? Surface?

R: "areas" refer to specific parts of the thin sections. To avoid misunderstandings, "*in specific areas*" was deleted (see L. 249 of the revised manuscript).

L. 259: Add closing bracket after "present".

R: A closing bracket was added.

Section 5.4 (and actually everywhere): Please specify, if your reported errors are 1sigma or 2sigma uncertainties.

R: Reported errors are 1σ uncertainties. Conversely, ^{21}Ne/^{22}Ne$_{Ex}$ errors are 2σ uncertainties which is specified in Figure 10 and Table 2. This information was added at the beginning of section 5.4 (see L. 297-298 of the revised manuscript) and in Table 2.

L. 311: A positive correlation between 40Ar* and 4He is trivial if you have only mantle gases.

R: The phrase "are positively correlated" was deleted and the text was edited accordingly (see L. 302 of the revised manuscript).

L. 316: Maybe I missed that: Can you explain the meaning of "N2*"?

R: N_2* means nitrogen corrected for atmospheric contamination. We erroneously included this term in the main text. N_2* was deleted.

L. 331ff: Add errors to your values.

R: Errors were added (see L. 317 and L. 323 of the revised manuscript)

L. 332/333: Write simply "expressed as d13C(V-PDB)".

R: The text has been modified accordingly. L. 325 of the revised manuscript.

L. 488: "Therefore, we consider it possible…"

R: The text has been modified accordingly.

L. 588: "noble gas systematics"

R: The text has been edited as follow: *"However, some studies on noble gas systematics (including our results) …"* (see L. 508 of the revised manuscript).

L. 622: …"a process, which…"

R: The text has been modified accordingly

Reviewer #2: Review of "The composition of fluids stored in the central Mexican lithospheric mantle: inferences from noble gases and CO2 in mantle xenoliths" by Sandoval-Velasquez et al.,

This manuscript from Sandoval-Velasquez and co-authors presents new noble gas and carbon isotopes, together with Raman spectrometry of fluid inclusions in mantle xenoliths from Central Mexico. The authors find that the noble gas signature of the fluid inclusions is consistent with mixing between and upper mantle (MORB) source and atmosphere, with a potentially subducted origin. The authors conclude that the upper mantle like noble gas signatures indicate that episodes of subduction have had little effect on the composition of the SCLM, or that a subsequent metasomatic event resulting from the Basin and Range extension overprinted the original subducted signature.

The data in the manuscript appear to be of high quality and the conclusions drawn by the authors are for the most part consistent with the data presented. One major criticism of the paper is that it is overly long and the structure could be improved to make it easier for readers to follow the author's arguments. The other major point is that the discussion concerning the recycled atmospheric component in the samples is not fully backed up by the data and the authors should revise this section (see comments below).

In principle I am of therefore of opinion that this manuscript should be accepted following moderate revisions. I have set out below sections of the manuscript that I think could be improved.

Minor Comments

Highlights:

Line 13 - Try not to use abbreviation in the highlights. These are meant to show the reader the major points without having to read the paper but that is impossible to do if you use abbreviations.

R: Abbreviations such as FI (fluid inclusions) and JH (Joya Honda maar) were removed from the highlights.

Line 18 - Is "subduction retreating" a common term? Perhaps the "retreat of the Farallon slab" is better.

R: "subduction retreating" was replaced by "retreat of the Farallon slab".

Line 22 - Replace "by" with "from" and change to "the subducting Farallon plate"

R: Done

Main Text:

Line 18 - Is it really necessary to abbreviate "fluid inclusions"? In fact the excessive use of abbreviations throughout the manuscript makes it very difficult to follow at times.

R: In order to make the text easier to read, the abbreviation FI was removed.

Line 20 - Change "over-imposed" to "superimposed"

R: Corrected

Line 37 - Delete "by" in the sentence "is consistent by with...."

R: "by" was deleted

Line 51 - Change "consumption" to "subduction"

R: "subduction" was added.

Line 61 - Change to "now allow the composition of the local lithospheric mantle to be probed."

R: The text has been modified accordingly

Line 80 - No need to abbreviate "melt inclusions"

R: The abbreviation for melt inclusions was removed.

Line 84 - I appreciate the citation but I think the authors may have the wrong paper here. Broadley et al., 2020 is about the noble gas signature of Ureilite meteorites. Perhaps a better paper to cite here would be Broadley et al., 2018 End-Permian extinction amplified by plume-induced release of recycled lithospheric volatiles, Nature Geoscience.

R: The Broadley et al. (2020) reference was deleted from the main text. We agree that this reference is not appropriate for this paper.

Line 88 - If the authors insist on abbreviating all the localities then at least use it consistently. Here you use Joya Honda maar even though you have used the abbreviation JH earlier in the paper.

R: "Joya Honda maar" was replaced by "JH".

Line 100 - What does physiographic province actually mean?

R: In North America, a physiographic province is defined as a geographic region with a characteristic geomorphology that differs significantly from that of adjacent regions (see Atwood, 1940 for more details). In the case of Mexico, La Mesa Central was previously defined as a physiographic province by Raisz (1959) and Nieto-Samaniego et al. (2005) to describe ""a basin surrounded by higher mountains which is higher and flatter than the Basin and Range province (located to the north). Instead of elongated mountains, this has low elevation areas, mainly dissecting ancient volcanic rocks". However, we removed this term from the text to avoid further details increasing the length of the manuscript.

Line 111 - Try and be consistent with your units. You use metres here but kilometres earlier in the paragraph.

R: The units were changed from meters (m) to kilometers (km) to be consistent.

Line 114/115 - Inconsistent use of abbreviations.

R: The name "Joya Honda maar" was replaced by the abbreviation "JH".

Line 118 - Try and avoid superlatives and opinions such as "most spectacular". If this has common usage for this are then maybe provide a citation of who said it first.

R: In fact, the superlative "most spectacular" was used by Saucedo et al. (2017). This reference was included in the text (see L. 120 of the revised manuscript).

Figure 1 - The map is very small and difficult to read. Consider making the map and its text larger and the photo smaller as it is not as important to the paper.

R: The figure was modified accordingly. The map and the text have been enlarged and the figure caption was edited accordingly.

Line 145 - 174 - This section is overly long especially since the majority of it comes from one previous publication (Liang and Elthon, 1990). This whole section could be condensed by 50% by only focussing on the most important points and then referring the readers to Liang and Elthon, 1990 if they require further insights in to these samples.

R: As suggested by the Reviewer, Section 3 was condensed focussing on the main petrological characteristics reported by Liang and Elthon (1990), especially in mineral chemistry results and subsequent interpretations.

Line 202 - Not necessary to cite every publication that has used the same analytical procedure. Focus on the first or any further publication that improved upon the method.

R: The main text was edited accordingly. We focused on the publication of Rizzo et al (2018) and Faccini et al. (2020) for noble gas analysis and Gennaro et al. (2017) and Rizzo et al. (2018) for CO_2 isotopic determinations.

Line 209 - How was the gas "purified"?

R: After removing CO_2, the residual gas mixture was purified under Zr-Al getter pumps in a UHV stainless-steel preparation line. Then, Ar, Kr and Xe were removed in a "cold finger" with active charcoal immersed in liquid nitrogen. Finally, He and Ne were adsorbed in a cold head with active charcoal cooled at 10K and then moved at 40 and 80K to release first He and then Ne, respectively.

This section was added, and the text was modified accordingly. See section 4 (L. 202 – 205 of the revised manuscript).

Line 211 - Admitted may be better than injected since it is a static mass spectrometer.

R: "injected" was changed by "admitted"

Line 212 - How was the CO2 concentration determined?

R: The moles of CO_2 were quantified by measuring the total pressure of gas $(CO_2 + N_2 + O_2 + noble$ gases) released during crushing, using an IONIVAC Transmitters ITR90, in a known volume of the system, then subtracting the residual pressure of $N_2 + O_2 + noble$ gases after freezing CO_2 in a "cold finger" immersed in liquid nitrogen.

This section was added to the main text. L. 199 – 202 of the revised manuscript.

Line 240 - The same paragenesis as what?

R: "*The same paragenesis*" refers to the same mineralogy observed in the samples. In order to avoid misunderstandings, the word "paragenesis" was replaced by "mineralogy" and the text was edited as follows (L. 235 of the revised manuscript):

"The suite of xenoliths exhibits the same mineralogy"

Section 5.1 - A lot of this is repetition of what has been reported earlier in section 3. Try and condense these sections such that there is as little overlap as possible. For example if you find the exact same texture, size, shape etc as has been previously reported then it is fine to just state this. There is no need to repeat it.

R: As mentioned above, section 3 was condensed to avoid overlapping. As suggested by the reviewer, petrographic characteristics of mantle xenoliths were removed from section 4 (now section 3) and are only presented in section 5.4.

Line 284 - Should be "... among which there is an opaque phase."

R: The text has been modified accordingly

Line 292 - Do you have an explanation as to why the dolomite vibrations are "unexpectedly weak"?

R: weak vibrations could be associated with strong Raman scattering because of disorder (see Frezzotti et al., 2012a). This information is now provided in the main text (see L. 284 of the revised manuscript).

Line 295 - Consider adding a citation here.

R: The references Peccerillo and Frezzotti (2007), Carteret et al. (2009) and Frezzotti et al. (2012a) were added. L. 288 of the revised manuscript.

Line 296 - Can you link these analyses to the photomicrographs (figure 4)? For example is the olivine that was analysed shown in figure 4?

R: Yes. In fact, spectra presented in Figures 5A, 5B and 5C correspond to inclusions analysed in Figures 4C, 4D and 4B, respectively. Details are now provided in Figure 5 (see the figure caption).

Line 304 - Change "chemical" to "elemental" since this is the title of this section.

R: "chemical" was changed by "elemental".

Line 306-321 - Usually it is sufficient to report the concentrations of only the most abundant isotopes. If the reader needs the concentration of the less abundant isotopes we can go to the table or use the ratios to calculate. It just makes it easier for the reader to follow as they are not saturated with values.

R: As suggested by the reviewer, concentrations of the less abundant isotopes such as ^{3}He and ^{36}Ar were removed from the text.

Line 323 - Is this positive correlation shown in figure 8? If so maybe reference this figure here. Also looking at figure 8 it is hard to see any evidence of a positive correlation. Now this may be down to the use of a log scale on the x-axis but if you are claiming they are correlated then you should show that clearly to the reader.

R: We agree that a positive correlation between ^{4}He/^{40}Ar* and Rc/Ra values is hard to see. The statement "are positively correlated with Rc/Ra" was removed and the text was modified as follows (see L. 315 of the revised manuscript):

"The ^{4}He/^{40}Ar ratios vary between 0.14 and 3.11 (Figure 8), which overlaps in part the typical production ratio of the mantle"*

Line 327 - I am confused by this statement. In the previous sentence you state that the highest 4/20 is 10483 but then you state that the CPX (which have the highest 4/20) max out at 2223. Are these averages? Either way state what these values represent (average, medium, max etc.)

R: Yes, these are averages. The text was modified accordingly (L. 318 – 320 of the revised manuscript):

"^{4}He/^{20}Ne values range from 2.4 to 10483; the highest values are recorded in Cpx and Ol (on average 2223.2 ± 3196.8 and 1498.6 ± 1306.1, respectively), while Opx exhibits considerably lower ratios (<639)"

Line 332 - Delta symbol appears to be missing.

R: Delta symbol was added.

Figure 6 - Again figure are hard to read and interpret. Try and make them bigger for the published version.

R: As suggested, the figure was made bigger for the published version.

Line 355 - What do you mean by we "stand on the above"?

R: With "stand on the above" we mean "based on". With this sentence we want to emphasize the importance of using both tools (petrography and isotopes) to properly discuss the characteristics of the local mantle. In order to avoid misunderstandings, the text was modified as follows (see L. 346 – 348 of the revised manuscript):

"In the discussion below, we combined the above petrographic evidence and the isotopic signatures (noble gases and CO_2) of the JH fluid inclusions to constrain volatile origin and mantle characteristics."

Section 6 - I would suggest you reorder the discussion a little. Personally I think it would be better if you discuss your new data in relation to the different mantle signatures and what this means for the different potential processes and then discuss the possible secondary processes. At the moment discussing secondary processes before you even identify the primary signature is bizarre.

R: We appreciate the reviewer suggestion. We reordered the discussion. First, the title "Secondary processes" was removed because we consider it ambiguous; second, the subsection 6.1.1 "*Atmospheric contamination*" is no longer considered as a secondary process since it is an intrinsic characteristic of the local mantle (see subsections 6.2 and 6.4.1, now merged in a unique section); the title of this subsection was replaced by "*Interaction with atmospheric fluids*" as suggested by Reviewer 1; third, Section 6.1.2 "Diffusive Fractionation", section 6.1.3 "*Exposure to cosmic rays*" and Section 6.2 "The effect of partial melting" were deleted from the main text and moved in supplementary information.

In summary, the discussion was reordered as follows:

6. Discussion

6.1 Inferences on the noble gas signature of the JH source mantle

> *6.1.1 Interaction with atmospheric fluids and evidence for a recycled atmospheric component 6.1.2 Noble gas signature of the JH mantle source.*

6.2 ^{3}He fluxes, ^{4}He production and the helium residence time for the Mexican lithospheric mantle.

> *6.2.1 Mantle CO_2 fluxes*

6.3 Inferences on CO_2 origin

Figure 7 - Again could be made bigger.

R: As suggested, the figure was made bigger for the published version.

Line 389 - Where is this CO_2 depletion shown. In a figure or table? Make reference to where the reader can find evidence for this depletion.

R: A reference was added, and the text was edited as follows: "*Some CO_2 depletion is also evident in sample V-I (Figure 6C)*". See L. 43 – 44, in supplementary material.

Line 424 - This section is irrelevant to your study. There is no evidence of cosmogenic noble gases in your study so there is no need for this section. Can be deleted.

R: We agree that section 6.1.3 is irrelevant, therefore this was removed from the main text and moved to supplementary information.

Line 452 - What do you mean by "sensibly lower than"?

R: We realize that this sentence is not clear. Our statement commented by the Reviewer was made by Rizzo et al. (2018), following the partial melting modeling discussed in e.g. Correale et al. (2016). The batch and fractional melting modeling is based on the crystal-melt partition coefficients of noble gases and $^4He/^{40}Ar*$ ratios measured in mantle xenoliths from the Yangtze Craton (China) and Lower Silesia (Poland). Following this approach, the degree of partial melting calculated from our $^4He/^{40}Ar*$ ratios would be considerably lower than that proposed by petrological studies (10-20%, Liang and Elthon, 1990). Nevertheless, since in this paper we are not dealing with these models, the phrase "*In fact, the calculated noble gas-based partial melting degrees do not match (are sensibly lower than) those obtained from lithophile elements-based models*" was deleted to avoid misunderstandings.

Line 465 - It has taken 465 lines to finally discuss the primary mantle origin of these samples. This section should be discussed earlier in the paper.

R: As mentioned above, the discussion was modified and the paper shortened.

Section 6.3.1 - Firstly, petrographic data cannot be used as evidence for a recycled origin for the atmospheric component. I do not think you have clearly distinguished between air contamination and recycling. There are methods to do this see Matsumoto et al., 2001 and Broadley et al., 2016 which both showed that the atmospheric At component was likely recycled due to the correlation between 3He and 36Ar.

Furthermore, Ne is not generally considered to be efficiently subducted so just by saying your Ne data look similar to Ne data from other localities that have been shown to contain a recycled component is not sufficient to conclude that your samples contain a recycled component. This section needs to be revised.

R: We agree with the Reviewer. As suggested, section 6.3.1 was modified (see section 6.1.1). We included the new diagrams ^{36}Ar vs ^3He and $^{20}Ne/^{22}Ne$ vs $^{40}Ar/^{36}Ar$ to properly evaluate the impact of subduction-related atmospheric fluids in our mantle xenoliths. We realized that a positive correlation between ^3He and ^{36}Ar exists (in samples with $^{40}Ar/^{36}Ar > 500$), as already observed in the papers suggested by the Reviewer#1 and #2. The variability of $^{20}Ne/^{22}Ne$ and $^{40}Ar/^{36}Ar$ ratios support the existence of an atmospheric component recycled in the local lithospheric mantle. Further details on the above considerations and on the modelling that led us to now estimate a

possible $^{40}Ar/^{36}Ar$ of the local mantle, are provided in the response to the comment 6 of Reviewer #1 and in the main text (see L. 383 – 400 of the revised manuscript).

Besides, the sentence "*Moreover, since Ne isotopes of JH overlap the fields of data from WARS and European SCLM mantle xenoliths, the recycling of an atmospheric component in the lithospheric mantle may be common to many other geodynamic contexts*" was deleted to avoid misunderstandings.

Section 6.3.3 - This should be combined with the previous section as a general section on the mantle origin of the samples.

R: As suggested by the Reviewer, section 6.3.3 and section 6.3.2 were combined. The new section (6.1.2) was entitled "*Noble gas signature of the JH mantle source*"

Line 524 - Broadley et al., 2016 also reported average 3He/4He values of 8.7 +/- 0.3 for WARS xenoliths.

R: According to the study of Correale et al. (2019), which followed that of Broadley et al. (2016), we added the average estimated by Broadley et al. (2016) for those values not affected by the release of cosmogenic helium (Baker Rocks and Browning Pass samples; 7.5 $\pm$ 0.45 Ra). We also updated Figures 7, 8 and 10 with this information. The text was edited as follows (L. 443 – 444 of the revised manuscript):

"*This $^3He/^4He$ signature is similar to that measured at the WARS (7.5 $\pm$ 0.45 Ra and 7.1 $\pm$ 0.4 Ra; Broadley et al., 2016; Correale et al., 2019) …*"

Line 533 - I see no evidence for a recycled Ne signature.

R: As mentioned above, the existence of an atmospheric component recycled in the local mantle is supported by the correlation between ^3He - ^{36}Ar contents and $^{20}Ne/^{22}Ne$ – $^{40}Ar/^{36}Ar$ ratios. However, to avoid misunderstandings the text was modified as follows (L. 454 – 456 of the revised manuscript):

"*If this interpretation is correct, then past subduction events would only have added a recycled atmospheric component into the mantle (cfr 6.1.1).*"

Line 534 - Doesn't require the addition of crustal material. You can add recycled air in fluids without any need for crustal material.

R: The word "crustal" was removed to avoid misunderstandings. L. 457 of the revised manuscript.

Line 560 - What do you mean by "Independently on..."?

R: We mean that, even if our hypothesis about the influence of subduction in the local mantle is erroneous, the petrographic evidence does demonstrate a metasomatic event affecting our mantle

xenoliths. However, we replaced "Independently on" with "Irrespective of", with the hope to have clarified the meaning of this sentence.

Line 597 - Is there plans to publish this data ? I am not sure what the journals rules are concerning unpublished data but maybe the editor can advice whether this is appropriate.

R: Yes, we plan to publish this data soon. According to the Guide for Authors "Unpublished results and personal communications are not recommended in the reference list, but may be mentioned in the text".

Line 606 - It is not immediately clear to me how these fluxes are calculated. More detail on how these calculations were done should be provided.

R: More details on the subcontinental mantle mass as well as the total mass of ^{3}He considered in the calculations are now provided in subsection 6.2 (see L. 508 – 536 of the revised manuscript). The formulas used to estimate ^{3}He flux, ^{4}He production and the helium residence time (Rt) were included and described in the text.

Figure 10 - It might be useful to scale the flux to the area in another box. That way you can show how efficient degassing is at each site.

R: Fluxes were scaled to the area and plotted in Figures 11B and 11D. The text and the figure caption were edited accordingly.

1 **THE COMPOSITION OF FLUIDS STORED IN THE CENTRAL MEXICAN LITHOSPHERIC MANTLE:**

2 **INFERENCES FROM NOBLE GASES AND CO$_2$ IN MANTLE XENOLITHS**

3 A. Sandoval-Velasquez[1], A.L. Rizzo[2], M. Frezzotti[3], R. Saucedo[4] and A. Aiuppa[1,2].

4

Highlights

6 • Fluid inclusions are used to study the chemical signature of the Mexican subcontinental
7 mantle

8

9 • Inclusions identified in the xenoliths are composed of $glass \pm CO_2 \pm carbonates \pm pyrite$

10

11 • Isotopes reveal a mixing of atmospheric, MORB-like and carbonate-rich fluids

12

13 • Mantle refertilization would occur after the retreat of the Farallon slab

14

15 • Carbonates and atmospheric fluids are inherited from the subducting Farallon plate.

16

17

1 **THE COMPOSITION OF FLUIDS STORED IN THE CENTRAL MEXICAN**
2 **LITHOSPHERIC MANTLE: INFERENCES FROM NOBLE GASES AND CO$_2$ IN MANTLE**
3 **XENOLITHS**

4 A. Sandoval-Velasquez[1], A.L. Rizzo[2], M. Frezzotti[3], R. Saucedo[4] and A. Aiuppa[1,2].

5

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16

17 **ABSTRACT**

18 We present the first isotopic (noble gases and CO$_2$) characterization of fluid inclusions (FI) ~~c~~coupled
19 to Raman microspectroscopy analyses in mantle xenoliths from Central Mexico, a geodynamically
20 complex area where the Basin and Range extension was ~~over imposed~~superimposed on the Farallon
21 subduction (terminated at 28 Ma). To characterize the isotopic signature of the Central Mexican
22 lithospheric mantle, we focus on ~~FI~~ fluid inclusions entrapped in mantle xenoliths found in deposits
23 of the Joya Honda maar (JH), a Quaternary monogenetic volcano belonging to the Ventura Espiritu
24 Santo Volcanic Field (VESVF) in the state of San Luis Potosí (central Mexico). Thirteen ultramafic
25 plagioclase-free xenoliths were selected, all exhibiting a paragenesis Ol> Opx> Cpx >> Sp, and being
26 classified as spinel-lherzolites and harzburgites. All xenoliths bring textural evidence of interstitial
27 glass veins bearing dendritic trails of secondary melt and fluid inclusions (composed of silicate glass
28 $\pm$ CO$_2$ $\pm$ Mg-Ca carbonates $\pm$ pyrite). These are related to pervasive mantle metasomatism driven by
29 carbonate-rich silicate melt. The Ar and Ne systematics reflect mixing between MORB-like upper
30 mantle and atmospheric fluids, the latter interpreted as reflecting a recycled air component possibly
31 inherited from the Farallon plate subduction. The ^{3}He/^{4}He ratios vary between 7.13 and 7.68 Ra,
32 within the MORB range (7-9 Ra), and the ^{4}He/^{40}Ar* ratios (0.4 - 3.11) are similarly close to the
33 expected range of the fertile mantle (1-5). Taken together, these pieces of evidence suggest that (i)
34 either the mantle He budget was scarcely modified by the Farallon plate subduction, and/or (ii) that
35 any (large) crustal contribution was masked by a later metasomatism/refertilization episode, possibly
36 during the subsequent Basin and Range extension. A silicate melt-driven
37 metasomatism/refertilization (revealed by the association between glass veins and ~~FI~~fluid inclusions)
38 is consistent ~~by~~ with calculated helium residence time for the Mexican lithospheric mantle (20 to

39 60Ma) that overlaps the timing of the above geodynamic events. We propose that, after the
40 refertilization event (e.g., over the last ~20Ma), the lithospheric mantle has evolved in a steady-state,
41 becoming slightly more radiogenic. We also estimated ^{3}He fluxes (0.027 - 0.080 mol/g), ^{4}He
42 production rates (340 - 1000 mol/yr), and mantle CO_2 fluxes (3.93 x 10^7 mol/yr to 1.18x10^8 mol/yr)
43 using the helium isotopic values measured in JH mantle xenoliths. Finally, the JH xenoliths exhibit
44 CO_2/^{3}He ratios comparable to those of the upper mantle (from 3.38 x 10^8 to 3.82x10^9) but more
45 positive δ^{13}C values (between -1.0 and -2.7‰), supporting the involvement of a crustal carbonate
46 component. We propose that the metasomatic silicate melts recycled a crustal carbonate component,
47 inherited by the Farallon plate subduction.

48 **Keywords:** *Mexican mantle xenoliths; fluid inclusions; noble gases; CO₂; mantle refertilization; carbonate*
49 *recycling.*

50

51 **1. INTRODUCTION**

52 The ~~consumption~~ subduction of the Farallon oceanic slab under the North American plate, during the
53 late Oligocene and Middle Miocene, has given rise to enormous changes in the tectonic configuration
54 of the northwestern coast of Mexico. These include the transition from a compressive to a transform
55 margin, and the beginning of a regional extension that produced the Basin and Range Province
56 (Atwater, 1989; Ferrari et al., 2012; Henry and Aranda-Gomez, 1992; Sedlock, 2003).

57 The Basin and Range extension started about 30Ma and was accompanied by intraplate magmatism,
58 which generated several volcanic fields north of the Transmexican Volcanic Belt (TMVB; Aranda-
59 Gómez and Ortega-Gutiérrez, 1987; Luhr and Aranda-Gómez, 1997; Henry and Aranda-Gomez,
60 1992). These fields are typically monogenetic complexes associated with the eruption of alkaline
61 basalts and basanites that have brought to the surface significant amounts of ultramafic xenoliths that
62 now allow the composition of the local lithospheric mantle to be probed ~~probing the composition of~~
63 ~~the local lithospheric mantle~~.

64 The Ventura Espiritu Santo Volcanic Field (VESVF), located in the San Luis Potosí state (central
65 Mexico), is one of the best-known examples of this volcanism, and is characterized by spectacular
66 volcanic structures like the Joya Honda maar (JH), and by frequent ultramafic nodules found in its
67 deposits. Other mantle xenoliths-bearing alkali basalt localities are the Santo Domingo Volcanic
68 Field (SDVF) also located in the San Luis Potosí state, the Pinacate Volcanic Field (PiVF), Las
69 Palomas Volcanic Field (PaVF), the Potrillo maar (Po), the Camargo Volcanic Field (CVF), the
70 Durango Volcanic Field (DVF), the San Quintin Volcanic Field (SQVF) and Isla Isabel (II; Figure
71 1; Basu, 197~~6~~7; Gutmann, 1986; Aranda-Gómez and Ortega-Gutiérrez, 1987; Luhr et al., 1989; Pier
72 et al., 1992; Luhr and Aranda-Gómez, 1997; Housh et al., 2010).

73 These volcanic structures in the central and NW portion of Mexico, and the textural and petrological
74 characteristics of their ultramafic xenoliths, have already been discussed elsewhere (Aranda-Gómez
75 and Ortega-Gutiérrez, 1987; Luhr and Aranda-Gómez, 1997; Henry and Aranda-Gomez, 1992).
76 These previous studies have revealed a complex (multi-stage) history of deformation, melting and
77 metasomatism, and opened new questions on the evolution of the Mexican lithospheric mantle.
78 Debate exists, however, on the provenance of the metasomatic fluids, and if and to what extent
79 subduction of the Farallon plate has modified mantle composition during the recent Mexican

80 geological history (Pier et al., 1989; Luhr and Aranda-Gómez, 1997; Dávalos-Elizondo et al., 2016).
81 Addressing these questions requires information on the chemical features of metasomatic fluids
82 present in the lithospheric mantle. Fluid- and melt inclusions ~~(FI and MI)~~ preserved in mantle
83 xenoliths are well known for being valuable sources of information to study the evolution of volatile
84 species trapped in ultramafic mantle rocks, and to derive inferences about the local lithospheric
85 mantle dynamics (Roedder, 1984; Andersen and Neumann, 2001; ~~Gautheron and Moreira, 2002;~~
86 Deines, 2002; Frezzotti et al., 2002a; Buikin et al., 2005; Gautheron et al., 2005a; Martelli et al.,
87 2011; Day et al., 2015; Broadley et al., 2016; Rizzo et al., 2018; Correale et al., 2019; Faccini et al.,
88 2020).

89 Here, we aim at filling this gap of knowledge on the volatile composition of the Mexican lithospheric
90 mantle, by reporting on the chemical and isotopic composition (He, Ne, Ar and CO_2) of ~~FI~~ fluid
91 inclusions entrapped in mantle xenoliths found in the ~~Joya Honda maar~~JH. Noble gases are sensitive
92 tracers that provide insights on fluid origin, the composition and evolution of the mantle, and their
93 relationship with different tectonic processes such as subduction (Matsumoto et al., 2001; Hopp et
94 al., 2007a; Hopp and Ionov, 2011; Martelli et al., 2014; Broadley et al., 2016; Faccini et al., 2020)
95 or mantle plumes (~~Farley and Neroda, 1998; Graham, 2002; Gautheron and Moreira, 2002;~~ Hopp et
96 al., 2004, 2007a, 2007b~~Gautheron et al., 2005a; Martelli et al., 2011; Correale et al., 2012, 2016,~~
97 ~~2019;~~ Buikin et al., 2005; Halldórsson et al., 2014; Boudoire et al., 2018, 2020~~; Day et al., 2015;~~
98 ~~Broadley et al., 2016; Rizzo et al., 2018; Faccini et al., 2020~~). In addition, studying CO_2 abundance
99 and isotopic composition contribute to assessing composition and provenance of metasomatic fluids
100 that may have interacted with these xenoliths (Sano and Marty, 1995; Correale et al., 2015; Gennaro
101 et al., 2017; Rizzo et al., 2018), for example revealing any addition to the mantle of carbonate-rich
102 fluids delivered by sediments and altered oceanic crust in the subducted slab (Plank and Manning,
103 2019).

104

105 **2. GEOLOGICAL SETTING**

106 The VESVF is located in the southern portion of the ~~physiographic~~ province known as the Mesa
107 Central (Raisz, 1959; Nieto-Samaniego et al., 2005); very close to the Sierra Madre Oriental province
108 (Figure 1). The Mesa Central, located north of the TMVB, comprises a portion of continental crust
109 that has a thickness of 32 km and is delimited by regional faults (Fix, 1975; Nieto-Samaniego et al.,
110 2005). The oldest rocks found in this province are muscovite schists from the Paleozoic (252 Ma),
111 superimposed by turbiditic sequences of the Triassic and volcano-sedimentary sequences of
112 continental origin formed during the mid-late Jurassic (Barboza-Gudiño et al., 1999; Morán-Zenteno
113 et al., 2005; Nieto-Samaniego et al., 2005). The most abundant outcrops correspond to sequences of
114 calcareous rocks of marine origin, formed during a transgression episode during the end of the late
115 Jurassic and the Cretaceous (Carrillo-Bravo, 1971; López-Doncel, 2003; Nieto-Samaniego et al.,
116 2005); these rocks make up the so-called Valles-San Luis Potosí Platform (PVSLP) and the Mesozoic
117 Basin of Central Mexico whose thickness can reach ~~5000~~ 5 km and 6 k~~000~~m, respectively. Cenozoic
118 rocks are mainly volcanic and sedimentary (of continental origin), the most recent being the alkaline
119 basalts of the VESVF, SDVF and DVF whose origin is related to a melting zone located 34 km deep
120 under the Mesa Central (Fix, 1975).

121 The VESVF is formed by some isolated scoria cones and three maars among which is the ~~Joya Honda~~
122 ~~maar~~JH (Aranda-Gómez et al., 2007; Saucedo et al., 2017). The JH is located at the intersection

between the PVSLP and the Mesozoic Basin of central Mexico (22 ° 25'4.97 "N and 100 ° 47'15.62" W), and is thought to have formed at about 311 ± 19 ka (Saucedo et al., 2017). This volcano is recognized as one of the most spectacular volcanic structure of the VESVFMexico (Saucedo et al., 2017), with its elliptical crater having vertical walls defining a 150 – 300 m deep depression (Figure 1). The maar formed through a series of mixed magmatic and phreatomagmatic eruptions that emplaced a sequence of pyroclastic falls and base surge deposits (having a maximum thickness of ~100 m). Magma–groundwater interaction is thought to have occurred during magma ascent through of a NE-SW normal fault system cutting folded limestones, calcareous mudstones, chert lenses and shales which are part of the Cuesta del Cura (Albian-Cenomanian) and Tamaulipas (Aptian) Formations (Aranda-Gómez and Luhr, 1996; Aranda Gómez et al., 2000; Saucedo et al., 2017). Saucedo et al. (2017) identified 5 eruptive phases, the last two of which generated deposits rich in mantle xenoliths. The erupted magmas are alkaline and mafic in composition (olivine-nepheline basanites and olivine basalts), and their origin is thought to be associated with decompressional melting of the asthenosphere and lithospheric mantle under la Mesa Central, as proposed for other volcanic fields associated to the Basin and Range extension (Aranda-Gómez and Ortega-Gutiérrez, 1987; Luhr et al., 1989; Lee, 2005; Aranda-Gómez et al., 2007).
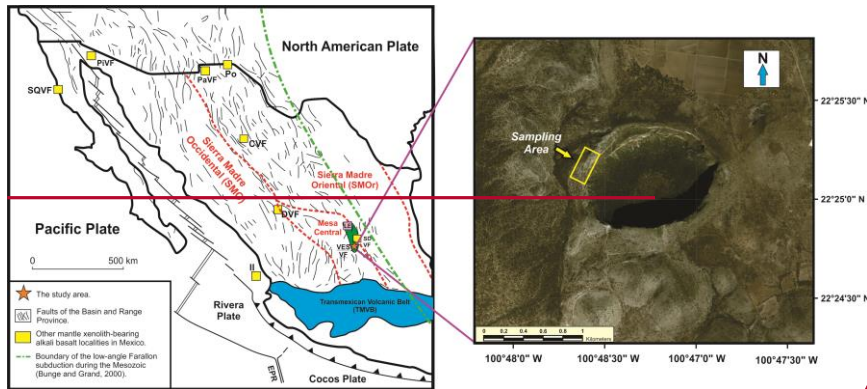

Figure 1. Location of the Joya Honda maar (JH) and geodynamic setting. The *left image* shows the Mexican part of the Basin and Range Province which has an extension of 9.4 x 10⁵ km² (Henry and Aranda-Gomez, 1992); the image was adapted from Aranda-Gómez et al. (2000). The green area is the area used to estimate the ⁴He production, the helium residence time and ³He CO₂ fluxes for the lithospheric mantle located under San Luis Potosí state (see sections 6.2.3 and 6.2.4). The pink square represents the location of the Los Encinos Volcanic Field (LE); although this is a monogenetic volcanic field associated with the Basin and Range extension, this lacks mantle xenoliths. Contours of Sierra Madre Occidental, Sierra Madre Oriental, the Transmexican Volcanic Belt and Mesa Central provinces were build based on Gómez-Tuena et al. (2007). VESVF: Ventura Espiritu Santo Volcanic Field, SDVF: Santo Domingo Volcanic Field, PiVF: Pinacate Volcanic Field, PaVF: Las Palomas Volcanic Field, Po: Potrillo maar, CVF: the Camargo Volcanic Field, DVF: Durango Volcanic Field, SQVF: San Quintin Volcanic Field, II: Isla Isabel. *Right Image:* Google Earth image (February 20ᵗʰ, 2020) showing the Joya Honda maar morphology and sampling area.

3. PETROLOGICAL BACKGROUND

The JH mantle xenoliths have been previously studied and described as spinel lherzolites and harzburgites (Aranda-Gómez and Ortega-Gutiérrez, 1987; Liang and Elthon, 1990; Luhr and Aranda-Gómez, 1997). Petrographically, these authors have recognized a protogranular to equigranular

145 ~~texture with olivines (Ol), orthopyroxenes (Opx) and clinopyroxenes (Cpx) crystals with size > 2~~
146 ~~mm.~~ The modal composition indicates a relatively constant paragenesis: Ol is the most abundant
147 phase (55-88%), followed by Opx (17-32%), Cpx (1-17%) and Spinel (Sp; 0.3 - 5%); in very few
148 cases, the presence of ~~ph~~flogopite is also reported with percentages below 1% (Luhr and Aranda-
149 Gómez, 1997). Compositionally, Ol has a Mg# (Mg# = 100 x Mg/(Mg + $\sum$Fe)) ranging from 87.5 to
150 91, Opx from 88.6 to 91.2, Cpx from 87.7 to 91.4 and Sp~~in~~ from 75.5 to 82.5 (Liang and Elthon,
151 1990). These authors also report the development of Na-Al poor spongy rims on Opx, Cpx and spinel,
152 explained as due to variable degrees of partial melting that have affected the local upper mantle.

153 Liang and Elthon (1990) classified the xenoliths into two groups based on their modal and
154 geochemical compositions (groups Ia and Ib). ~~In group Ia peridotites, olivines have Mg# (Mg#~~
155 ~~=Mg/Mg+Fe * 100) ranging from 89.40 to 90.41, $\sum$FeO values from 9.42 to 10.38 wt%, and NiO~~
156 ~~from 0.38 to 0.43 wt%. Mg# in orthopyroxenes vary between 89.86 and 91.21, $\sum$FeO values range~~
157 ~~from 5.69 to 6.57 wt%, Na$_2$O values from 0.08 to 0.15 wt%, and CaO from 0.67 to 0.90 wt%. Cores~~
158 ~~of Ia clinopyroxenes have high Mg# (89.7 – 91.4), elevated CaO contents (19.27 – 21.43 wt%), Na$_2$O,~~
159 ~~and Al$_2$O$_3$ (0.88 – 1.79 wt% and 6.04 – 7.01 wt%, respectively) and LREE (Light Rare Earth~~
160 ~~Element) depleted patterns ((La/Yb)$_N$ <0.8). Chromian spinels were reported in both groups of~~
161 ~~peridotites: spinels of group Ia exhibit Cr# values (Cr# = 100 x Cr/(Cr + Al)) between 79.66 and~~
162 ~~82.56 which are negatively correlated with Ol Mg# values.~~ Mantle xenoliths from group Ia are
163 interpreted as mantle residues generated by different degrees of partial melting and extraction of
164 picritic melts in the upper mantle; these authors calculated a degree of partial melting between 7%
165 and 22% for Ia xenoliths, using melting models based on bulk-rock MgO, Ni and Sc abundances.
166 Group Ib peridotites exhibit similar degrees of partial melting (1-20%) followed by metasomatic
167 enrichment (Liang and Elthon, 1990). One of the most important characteristic of Ib xenoliths is the
168 extreme core-to-rim chemical zoning (and LREE-enriched patterns; (La/Yb)N> 0.8) in
169 clinopyroxene, revealed by a decrease of of Al$_2$O$_3$ and Na$_2$O towards the rim, while Mg#, CaO, TiO$_2$
170 and Cr$_2$O$_3$ tend to increase (Liang and Elthon, 1990). According to these authors, high FeO-Na$_2$O
171 contents in the cores of Ib minerals and LREE enrichment in Cpx crystals suggest interaction between
172 silicate melts (basanitic in composition) and a residual mantle similar to group Ia xenoliths.
173 Additionally, they explain the extreme core-to-rim chemical zoning, and reaction rims in Cpx, by the
174 reaction with H$_2$O-rich fluids depleting Cpx rims in Na$_2$O and Al$_2$O$_3$ (also increasing TiO$_2$ contents).

175

176 ~~Generally, Ib olivines have lower Mg# values ranging from 87.76 to 89.32, ($\sum$FeO from 10.37 to~~
177 ~~11.89 wt%), and NiO contents from 0.38 to 0.40 wt%. Ib orthopyroxenes also exhibit lower Mg# and~~
178 ~~higher Na$_2$O and $\sum$FeO contents if compared with group Ia peridotites; Mg# values vary from 88.61~~
179 ~~to 89.75, $\sum$FeO from 6.56 to 7.26 wt%, Na$_2$O values from 0.19 to 0.22 wt% and CaO from 0.72 to~~
180 ~~0.80 wt%. Ib clinopyroxenes core analysis reveal low Mg# (87.78 – 88.99), low CaO (17.41 – 18.58~~
181 ~~wt%), high Na$_2$O (2.40 – 2.74 wt%) and high Al$_2$O$_3$ contents (7.21 – 7.67 wt%) if compared with Ib~~
182 ~~clinopyroxenes. Finally, chromian spinels have relatively low Cr# (75.59 – 79.87) and are positively~~
183 ~~correlated with Mg# values measured in olivines. One of the most important characteristic of Ib~~
184 ~~xenoliths is the extreme core-to-rim chemical zoning (and LREE-enriched patterns; (La/Yb)N> 0.8)~~
185 ~~in clinopyroxene, revealed by a decrease of of Al$_2$O$_3$ and Na$_2$O towards the rim, while Mg#, CaO,~~
186 ~~TiO$_2$ and Cr$_2$O$_3$ tend to increase (Liang and Elthon, 1990). Group Ib peridotites exhibit similar~~
187 ~~degrees of partial melting (1-20%) followed by metasomatic enrichment (Liang and Elthon, 1990).~~

188 ~~According to these authors, high FeO Na₂O contents in the cores of Ib minerals and LREE~~
189 ~~enrichment in Cpx crystals suggest interaction between silicate melts (basanitic in composition) and~~
190 ~~a residual mantle similar to group Ia xenoliths. Additionally, they explain the extreme core to rim~~
191 ~~chemical zoning, and reaction rims in Cpx, by the reaction with H₂O rich fluids depleting Cpx rims~~
192 ~~in Na₂O and Al₂O₃ (also increasing TiO₂ contents).~~

193

194

4. SAMPLES AND METHODS

196 Samples were collected from the eastern part of the JH (Figure 1), where units IV and V emerge
197 according to the stratigraphy described by Saucedo et al. (2017). These units are composed of
198 pyroclastic fall and flow deposits where the highest concentration of mantle xenoliths is found. The
199 nodules are usually dispersed within or hosted in basanitic lavas. Thirteen fresh nodules were selected
200 with diameters between 5 and 10 cm; additionally, a pyroxenite sample was studied (sample V-C)
201 and was only used for noble gas analysis due to its small diameter (<5 cm). Eight nodules were
202 selected for petrographic analysis on thin and polished sections. Petrographic analysis was performed
203 at the petrography laboratory of the University of Milano-Biccoca based on the textural classification
204 proposed by Mercier and Nicolas (1975); the modal composition was carried out by point counting
205 (from 4000 to 7000 points per section).

206 Two double-polished rock sections of about 130 μm thickness were selected for the Raman of fluid
207 inclusions. Analyzed ~~FI~~ fluid inclusions are located at 10 to 20 μm depth below the sample surface.
208 Analyses were performed using a Labram Evolution (Horiba Scientific, Japan) at the Dipartimento
209 di Scienze dell'Ambiente e della Terra, Università Milano Bicocca. The polarized Raman spectra
210 were excited using a green Ar-ion laser operating at 532 nm, with 50-70 mW emission power. Spectra
211 acquisition was performed with a backscattered geometry and a 600 g/mm diffraction grating. A
212 transmitted light Olympus B40 microscope with a $100 \times$ objective (Numerical aperture, N.A., = 0.90)
213 was used for all the acquisitions (spatial resolution < = 1μm). Confocality was maintained with a
214 pinhole of 100 μm. Spectra were collected with variable acquisition times (from 20 to 30 sec). The
215 spectrometer was calibrated using a Silicon standard. To increase band attribution accuracy better
216 than 0.2 cm^{-1}, spectra were baseline corrected and processed by statistical analysis (Fityk software;
217 Wojdyr, 2010) using a Voigt Pseudo-function, a convolution of a Lorentzian with a Gaussian line
218 shape. Mineral and fluid identification has been based on our reference spectra database (Frezzotti et
219 al., 2012a).

220 Noble gas and CO_2 isotopic determinations were performed at the noble gas and stable isotopes
221 laboratories of INGV, Sezione di Palermo, following the preparation methods and analytical
222 procedures described in ~~Nuccio et al. (2008),~~ Gennaro et al. (2017), ~~and~~ Rizzo et al. (2018) and
223 Faccini et al. (2020)~~Correale et al. (2015, 2019), Gennaro et al. (2017), Rizzo et al. (2018), and~~
224 ~~Faccini et al. (2020)~~. All xenoliths were crushed and sieved with the aim of hand-picking crystals
225 with diameters >0.5 mm. Thirty-five aliquots (13 Ol, 11 Opx and 13 Cpx) of crystals (weights of
226 0.05 to 2 g) were selected for noble gas isotopic analysis. Before analysis, samples were cleaned
227 ultrasonically in 6.5% HNO_3 (for CO_2 analysis samples were cleaned in HCl), deionized water and
228 high-purity acetone. After drying, samples were accurately weighed and loaded into an ultra-high-
229 vacuum (UHV) crusher for noble gas analyses that was pumped and backed for 48h at 120°C. As

230 soon as the ultra-high-vacuum was reached, fluid inclusions were released by single-step crushing at
231 about 200 bar and room temperature (21°C). ~~After drying, samples were accurately weighed and~~
232 ~~loaded into an ultra-high-vacuum crusher for noble gas analyses; FI were released by single-step~~
233 ~~crushing at about 200 bar and room temperature (21°C)~~ Single step technique was used to minimize
234 the addition of secondary helium (cosmogenic ^{3}He and radiogenic ^{4}He) accumulated in the crystal

235 lattice (Kurz, 1986; Graham, 2002, Rizzo et al., 2018; Correale et al., 2019 ~~–~~); this is supported by

236 the homogeneity of the dataset (more details about the effect of secondary helium in our samples are
237 provided in supplementary material). The moles of CO_2 were quantified by measuring the total
238 pressure of gas (generally $CO_2+N_2+O_2$+noble gases) released during crushing (by an IONIVAC
239 Transmitters ITR90) in a known volume of the system, then subtracting the residual pressure of
240 N_2+O_2+noble gases after removing CO_2 in a "cold finger" immersed in liquid nitrogen. For noble
241 gas analysis, the residual gas mixture was purified under Zr-Al getter pumps in a UHV stainless-steel
242 preparation line. After then, Ar (and Kr and Xe) was removed in a "cold finger" with active charcoal
243 immersed in liquid nitrogen. Finally, He and Ne were adsorbed in a cold head with active charcoal
244 cooled at 10K and then moved at 40 and 80K in order to release first He and then Ne, respectively.
245 ~~For noble gas analysis, the gas mixture extracted from crystals was purified in a stainless-steel~~
246 ~~preparation line to separate He, Ne, and Ar from other species (N₂, H₂, H₂O, CO₂). He, Ne, and Ar~~
247 ~~were separated using cryogenic and active carbon traps and then injected into mass spectrometers.~~
248 ~~At the time of crushing, a first estimate of the concentration of CO₂ in FI was performed).~~ He and
249 Ne isotopes were analyzed using two different split-flight-tube mass spectrometers (Helix SFT-
250 Thermo), while Ar isotopes were analyzed by a multi-collector mass spectrometer (Argus, GVI). The
251 measured ^{3}He/^{4}He ratios are expressed as R/Ra (where R is the ratio of the sample and Ra the He
252 isotopic ratio of air = 1.39×10^{-6}); this ratio was corrected for atmospheric contamination based on
253 the measured ^{4}He/^{20}Ne ratio and the values are expressed as Rc/Ra (eq.1);

254 $$R_c/R_a = ((R_M/R_a)(He/Ne)_M - (He/Ne)_A)/((He/Ne)_M - (He/Ne)_A) \qquad eq.1$$

255 where R_M/R_a and $(He/Ne)_M$ are the measured values and $(He/Ne)_A$ refers to the atmospheric
256 theoretical value (0.318). ^{40}Ar values were also corrected for atmospheric contamination:

257 $$^{40}Ar^* = {}^{40}Ar_{sample} - ({}^{36}Ar_{sample} \cdot ({}^{40}Ar/{}^{36}Ar)_{air}) \qquad eq.2$$

258 where ^{40}Ar* is the corrected ^{40}Ar, ^{40}Ar/^{36}Ar$_{air}$ = 295.5 and ^{21}Ne/^{22}Ne$_{air}$ = 0.029 (Steiger and Jäger,

259 1977; Ozima and Podosek, 2002). Values of ^{20}Ne, ^{21}Ne, ^{22}Ne, ^{36}Ar, and ^{38}Ar are also reported.
260 Analytical uncertainties (1σ) for ^{3}He/^{4}He, ^{20}Ne/^{22}Ne, ^{21}Ne/^{22}Ne, ^{40}Ar/^{36}Ar, and ^{38}Ar/^{36}Ar ratios are
261 <2.7%, <6.3%, <7.5%, <2.0%, and <1.7%, respectively. The ^{20}Ne/^{22}Ne and ^{21}Ne/^{22}Ne ratios are
262 corrected for isobaric interferences at m/z values of 20 (^{40}Ar^{2+}) and 22 (^{44}CO2^{+2}) (Rizzo et al., 2018;
263 Faccini et al., 2020).

264 Based on the results of the initial CO_2 measurements, twelve aliquots with the highest concentrations
265 were selected for isotopic CO_2 analysis. After crushing, the gas released was cleaned using a
266 purification line composed by two cryogenic traps and by a 626B Baratron® Absolute Capacitance
267 Manometer MKS (measuring range 10^{-3}–10 mbar) to remove H_2O and any atmospheric component,
268 and to quantify the gas released (Gennaro et al., 2017; Rizzo et al., 2018). The purified CO_2 was
269 condensed in a glass sampler (adjusted to atmospheric pressure by adding pure helium), and this was
270 transferred to the mass spectrometer. The ^{13}C/^{12}C isotope ratio was determined using a Thermo
271 (Finnigan) Delta Plus XP CF-IRMS connected to a Trace GC gas chromatograph and a Thermo

274

5. RESULTS

5.1 Petrography

The suite <u>of</u> ~~of~~ xenoliths ~~is formed by~~<u>exhibits</u> the same ~~paragenesis~~<u>mineralogy</u>: Ol> Opx> Cpx >> Sp. All samples are plagioclase-free and are classified as spinel lherzolites and harzburgites (Figure 2). Peridotites show protogranular to porphyroclastic textures, in which two generations of Ol, Opx and Cpx crystals are observed (Figure 3): the first generation corresponds to large, elongated and deformed crystals of sizes greater than 3 mm (porphyroclasts); the second generation corresponds to smaller crystals with polygonal shapes (neoblasts $\leq$ 3mm), which occur in the rock as a consequence of an intense recrystallization process.

Olivines are present as translucent crystals without alteration. Ol porphyroclasts exhibit anhedral forms (size <4.5 mm) with curved grain boundaries, kink bands and numerous fractures due to deformation (Figure 3A); some crystals have Opx and Cpx inclusions (<1mm) with rounded shapes. Most of the neoblasts are less than 2 mm long and are characterized by straight borders and subhedral forms. Orthopyroxenes exhibit light brown colours without alteration; opx porphyroclasts are characterized by anhedral and elongated forms with curved grain boundaries and diameters $\leq$ 4.5 mm (Figure 3B, 3C and 3D). Neoblasts exhibit euhedral forms with well-developed straight boundaries and sizes less than 2 mm; Opx tends to concentrate forming clusters of three or more crystals ~~in specific areas~~, where vermicular spinel is commonly observed (Figure 3E and 3F); some Opx may contain small Cpx inclusions (<0.2mm). Opx may exhibit a rough areas (especially over the rims) that resembles spongy rims, which may expand over the entire crystal (Figure 3B, 3C and 3F). Cpx crystals are light green, with subhedral to anhedral forms, sizes $\leq$ 2 mm (rare crystals with diameters greater than 4 mm are present<u>)</u>. Spongy textures along crystal rims in Cpx are very common and varies in thickness, this texture sometimes develops as bands or affecting the entire crystal surface (Figure 3C and 3G). Finally, spinel occurs as dark brown crystals with irregular shapes (anhedral forms with curved grain borders), sizes $\leq$ 2 mm and develop as vermicular intergrowths in pyroxene clusters (Figure 3E and 3F).

Peridotites cut by glass veins that develop along the crystal borders, extending into single crystals as micro-fractures. Veins have variable thicknesses, the largest being 0.3 mm thick (Figure 3D, 3F and 3H). Veins do not show a genetic relation with the host lava and are mainly formed by glass and may contain relatively large ($\leq$ 0.25 mm) crystals of Cpx, tiny crystals with high birefringence, identified as carbonates; and rare opaque minerals.
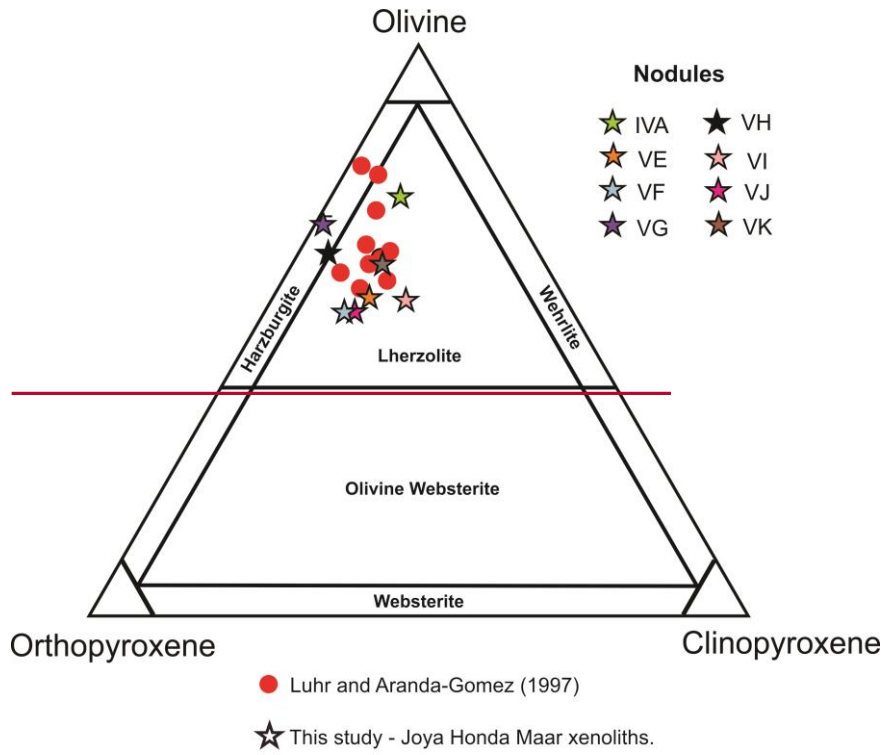
306

Figure 2. *Ternary classification for ultramafic and mafic rocks, from Streckeisen (1976).*
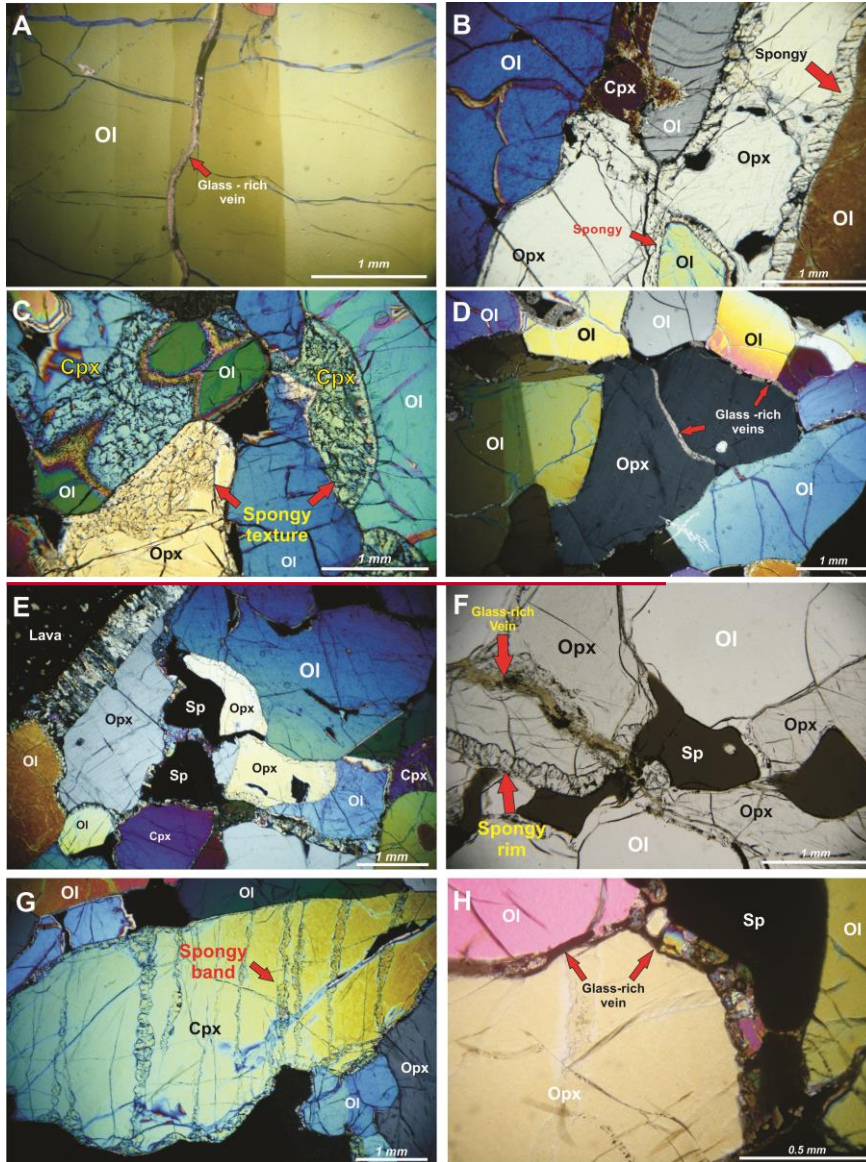
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308

Figure 3. *Microphotographs of the JH mantle xenoliths in cross-polarized light (A, B, C, D, E, G, H) and transmitted plane-polarized light (F). Ol: olivine, Opx: orthopyroxene, Cpx: clinopyroxene, Sp: spinel. A) Ol porphyroclast with well-developed kink bands and glass-rich veins. B) Spongy rims developed in Opx crystals; C) Cpx and Opx crystals are almost and totally replaced by the spongy rim. D) Porphyroclastic texture; Opx crystal being cut by a glass-rich vein. E) Opx cluster. F) Opx cluster cut by a vein composed of light brown glass and some opaque minerals, note the presence of spongy rims in Opx. G) Cpx porphyroclast with development of spongy bands. H) Glass-rich veins around Opx porphyroclast.*

5.2 Fluid and melt inclusions

Olivine crystals contain abundant dendritic trails of secondary inclusions consisting of glass, mineral phases, and a fluid phase. Dendritic inclusion trails are intragranular and typically originate from the glass/carbonate microveins permeating the rocks (Figure 4A). Figure 4 shows this peculiar texture resulting from the association of large (15-30 µm) irregularly-shaped inclusions containing silicate glass (melt) with subordinate crystals and a fluid phase in variable proportions, along with smaller (<20 µm) inclusions dominated by glass (melt) or fluid, ± crystals. Similar inclusion textures are also observed in orthopyroxene and clinopyroxene, while fluid inclusions in the absence of glass, generally observed in peridotites (Andersen and Neumann, 2001; Frezzotti and Touret, 2014), are extremely rare. In inclusions, the silicate glass is colorless, isotropic, and does not show any devitrification (Figure 4B). Mineral phases (< 30 µm) are high birefringent and texturally associated with the glass (Figure 4C). The fluid is CO_2-rich, one or two phases (L, or L+V). Fluid-dominated inclusions may contain tiny mineral grains, among which there is an opaque phase (Figure 4D).
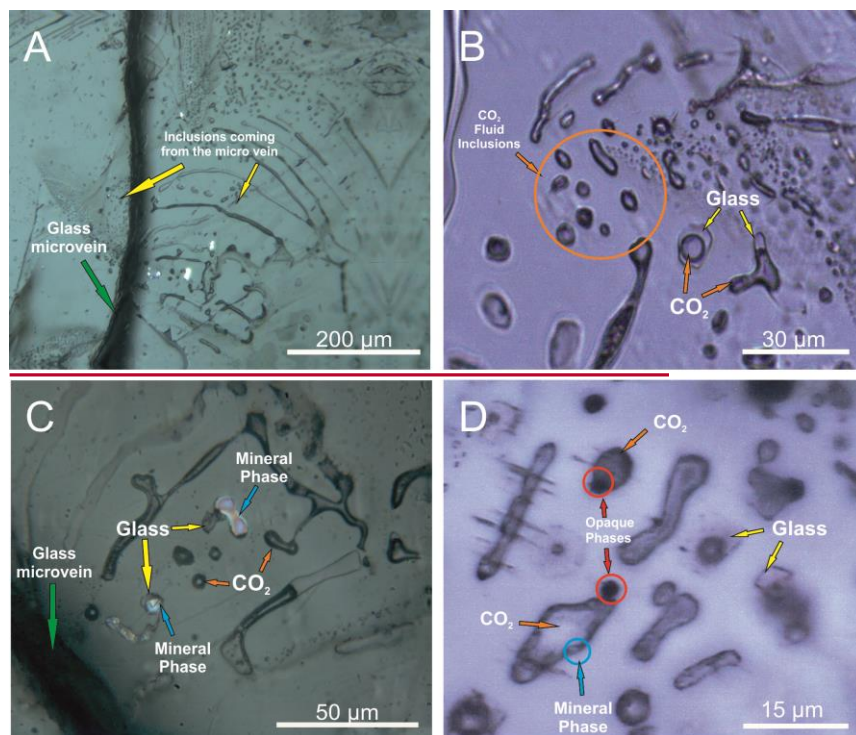

Figure 4. Microphotographs of inclusions identified in olivine. A) Melt and fluid inclusions originating from microveins. B) Intragranular trail of dendritic inclusions. C) Inclusions composed by glass and high birefringent mineral phases (cross polarized light illumination). D) Opaque phases associated to fluid inclusions.

5.3 Raman microspectroscopy

Raman microspectroscopy analyses of dendritic inclusions reveal that mineral phases texturally associated with silicate glass are Mg-calcite (Figure 5A; vibrations at 1088, 714, 284, 158 cm^{-1}). The fluid is pure CO_2 (Figure 5B; Fermi doublet at about 1282 -1387 cm^{-1}). Interestingly, in most CO_2 inclusions, Raman spectra also reveal the presence of dolomite (Figure 5C; vibrations at 1094-1096, 722-723, 299-300 cm^{-1}). Dolomite vibrations, however, are unexpectedly weak (likely linked to disorder; Frezzotti et al., 2012a) and broad (full width at half maximum up to 15 cm^{-1}) (Figure 5C). Also, the main vibration at 1098 cm^{-1} is downshifted from 2 to 4 cm^{-1}. These spectral characteristics indicate a relevant order decrease in the crystalline structure as it occurs in decomposing carbonates (Frezzotti and Peccerillo, 2007; Carteret et al., 2009; Frezzotti et al., 2012a).

The tiny mineral grains observed in a few CO_2 inclusions are magnesite (Figure 5D; vibrations at 1094, 723, 322, 202 cm^{-1}). An opaque mineral has been identified as pyrite (Figure 5D; vibrations at 342 and 377 cm^{-1}). The association of Mg-carbonate ± pyrite in CO_2-rich inclusions is suggestive of fluid inclusion-host olivine reactions at low temperatures (Frezzotti et al., 2012b), probably during host lava cooling at the surface.

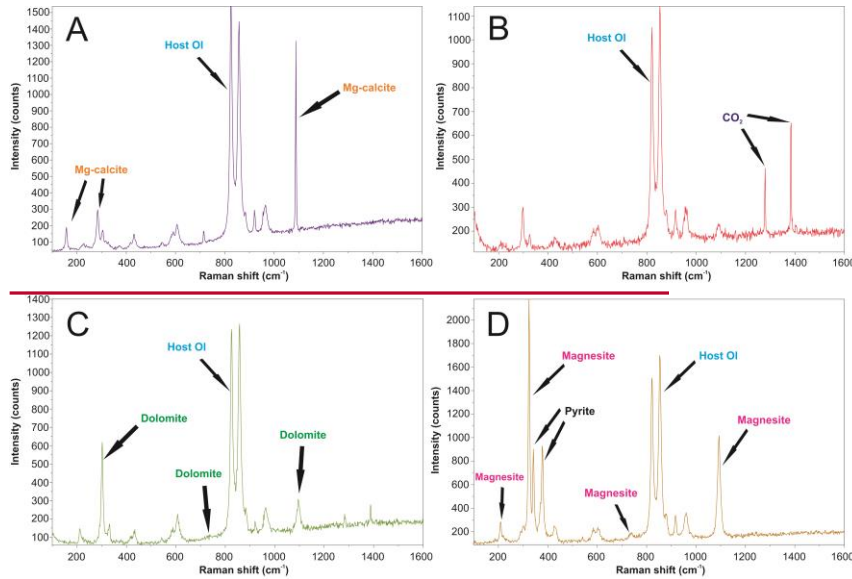Figure 5: Raman spectroscopy applied in olivine inclusions. Further details are discussed in section 5.2.

5.4 Elemental and Isotopic composition

The chemical elemental and isotopic composition of the crystal-hosted FI fluid inclusions in the JH mantle xenoliths are reported in Table 2; reported errors are 1σ uncertainties, except for $^{21}Ne/^{22}Ne_{ext}$ ratios whose errors are 2σ uncertainties. ^{4}He concentrations range between 8.56 x 10^{-14} and 1.29 x

345 10^{-11} mol/g where the highest concentrations are observed in Cpx (~4.28 x 10^{-12} mol/g) followed by

346 Ol (~2.21 x 10^{-12} mol/g) and Opx (~2.06 x 10^{-12} mol/g). ~~[3]He contents vary from 7.37 x 10^{-19} to 1.29~~

347 ~~x 10^{-16} mol/g, with the highest values also recorded in Cpx (4.04 x 10^{-17} mol/g), followed by Ol (2.28~~

348 ~~x 10^{-17} mol/g) and Opx (2.11 x 10^{-17} mol/g). [3]He and~~ [4]He concentrations for the V-I crystals are

349 significantly lower than those measured in other nodules. $^{40}Ar^*$ content ranges from 5.37 x 10^{-14} to

350 1.08 x 10^{-11} mol/g; in general, both $^{40}Ar^*$ and [4]He values ~~are positively correlated and~~ are similar to

351 those previously reported in mantle xenoliths from the European Subcontinental Lithospheric Mantle

352 (European SCLM~~); Gautheron et al. 2005; Martelli et al. 2011; Rizzo et al. 2018; Faccini et al., 2020),~~

353 ~~East African Rift (EAR; Halldorsson et al., 2014), and~~ the West Antarctic Rift System (WARS-

354 ~~SCLM; Correale et al., 2019),~~ the Eastern Australia SCLM and some regions belonging the East

355 African Rift (Northern/Southern Kenya rifts and the Ethiopia-Afar region; Figure 6A; Matsumoto et

356 al., 1998, 2000; Hopp et al., 2004, 2007a, 2007b; Buikin et al., 2005; Gautheron et al., 2005a;

357 Czuppon et al., 2009; Martelli et al., 2011; Halldórsson et al., 2014; Broadley et al., 2016; Rizzo et

358 al., 2018; Correale et al., 2019; Faccini et al., 2020~~; Figure 6A). The ^{36}Ar contents vary from 3.38 x~~

359 ~~10^{-16} to 4.14 x 10^{-14} mol/g. The highest concentrations of $^{40}Ar^*$, ^{36}Ar and N_2^* are also found in Cpx.~~

360 ^{20}Ne, ^{21}Ne and ^{22}Ne values tend to be high in Cpx and Opx; ^{20}Ne ranges from 1.42 x 10^{-16} to 5.08 x

361 10^{-14} mol/g, ^{21}Ne from 5.22 x 10^{-19} to 1.21 x 10^{-16} mol/g and ^{22}Ne from 1.34 x 10^{-17} to 4.90 x 10^{-15}

362 mol/g. CO_2 is the most abundant gas, on average its contents are higher in Cpx and Opx (1.02 x 10^{-7}

363 and 3.18 x 10^{-8} mol/g, respectively) than in Ol (3.43 x 10^{-9} mol/g); CO_2 contents are positively

364 correlated with ~~[3]He,~~ [4]He, $^{40}Ar^*$, ^{20}Ne, ^{21}Ne and ^{22}Ne, but are lower than those observed in European

365 SCLM xenoliths (Figure 6B and 6C).

366 In detail, the Rc/Ra values vary as follows: Ol from 7.13 to 7.68 Ra, Opx from 6.15 to 7.54 Ra, and

367 Cpx from 5.40 to 7.59 Ra. The $^4He/^{40}Ar^*$ ratios ~~are positively correlated with Rc/Ra and~~ vary

368 between 0.14 and 3.11 (Figure 8), which overlaps in part the typical production ratio of the mantle

369 ($^4He/^{40}Ar^* = 1 - 5$; Yamamoto et al., 2009; Marty, 2012); on average the highest values belong to Ol

370 crystals (1.51 ± 0.76), compared to Opx (0.72 ± 0.25) and Cpx (0.78 ± 0.40). $^4He/^{20}Ne$ values range

371 from 2.4 to 10483; the highest values are recorded in Cpx~~(~2223.2)~~ and Ol (on average 2223.2 ±

372 3196.8 and ~~~~1498.6~~.6~~ ± 1306.1, respectively), while Opx exhibits considerably lower ratios (<639).

373 This tendency is also observed for $^{40}Ar/^{36}Ar$ ratios that vary from 303 to 8231 in Cpx, from 392 to

374 2518 in Ol, and from 340 to 1436 in Opx. It should be noted that those samples with the lowest values

375 of Rc/Ra, also are depleted in $^4He/Ar^*$, $^{40}Ar/^{36}Ar$ and $^4He/^{20}Ne$. On average $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$

376 ratios ~~vary from~~are 10.2 ± 0.50 and ~~9.8 to 12.1 and from~~ 0.~~0288-~~0332 ± 0.0058~~to 0.0553~~, respectively;

377 in both cases, the values are slightly higher in Cpx compared to Ol and Opx. Finally, the isotope

378 composition of CO_2 expressed as δ~~—~~^{13}C values (in per mil vs V-PDB) varies between -0.97 and -

379 2.86‰ and does not exhibit a systematic variation between Ol, Opx and Cpx. The most negative

380 value (-2.86‰) was reported in IV-A Opx while the most positive values belong to two aliquots of

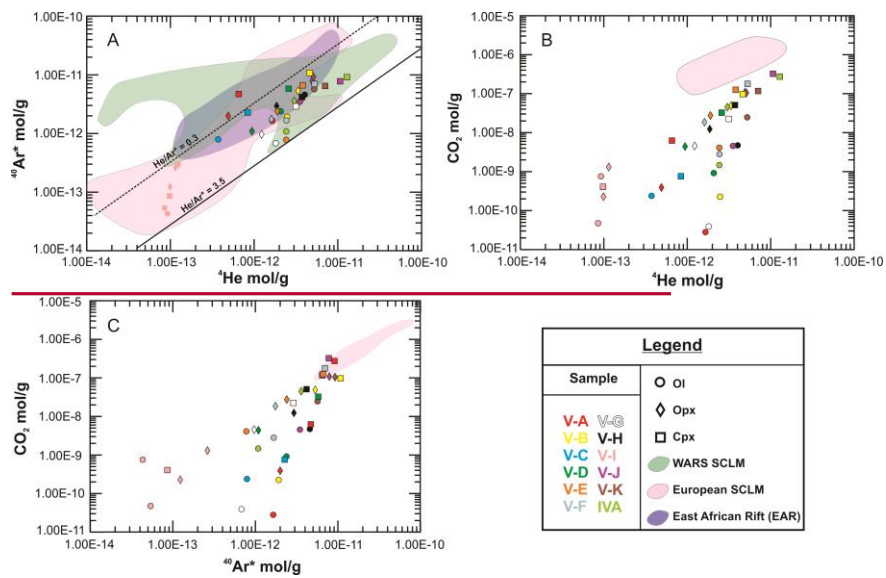381 the same nodule: V-K Ol (-1.10) and V-K Opx (-0.97).

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6. Discussion

Present textual and Raman spectroscopy observations indicate that the JH ~~FI~~ fluid inclusions are CO_2-dominated (Figure 5) and, even more importantly, that they are strictly associated with the pervasive infiltration of glass veins (Figures 3, 4). The inclusions typically exhibit the coexistence of glass, mineral phases, and a fluid phase, and form dendritic trails of ~~FI~~ fluid inclusions originating from the glass/carbonate microveins permeating the rocks (Figure 4A). The close association between glass and ~~FI~~fluid inclusions, and their originating from the glass microveins, are strongly suggestive of trapping of fluids delivered by degassing of a carbonate-rich silicate melt at mantle depth. Textural observations and preliminary compositional information (indicating that glass veins contain 59 ± 3 wt % SiO_2) clearly exclude that the glass veins are related to the basanitic to basaltic host magma.

In view of the above, and in line with previous work (Liang and Elthon, 1990; Luhr and Aranda-Gómez, 1997), we relate the ~~FI~~ fluid inclusions trapped in JH xenoliths to a melt-related metasomatic event deep in the source mantle. The overprinted textures in Cpx along crystal rims (named as spongy rims by Luhr and Aranda-Gómez, 1997) (see Figure 3) have also been associated to this metasomatic event (Liang and Elthon, 1990).

In the discussion below, we combined ~~stand on~~ the above petrographic evidence ~~while we use~~and the isotopic signatures (noble gases and CO_2) of the JH ~~FI~~fluid inclusions to constrain volatile origin and mantle characteristics. However, ~~before the origin of noble gases and carbon can be explored, an initial~~an initial screening of the dataset ~~is~~was necessary~~required~~ to filter out ~~any~~ samples that have suffered from~~effect related~~ to secondary processes affecting ~~the xenoliths~~fluid inclusion compositions (see~~. The details on the above screening are reported in~~ Supplementary information)~~, while the processes are reported in the main figures, when recalled~~. The filtered dataset is used below to infer volatile sources ad processes deep in the mantle.

6.1 Diffusive Fractionation

~~As shown in Figure 6, the lowest noble gas concentrations (especially helium) were measured in V-I crystals and, to a minor extent, in V-A and V-C (He<10^{-12} mol/g). Some CO_2 depletion is also evident in sample V-I (Figure 6C). When plotting ^{3}He, ^{4}He, ^{40}Ar*, and ^{4}He/^{40}Ar* vs. Rc/Ra (Figures 8 and 10A-10C), we find that in sample V-I the He and Ar depletion is also accompanied by ^{3}He/^{4}He (<6.15 Ra) sensibly lower than the dataset average (7.39 ± 0.14 Ra). In samples V-A and V-C, the ^{3}He/^{4}He decrease is less important. It is worth noting that the lower Rc/Ra values mostly correspond to pyroxenes (Opx and Cpx) from the same nodule, while Ol crystals are less or not modified. Indeed, Ol from V-I show ^{3}He/^{4}He values (7.25 – 7.37 Ra) that are comparable to the rest of the dataset (7.21 – 7.36 Ra).~~

~~Following Burnard et al. (1998), Burnard (2004), and Yamamoto et al. (2009), this data variability can be interpreted as due to preferential loss of He (relative to Ar and CO_2) due to diffusive fractionation. In fact, in case of radiogenic ^{4}He in growth or addition to fluid inclusions, an increase of ^{4}He concentration with decreasing ^{3}He/^{4}He values should be expected, without any relative decrease of ^{3}He, ^{40}Ar*, and ^{4}He/^{40}Ar*. We highlight that He diffusion into the fast-flowing melt-filled dissolution channels cutting the mantle is commonly invoked during partial melting (Burnard, 2004; Yamamoto et al., 2009; Faccini et al., 2020) and/or metasomatism of solid mantle that~~

431 prevalently affects pyroxene crystals. Some studies conclude that the ^{4}He diffusion coefficient is
432 considerably higher than that of ^{40}Ar (D_{4He}/D_{40Ar} = 3.16 in solid mantle; Burnard, 2004; Yamamoto
433 et al., 2009); this is especially true assuming that only the relative atomic mass controls the difference
434 in diffusion coefficients. Likewise, the difference in mass between ^{3}He and ^{4}He implies important
435 differences in their diffusivities (D_{3He}/D_{4He} = 1.15; Trull and Kurz, 1993; Burnard, 2004; Yamamoto
436 et al., 2009). Hence, in case of diffusive loss of He, a decrease in ^{3}He/^{4}He and ^{4}He/^{40}Ar* is expected,
437 as observed in V-A and V-I pyroxenes. Because the clearest evidence of diffusive fractionation are
438 observed in pyroxenes, we exclude V-C because Ol from this sample show ^{3}He/^{4}He values (7.13 Ra)
439 comparable to Opx (7.33 Ra) from the same nodule (although Ol have lower He concentrations). In
440 any case, in order to properly interpret the origin of the He in the following sections of the discussion,
441 pyroxenes from V-I and V-A nodules will not be discussed further.

442 To support the hypothesis of a diffusive fractionation, in Figures 8 and 10A-B-C we model this
443 process based on the approach proposed by Burnard et al. (1998), Burnard (2004), Yamamoto et al.
444 (2009), and already applied in Boudoire et al. (2020) and Faccini et al. (2020). We consider a starting
445 mantle composition of ^{3}He = 1.56 x 10^{-17} mol/g, ^{4}He = 1.5 x 10^{-12} mol/g, and ^{40}Ar* = 6 x 10^{-13} mol/g,
446 which corresponds to the lowest concentrations of these species in nodules not evidently modified
447 by diffusion. We additionally use a starting ^{4}He/^{40}Ar* = 2.5 (the average mantle production ratio),
448 and a ^{3}He/^{4}He = 7.5 Ra, which is within the Rc/Ra variability of the dataset. According to our
449 modeling, diffusive fractionation is able to justify the data variability observed in pyroxene from V-
450 A and V-I samples, which will not be discussed anymore.

451

452 **6.1 Secondary processes**

453 **6.1.16.2 Atmospheric ContaminationInteraction with atmospheric fluids**

454 **6.1 Inferences on the noble gas signature of the JH source mantle**

455 *6.1.1 Interaction with atmospheric fluids and eEvidence for a recycled atmospheric component*

456 In order to correctly interpret the noble gas data obtained in FI fluid inclusions from the JH mantle
457 xenoliths, it is necessary to evaluate the atmospheric contamination in our samplesinteraction with
458 atmospheric fluids. It is well known that Ar and Ne are more susceptible (relative to He) to
459 contamination, due to their higher abundances in atmosphere relative to the mantle fluids. For this
460 reason, tracers such as ^{40}Ar and ^{36}Ar, ^{4}He/^{20}Ne, ^{20}Ne/^{22}Ne, ^{21}Ne/^{22}Ne, and ^{40}Ar/^{36}Ar are normally used
461 to investigate the isotopic contribution from the atmosphere (Matsumoto et al., 2001; Gurenko et al.,
462 2006; Hopp et al., 2004, 2007a, 2007b; Nuccio et al., 2008; Martelli et al., 2014; Oppenheimer et al.,
463 2014; Rizzo et al., 2018)(Gurenko et al., 2006; Nuccio et al., 2008; Martelli et al., 2014;
464 Oppenheimer et al., 2014; Rizzo et al., 2018).

465 He, Ne and Ar systematics suggest the existence of an atmospheric component in our samplesWe
466 find that most of the samples exhibit low air contamination (except speciallyespecially for in nodule
467 V-I). Indeed, the differences between R/Ra and Rc/Ra are negligible, except for V-I pyroxenes that
468 also show the lowest ^{4}He/^{20}Ne values of the dataset (≤10). In general, the measured R/Ra and
469 ^{4}He/^{20}Ne values fall along an binary mixing air-MORB mixing curve, and overlap with those
470 measured in mantle xenoliths from the European SCLM, the East African Rift (EAR), the West

471 Antarctic Rift System (WARS), Eastern Australia, Red sea region and N/S Kenya rifts~~and WARS~~ ,
472 ~~except for a few samples that show among the highest ever measured ^{4}He/^{20}Ne ratios for the SCLM~~
473 ~~(up to 10483) (Figure 7A)~~(Figure 7A). ~~This evidence~~The existence of such an
474 ~~atmopsheric~~atmospheric component ~~of a limited atmospheric contribution~~ is corroborated by ~~low~~the
475 high ^{40}Ar/^{36}Ar and ^{3}He/^{36}Ar values (up to 8231 and 0.07, respectively; Figure 7B), which in turn
476 support the robustness of the ^{40}Ar* correction (e.g. Martelli et al., 2014; Rizzo et al., 2015, 2018).
477 However, ~~our~~ ^{40}Ar/^{36}Ar and ^{20}Ne/^{22}Ne ratios ~~which are~~ significantly below the expected MORB
478 value~~s~~ (44~~.~~,000 and 12.5, respectively; ~~-~~ Burnard, 1997; Moreira, 1998; Sarda, 2004)~~Burnard, 1997;~~
479 ~~Moreira et al., 1998)~~. As shown in Figure 7B, ^{40}Ar/^{36}Ar ~~correlate with~~and ^{3}He/^{36}Ar values~~, and~~ also
480 fall along a two-component mixing between a MORB-like upper mantle and atmosphere ~~well fits the~~
481 ~~Ar-He dataset~~. (~~whereas~~ He/Ar* ratios ~~between~~of 0.14 ~~and~~to 3.5 ~~are able to~~explain the whole data
482 variability; see also Figure 9B~~; see Fig. /b)~~ ~~(with the exception of a few samples that exhibit ^{4}He/^{40}Ar*~~
483 ~~ratios affected by other processes; see Section 6.3)~~. Likewise, samples fit the binary mixing air-
484 MORB when using the three-isotope neon plot (Figure 7C), confirming the existence of atmospheric
485 fluids in our inclusions. The atmospheric component~~Atmospheric contamination~~ is especially notable
486 ~~only~~ in nodule V-I that exhibits an isotopic signature close to that of air with ^{4}He/^{20}Ne ratios below
487 10 (for Opx and Cpx) and ^{40}Ar/^{36}Ar values below 392. These compositions confirm that this nodule
488 likely suffered secondary processes that modified its pristine mantle signature. This sample is
489 therefore not considered ~~not anymore~~ representative of the local SCLM (and omitted from the
490 following discussion).

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6.1.2 Diffusive Fractionation

As shown in Figure 6, the lowest noble gas concentrations (especially helium) were measured in V-I crystals and, to a minor extent, in V-A and V-C (He<10^{-12} mol/g). Some CO_2 depletion is also evident in sample V-I. When plotting ^3He, ^4He, $^{40}Ar*$, and $^4He/^{40}Ar*$ vs. Rc/Ra (Figures 8 and 9A-9C), we find that in sample V-I the He and Ar depletion is also accompanied by $^3He/^4He$ (<6.15 Ra) sensibly lower than the dataset average (7.39 ± 0.14 Ra). In samples V-A and V-C, the $^3He/^4He$ decrease is less important. It is worth noting that the lower Rc/Ra values mostly correspond to pyroxenes (Opx and Cpx) from the same nodule, while Ol crystals are less or not modified. Indeed, Ol from V-I show $^3He/^4He$ values (7.25 – 7.37 Ra) that are comparable to the rest of the dataset (7.21 - 7.36 Ra).

Following Burnard et al. (1998), Burnard (2004), and Yamamoto et al. (2009), this data variability can be interpreted as due to preferential loss of He (relative to Ar and CO_2) due to diffusive fractionation. In fact, in case of radiogenic ^4He in growth or addition to FI, an increase of ^4He concentration with decreasing $^3He/^4He$ values should be expected, without any relative decrease of ^3He, $^{40}Ar*$, and $^4He/^{40}Ar*$. We highlight that He diffusion into the fast flowing melt filled dissolution channels cutting the mantle is commonly invoked during partial melting (Burnard, 2004; Yamamoto et al., 2009; Faccini et al., 2020) and/or metasomatism of solid mantle that prevalently affects pyroxene crystals. The ^4He diffusion coefficient is considerably higher than that of ^{40}Ar ($D_{4He}/D_{40Ar} = 3.16$ in solid mantle; Burnard, 2004; Yamamoto et al., 2009). Likewise, the difference in mass between ^3He and ^4He implies important differences in their diffusivities ($D_{3He}/D_{4He} = 1.15$; Trull and Kurz, 1993; Burnard, 2004; Yamamoto et al., 2009). Hence, in case of diffusive loss of He, a decrease in $^3He/^4He$ and $^4He/^{40}Ar*$ is expected, as observed in V-A and V-I pyroxenes. Because the clearest evidences of diffusive fractionation are observed in pyroxenes, we exclude V-C because Ol from this sample show $^3He/^4He$ values (7.13 Ra) comparable to Opx (7.33 Ra) from the same nodule (although Ol have lower He concentrations). In any case, in order to properly interpret the origin of the He in the following sections of the discussion, pyroxenes from V-I and V-A nodules will not be discussed further.

To support the hypothesis of a diffusive fractionation, in Figures 8 and 9A-B-C we model this process based on the approach proposed by Burnard et al. (1998), Burnard (2004), Yamamoto et al. (2009), and already applied in Boudoire et al. (2020) and Faccini et al. (2020). We consider a starting mantle composition of $^3He = 1.56 \times 10^{-17}$ mol/g, $^4He = 1.5 \times 10^{-12}$ mol/g, and $^{40}Ar* = 6 \times 10^{-13}$ mol/g, which corresponds to the lowest concentrations of these species in nodules not evidently modified by diffusion. We additionally use a starting $^4He/^{40}Ar* = 2.5$ (the average mantle production ratio), and a $^3He/^4He = 7.5$ Ra, which is within the Rc/Ra variability of the dataset.

528 According to our modeling, diffusive fractionation is able to justify the data variability observed in
529 pyroxene from V-A and V-I samples, which will not be discussed anymore.

530

531 *6.1.3 Exposure to cosmic rays*

532 Several studies have shown that rocks exposed to cosmic rays (i.e. after eruption) favor the
533 accumulation of ^{3}He in the crystal lattices shifting the original ^{3}He/^{4}He ratios to higher values
534 (Kurz, 1986; Lal, 1987; Dunai and Baur, 1995; Dunai, 2010; Broadley et al., 2016; Nesterenok and
535 Yakubovich, 2016; Correale et al., 2019). According to e.g. Dunai and Baur (1995) and Correale et
536 al. (2019 and references therein), crystals with low He concentrations are more prone to changes
537 due to the diffusion of ^{3}He from lattices into the FI. However, in the case of the JH mantle
538 xenoliths, the aliquots with the lowest He contents (^{3}He <10^{-17} and ^{4}He < 10^{-12}; Figure 9A, 9B)
539 generally show an opposite effect, that is a decrease in ^{3}He/^{4}He compared to the samples with the
540 highest helium concentrations that we interpreted as the result of diffusive fractionation. The
541 eruption time of JH xenoliths (311 ± 19 ka; Saucedo et al., 2017) limits the exposure time to
542 cosmic rays. Finally, the single step crushing method prevents the contribution of secondary He
543 accumulated in the crystal lattice (cosmogenic ^{3}He and radiogenic ^{4}He), as evidenced by other
544 authors (Kurz, 1986; Graham, 2002; Gautheron et al., 2005; Rizzo et al., 2018; Correale et al.,
545 2019; Faccini et al., 2020). We therefore conclude that the effect of cosmogenic ^{3}He in our samples
546 is negligible.

547
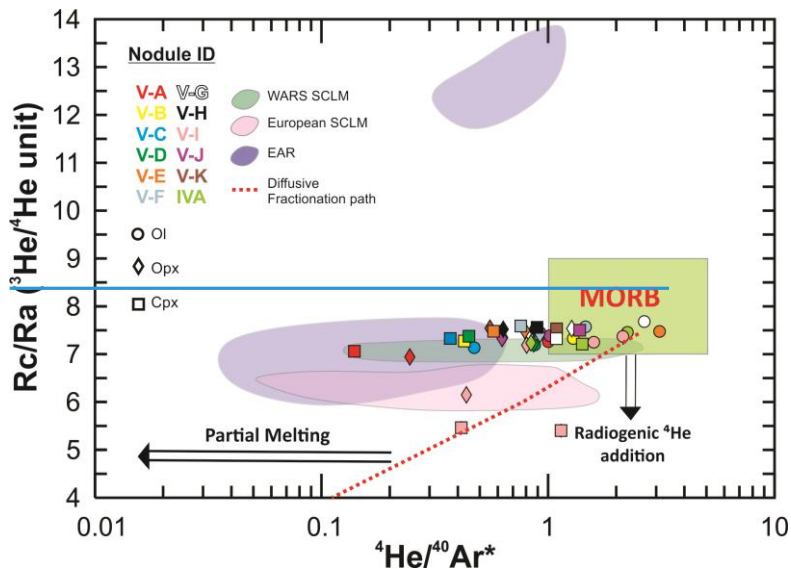
Figure 8. $^4He/^{40}Ar^*$ *vs* $^3He/^4He$ *corrected for air contamination (Rc/Ra) ratios of FI from JH mantle xenoliths. MORB range is reported at Rc/Ra = 8 ± 1 (Graham, 2002) and $^4He/^{40}Ar^*$ from 1 to 5 (Yamamoto et al., 2009). The WARS SCLM, European SCLM and EAR compositional ranges were built using FI data cited in Figure 6. The diffusive fractionation path was modeled using the diffusion coefficient (D) of ^3He, ^4He, and $^{40}Ar^*$ (D_{3He}/D_{4He}=1.15 andD_{4He}/D_{40Ar}=3.16 in solid mantle; Burnard, 2004; Yamamoto et al., 2009).*

6.2 3 The effect of partial melting

It has previously shown (Graham, 2002; Burnard, 2004; Yamamoto et al., 2009; Correale et al., 2012, 2016, 2019; Rizzo et al., 2018; Faccini et al., 2020) that the noble gas signature of mantle xenoliths depends to some extent on the melting history of the mantle source, and that the $^4He/^{40}Ar^*$ ratio is a useful tracer to understand partial melting degree in mantle xenoliths. The method stands on the different mineral/melt partition coefficients of the two elements (Heber et al., 2007). In detail, it has been verified that He is more incompatible than Ar, thus escaping the mantle more effectively during partial melting, and ultimately causing a $^4He/^{40}Ar^*$ decrease in the mantle residuum (Burnard, 2004; Heber et al., 2007; Yamamoto et al., 2009), as observed in Figure 8. However, Rizzo et al. (2018) first argued that estimating partial melting degrees based $^4He/^{40}Ar^*$ in FI fluid inclusions is tricky, because noble gases are not directly measured in crystals (i.e., dissolved in the solid matrix) but rather in the FI fluid inclusions hosted in crystals. In fact, the calculated noble gas-based partial melting degrees do not match (are sensibly lower than) those obtained from lithophile elements-based models. On the other hand, the relative $^4He/^{40}Ar^*$ variations observed in FI fluid inclusions are qualitatively consistent with those indicated by lithophile elements-based models, suggesting that an equilibrium between the noble gas in FI fluid inclusions and those dissolved in the crystals must exist (Rizzo et al., 2018; Faccini et al., 2020).

As noted in Figure 8, the variability of $^4He/^{40}Ar^*$ ratios in the JH nodules reflects processes that have mainly affected the pyroxenes. Indeed, the majority of Ol crystals have $^4He/^{40}Ar^*$ values within the typical production ratio of a fertile mantle ($^4He/^{40}Ar^* = 1$-5; Marty, 2012), while Opx and Cpx crystals exhibit slightly lower $^4He/^{40}Ar^*$ ratios, from 0.4 to 1.4. In general, the $^4He/^{40}Ar^*$ population of our samples implies that source mantle melting may have to some extent impacted the Opx and Cpx noble gas signature, but not that of Ol, ultimately suggesting a low degree of partial melting. We stress that the degrees of partial melting are not well constrained on petrological basis for the JH spinel lherzolites, as a wide range (7-22%) has been proposed in previous work (Liang and Elthon, 1990).

6.3 4 Inferences on the noble gas signature of the JH source mantle

6.3 4.1 Evidences for a recycled air atmospheric component: Ne and Ar: Ne and Ar

As stated in section 6.1.12, the Ne and Ar isotopic systematics strongly support the presence of an atmospheric component in the JH FIfluid inclusions. This air-derived component is mixed with fluids having a MORB-like signature (Figure 7B, C). A similar behavior is observed in mantle xenoliths from the European SCLM, the West Antartic Rift System (WARS), Eastern Australia SCLM, Red sea region, N/S Kenya rifts WARS and Ethiopia (Afar). and European SCLM mantle xenoliths, as well as in other portions of SCLM on Earth (e.g., Gurenko et al., 2006). Instead, samples from EAR

exhibit an enrichment in $^{20}Ne/^{22}Ne$ relatively to $^{21}Ne/^{22}Ne$, due to the presence of a primordial component in the local mantle (Halldórsson et al., 2014).

The atmospheric component identified in the FI fluid inclusions may derive from two main possible processes, as summarized by Nuccio et al. (2008), Martelli et al. (2011), Correale et al. (2012), and Rizzo et al. (2018), and Faccini et al. (2020): a) air entrapment in crystal fractures during or after eruption of transporting lava, and b) the interaction with subducted atmospheric fluids recycled in the upper mantle.

Although air entrapment in crystals microcracks cannot be totally discarded due to surface exposure of the xenoliths over the last 300 ky, athe positive correlation between ^{3}He and ^{36}Ar suggests our petrographic evidence of a close association between FI and glass veins (Figure 4) support a deep origin (Figure 9aA), i.ee.g., a recycled air atmospheric component in the local lithospheric mantle likely inherited from subduction (Matsumoto et al., 2001). . Indeed, there is petrological evidence that supports the interaction of the local upper mantle with metasomatic fluids possibly coming from the subducted oceanic crust (Pier et al., 1989; Luhr and Aranda-Gómez, 1997; Dávalos-Elizondo et al., 2016). In view of the above, and with the aim of constraining the $^{40}Ar/^{36}Ar$ signature expected for the local mantle, we also evaluated the relationship between $^{20}Ne/^{22}Ne$ and $^{40}Ar/^{36}Ar$ ratios (Figure 9bFigure 9BS1), using . We based on the approach used by Langmuir et al. (1978) and Hopp et al. (2007a), according tond the variability of our dataset. Considering an upper mantle $^{20}Ne/^{22}Ne$ ratio equal to 12.5 (Sarda et al., 1988; Moreira et al., 1998), $^{36}Ar/^{22}Ne$ ratios between 4.21 and 93.5, a maximum $^{4}He/^{20}Ne$ ratio of 11,000 and $^{4}He/^{40}Ar*$ ratios between 0.14 and 3.11 (as observed in our samples; see Figures 7A and 8), we realizcalculated that a local upper mantle with $^{40}Ar/^{36}Ar$ ratiosignature equal toof about 10,500 for the local upper mantlecan justify the variability of our xenoliths (see Figure 9B and Table 3). Assuming a MORB-like $^{40}Ar/^{36}Ar$ signature of This approach suggests that the original $^{40}Ar/^{36}Ar$ of the upperpristine upper mantle (~44,000; (Moreira et al.,1998), our evidencesthese calculations further support has decreased significantly and supports the existence of an atmospheric component in the Mexican lithospheric mantle, likely recycled during subduction events. Similar indications were observed in SCLM xenoliths from European localities, West Antarctic Rift System (WARS), Eastern Australia, Red sea region, N/S Kenya rifts and Ethiopia (Afar). (Matsumoto et al., 1998, 2000; Hopp et al., 2004, 2007a, 2007b; Buikin et al., 2005; Gautheron et al., 2005a; Czuppon et al., 2009; Martelli et al., 2011; Halldórsson et al., 2014; Broadley et al., 2016; Rizzo et al., 2018; Correale et al., 2019; Faccini et al., 2020).

Petrological evidence also supportshighlights the interaction of the local upper mantle with metasomatic fluids possibly coming from the subducted oceanic crust (Pier et al., 1989; Luhr and Aranda-Gómez, 1997; Dávalos-Elizondo et al., 2016).Subduction may have favored recycling of air-rich components in the interested portion of the SCLM. Even though the present-day plate geometry in central and southern Mexico implies ththen and at the oceanic crust subduction terminates beneath the TMVB (Figure 1; Pardo and Suárez, 1995; Ferrari et al., 2012) i.e. 200 km south JH, subduction of the Farallon plate beneath the western part of North America during the Mesozoic and Paleogene could have potentially modified the Mexican lithospheric mantle directly below la Mesa Central (Pier et al., 1989; Bunge and Grand, 2000). We consider tTherefore, we consider it possiblerealistic that the presence of an atmospheric component in FI fluid inclusions from JH is mostly attributable to a local SCLM feature. Moreover, since Ne isotopes of JH overlap the fields of data from WARS and European SCLM mantle xenoliths, the recycling of an atmospheric component in the lithospheric mantle may be common to many other geodynamic contexts.

6.4~~13.2~~ *Noble gas signature of the JH mantle source*~~No mantle plume component in the JH mantle source~~.

Ne isotopes can additionally be used, in combination with He isotopes, to resolve any potential influence of a mantle plume on the isotopic signature of the JH mantle xenoliths. To this aim, the relationship between the extrapolated neon isotope ratio (i.e. the air-free mantle ^{21}Ne/^{22}Ne ratio expressed as ^{21}Ne/^{22}Ne$_{EX}$) and the ^{3}He/^{4}He values was evaluated (e.g., Hopp et al., 2004, 2007b; Halldórsson et al., 2014). The ^{21}Ne/^{22}Ne$_{EX}$ values were calculated by extrapolating the measured ^{21}Ne/^{22}Ne ratios to Neon-B (^{20}Ne/^{22}Ne=12.5) using the methodology proposed by Graham (2002) and Halldórsson et al. (2014). Only those samples with ^{40}Ar/^{36}Ar ratios > ~~300~~ 500 and ^{20}Ne/^{22}Ne ratios distinguishable from air were selected. For comparison, the same calculation was made using the Ne isotopes previously reported for the European SCLM (Buikin et al., 2005; Gautheron et al., 2005a; Martelli et al., 2011; Rizzo et al., 2018; Faccini et al., 2020)~~M (Gautheron et al. 2005; Martelli et al. 2011; Rizzo et al. 2018)~~, the WARS ~~SCLM~~ (Broadley et al., 2016; Correale et al., 2019)~~(Correale et al., 2019)~~, Eastern Australia SCLM (Matsumoto et al., 1998, 2000), Red sea region (Hopp et al., 2004; Halldórsson et al., 2014)~~and, the EAR~~Ethiopia (Afar) region (Halldórsson et al., 2014) and N/S Kenya rifts (Hopp et al., 2007b; Halldórsson et al., 2014); as a result, the graph reported in the Figure ~~9D~~ 10A was obtained.

As evidenced in Figure ~~9D~~10A, samples V-K/VF Ol, VF Opx and V-E/V-H Cpx exhibit ~~our mantle xenoliths have~~ (^{21}Ne/^{22}Ne)$_{EX}$ and ^{4}He/^{3}He ratios close to the theoretical value for a MORB-like upper mantle (as observed for some mantle xenoliths from the Easter Australia SCLM and the Red sea region), the remaining values fall along the ~~binary mixing~~ MORB-Plume mixing line. ~~Concerning~~When comparing our samples with other portions of SCLM on Earth, ~~and are higher compared to typical plume-related values. Concerning~~ the WARS, ~~and the European SCLM values~~and the N/S Kenya rifts, we notice that JH nodules have similar (^{21}Ne/^{22}Ne)$_{EX}$ ~~and~~but lower ^{4}He/^{3}He values, confirming the presence of a ~~common~~dominating MORB component ~~for the three these localities and the less radiogenic nature of the Mexican lithospheric mantle. On the other hand, the~~T~~Instead, the ~~EAR~~Ethiopian xenoliths more clearly exhibit both (^{21}Ne/^{22}Ne)$_{EX}$ and ^{4}He/^{3}He ~~two groups of values, one group with (^{21}Ne/^{22}Ne)$_{EX}$ similar to the European SCLM and another group with~~ratios ~~similar~~close to ~~the a P~~plume endmember~~component~~.

~~Halldórsson et al. (2014) interpreted this variability by a binary mixing between these two end-members (SCLM and Plume), confirming the influence of a single mantle plume source~~In the case of JH mantle xenoliths, (^{21}Ne/^{22}Ne)$_{EX}$ ratios <0.05 would suggest a deep-mantle contribution of ~~plume-derived~~ Neon (<10%)~~;~~. ~~h~~However, it must be taken into account that the samples less contaminated by the atmospheric component fall within the AIR-MORB line when considering their error bars (Figure 7C). In addition, ~~this component does not affect~~the ^{3}He/^{4}He ratios ~~helium ratios which~~ reflect a homogeneous MORB-like ~~upper mantle~~ signature. Based on ~~noble gas signatures~~these evidences, we conclude that the upper mantle beneath JH is predominantly MORB-like with a minimum contamination by a recycled crustal component, although we cannot totally discard a deep-mantle ~~neon isotopic ratios from JH xenoliths do not totally exclude a plume~~ contribution~~, the local upper mantle is predominantly MORB with a minimum contamination by a recycled crust~~. This conclusion support the idea ~~. The helium and neon isotopic ratios from JH~~

~~xenoliths thus exclude a lower mantle contribution to the local SCLM. Rather, they point to a MORB-like source with a minimum contamination by a recycled crust, confirming~~ that the VESVF ~~is rather due to~~originates from extension and melting of the lithospheric mantle under the Mesa Central province.

~~6.3.3 A MORB-like ³He/⁴He ratio signature~~

As discussed above, the ~~³He/⁴He ratios measured in the xenoliths indicate a MORB-like signature (8±1 Ra, Graham, 2002; Figure 9~~10) for the JH mantle. The relative invariance of the Rc/Ra values suggests that the upper mantle under this portion of La Mesa Central is relatively homogeneous in terms of noble gases (Rc/Ra = 7.39 $\pm$~~±~~ 0.14; Figure 10B - D). This ^{3}He/^{4}He signature is similar to that measured at the WARS (7.5 ± 0.5 Ra and 7.1 ± 0.4 Ra; Broadley et al., 2016; Correale et al., 2019) and at the upper range of that inferred at the ~~WARS~~N/S Kenya rifts and Red Sea region (6.6 ± 0.7 Ra and 7.0 ± 0.9 Ra, respectively; Hopp et al., 2004, 2007b; Halldórsson et al., 2014), ~~(7.1 ± 0.4; Correale et al., 2019),~~ but manifestly less radiogenic than the European SCLM (6.1 $\pm$~~±~~ 0.9; Gautheron and Moreira, 2002; Buikin et al., 2005; Gautheron et al., 2005a; Martelli et al., 2011; Rizzo et al., 2018; Faccini et al., 2020)~~. ~~~~Gautheron and Moreira, 2002; Gautheron et al., 2005; Martelli et al., 2011; Rizzo et al., 2018).~~

The MORB-type ^{3}He/^{4}He ~~He~~signature at JH deserves some consideration in relation to the past geodynamic history of the area. We envisage two possible scenarios.

In scenario 1, the relatively homogeneous (MORB-like) ^{3}He/^{4}He ratios for the JH mantle xenoliths might be taken as indicative of a low-to-negligible recycling of crustal materials during the subduction of Farallon plate (20-40 Ma). A limited input of U-Th-bearing crustal materials would in fact explain well the low contribution of radiogenic ^{4}He in the local mantle. If this interpretation is correct, then past subduction events would only have added ~~only have altered the Ne and Ar isotopic budgets via the addition of~~ a recycled ~~air~~atmospheric component into the mantle (cfr 6.3~~1~~.1). Alternatively, one may consider a scenario (scenario 2) in which any addition of (subduction-related) ~~crustal~~materials during subduction of the Farallon plate was later (during the <20 Ma Basin and Range extensional phase) overprinted by an influx of MORB-like materials, rising from deeper (asthenospheric to deep SCL) mantle domains. This latter scenario is supported by the geodynamic reconstructions that indicate a metasomatism/refertilization of the lithospheric mantle during the Basin and Range extensional phase. Paleo-subduction reconstructions indicate that the Farallon plate subducted horizontally underneath Western North-America and Northern-Central Mexico between 74 - 40Ma, producing the Laramide orogeny in the United States and the mountain range known as the Sierra Madre Oriental (SMOr) east of the JH (Figure 1; Atwater, 1989; Cserna, 1989; Severinghaus and Atwater, 1990; Bunge and Grand, 2000; Eguiluz de Antuñano et al., 2000; Lee, 2005). This tectonic configuration would have changed at ~40-20Ma, however, when the retreating ~~subduction~~ of the Farallon slab occurred, a commonly invoked cause for initiation of the Basin and Range extension (Leeman and Harry, 1993; Nieto-Samaniego et al., 1999, 2005; Lee, 2005; Sedlock, 2003).~~(Leeman and Harry, 1993; Nieto-Samaniego et al., 1999; Lee, 2005; Nieto-Samaniego et al., 2005; Sedlock, 2003).~~ According to Nieto-Samaniego et al. (1999), retreating of the oceanic slab favored the influx of younger and hotter asthenospheric material that ultimately led to melt generation and extension at the base of the Mesa Central. Evidence of this process comes from the intense

714 normal faulting in the Mesa Central registered 30Ma, 23-24Ma 12-13Ma ago, and from the transition
715 from calc-alkaline volcanism (in the so-called Sierra Madre Occidental; SMO; Figure 1) to intraplate
716 alkaline volcanism (Henry and Aranda-Gomez, 1992; Nieto-Samaniego et al., 1999; Aranda Gómez
717 et al., 2000). Injection of ^{3}He-rich (MORB-like) asthenospheric melts during the mid-Cenozoic could
718 well have caused re-fertilization/re-juvenation of the Mexican lithospheric mantle in a model similar
719 to that proposed for the lithospheric mantle beneath the Yangtze craton and the WARS (Correale et
720 al., 2016, 2019; Faccini et al., 2020). This scenario is possible if we assume that almost all ^{3}He comes
721 from asthenospheric melts, as proposed by Gautheron and Moreira (2002) and Gautheron et al.
722 (2005a) Gautheron and Moreira (2002) and Gautheron et al. (2005) to explain the noble gases
723 systematics of the European SCLM (a steady-state model).
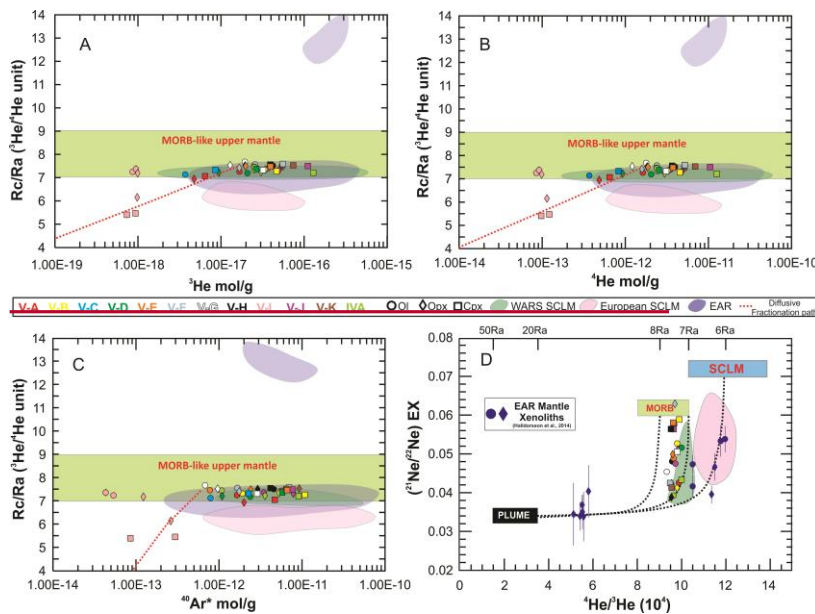
Figure 9. A) ^{3}He, B) ^{4}He and C) ^{40}Ar* vs ^{3}He/^{4}He corrected for air contamination (Rc/Ra). MORB range is reported at Rc/Ra = 8 ± 1 (Graham, 2002). D) ^{21}Ne/^{22}Ne ex ratios vs ^{4}He/^{3}He ratios, adapted from Halldórsson et al. (2014). Dotted lines are binary mixing between three endmembers: 1) Plume, at 20Ra and ^{21}Ne/^{22}Ne ex = 0.034 ± 0.001, 2) MORB-like upper mantle at 8 ± 1 Ra and ^{21}Ne/^{22}Ne ex = 0.06 ± 0.001 and SCLM at 6.1 ± 0.9 Ra and ^{21}Ne/^{22}Ne ex = 0.07 ± 0.001.

724 Independently on respective if of subduction is considered to have (scenario 2) or have not (scenario
725 1) impacted the He mantle budget, there is unquestionable petrographic evidence (this study; Liang
726 and Elthon, 1990; Luhr and Aranda-Gómez, 1997) for a melt-related metasomatic event affecting the
727 JH, potentially during Basin and Range extensional phase (Nieto-Samaniego et al., 1999).

728

6.2~~45~~ ^{3}He fluxes, ^{4}He production and the helium residence time for the Mexican lithospheric mantle

The MORB-type He signature of JH xenoliths can quantitatively be interpreted in light of the SCLM model of Gautheron and Moreira, (2002). According to the authors (see ~~also~~ (also (Griffin et al., 1999, 2009), ~~Griffin et al., 1999, 2009),~~ the geochemical and isotopic characteristics of the SCLM are the ultimate result of any past interaction with fluids and melts coming from (i) deeper mantle sources and/or (2) recycled slab components that have alternated over geological time (Griffin et al., 1999). In terms of helium isotopes, Gautheron and Moreira (2002) argued that the SCLM is globally homogeneous (6.1±0.9 Ra). They based this inference on the study of suites of ultramafic xenoliths and alkali basalts collected from different continental settings (Europe, USA, Antarctic, Australia, and West Africa).

In order to explain its helium isotopic homogeneity, Gautheron and Moreira (2002) proposed the global lithospheric mantle is in steady state for helium. In their model, the global SCLM is continuously metasomatized by melts and fluids with a MORB-like helium signature coming from the asthenosphere (affecting the entire reservoir); eventually, this signature becomes more radiogenic due to U and Th decay resulting in lower ^{3}He/^{4}He ratios (e.g. 6.1 ± 0.9 Ra). Thus, the steady-state model is based on the balance between the He flux from the asthenosphere and the in-situ production in the lithosphere of radiogenic ^{4}He. From this model, it is possible to estimate the helium residence time in the lithospheric mantle (Rt), the ^{3}He flux (F) and the ^{4}He production (P*). The model uses the dimensions of the SCLM (thickness, surface and density) assuming a constant U + Th concentration. These authors reported a Rt = ~200 Ma, F= 270 mol/yr and P* = 6.8x10^6 mol/yr for the global SCLM, while Gautheron et al. (2005) obtained a Rt = 5-150 Ma, F= 3.5 x10^4 at/m^2/s (~ 1 mol/yr) and P* ~ 3 x 10^4 mol/yr for the European SCLM.

However, some studies on noble gas systematics (including our results) ~~our data and a recent study on West Antarctic Rift (Correale et al., 2019)~~ support a more fertile signature (^{3}He/^{4}He> 7.0 Ra) for some portions of the SCLM on Earth (e.g., Southern Australia and West Antarctic Rift; Matsumoto et al., 1998; Broadley et al., 2016; Correale et al., 2019). Therefore, we argue that the steady state model proposed by Gautheron and Moreira (2002) should be applied in local portions of SCLM to eventually detail their interactions with the asthenosphere. Using this steady-state model, and considering the ^{3}He/^{4}He signature of the JH mantle xenoliths, we estimated the helium residence time, the ^{3}He flux and the ^{4}He production for the lithospheric mantle located under the San Luis Potosí state (central Mexico) ~~following Gautheron and Moreira (2002)~~:

$$F = \frac{P^*}{\left(\frac{^4He}{^3He}\right)_{SCLM} - \left(\frac{^4He}{^3He}\right)_{MORB}} \qquad \text{eq.3}$$

In eq. 3, F is the ^{3}He flux (cc STP/yr) and P* is the ^{4}He production (P*= 2.8 *10^{-14} * (4.35+Th/U) * U * M). U is the concentration of uranium in ppm and M is the mass of the subcontinental mantle. The helium residence time Rt is defined as:

$$Rt = \frac{Total\ ^3He\ in\ the\ SCLM\ (cc\ STP)}{F} \qquad \text{eq.4}$$

The parameters used in the calculation are as follows: 1) the average of the ^{3}He~~^{4}He~~/^{3}^{4}He ratios measured in JH mantle xenoliths equal to (97,500 (7.38~~7.38~~ Ra) and a MORB endmember equal to 84,600 (8.5 Ra). The latter value is higher than that assumed by Gautheron and Moreira (2002) (8.0

769 Ra) because preliminary results for mantle xenoliths from other localities in central Mexico yield
770 Rc/Ra values of $\leq$ 8.35 (unpublished data); 2) U contents between 0.01 and 0.03 ppm as previously
771 reported for mantle xenoliths from central Mexico (Dávalos-Elizondo et al., 2016) and a Th/U = 3
772 as assumed by Gautheron and Moreira (2002); 3) A subcontinental mantle mass equal to 3.66×10^{21}
773 g. This mass was estimated assuming a thickness of the local lithospheric mantle ~of ~150km
774 (density of 3.3×10^6 g/m^3; Gautheron and Moreira, 2002) and a; 4) A surface of 7.4×10^9 m^2 that
775 includes all the Cenozoic intraplate monogenetic volcanic fields located in the San Luis Potosí state
776 (VESVF, SDVF and Los Encinos volcanic field; see Figure 1; Aranda-Gómez et al., 2007); 5) A
777 upper mantle ^{4}He concentration =equal to 1 x 10^{-6} ccSTP/g (4.5 x 10^{-11} mol/g), which corresponds
778 to the maximum value identified for continental mantle xenoliths (Gautheron and Moreira, 2002);
779 this value is equivalent to a ^{3}He concentration =1.0 x 10^{-11} ccSTP/g (4.5 x 10^{-16} mol/g) assuming a
780 Rc/Ra = 7.38; thus the total ^{3}He estimated for the local SCLM is 1.64×10^6 mol (3.66×10^{10} cc STP).
781 .-The results obtained are reported in Table 34.

782 The calculated ^{3}He fluxes for the Mexican lithospheric mantle vary from 0.027 to 0.080 mol/g
783 (Figure 10A11A). These fluxes are very low if compared with the values reported for the global
784 SCLM, the European SCLM or MORB values (800-1300 mol/g; Marty and Jambon, 1987; Javoy et
785 al., 1989; Michael and Graham, 2015; Tucker et al., 2018). When scaled to the surface area (7.4×10^9
786 m^2) of volcanism in the San Luis Potosí state, our specific fluxes vary between 6.9 and 20.7 at/s/cm^2
787 (Figure 11B) which are well above the MORB and the global SCLM values (4.8 at/s/cm^2 and 3.5
788 at/s/cm^2, respectively; Craig et al., 1975; Gautheron and Moreira, 2002) confirming a high ^{3}He
789 contribution from the asthenosphere under central Mexico.

790 The associated Rt values range from 20 to 60 Ma. These estimates are lower if compared to the global
791 SCLM and would explain the less radiogenic character of the Mexican lithospheric mantle. In this
792 model, the Rt values do not depend on the area but have a close relationship with the average of the
793 ^{3}He/^{4}He ratios measured in the mantle xenoliths. It is reasonable to think that the smaller the ^{3}He/^{4}He
794 ratio measured in the xenoliths (7.38 Ra for JH xenoliths and 6.1Ra for the SCLM), the longer the
795 helium residence time in the lithospheric mantle should be. Therefore, low Rt values implies low ^{4}He
796 production and high ^{3}He/^{4}He ratios, as observed in JH mantle xenoliths. Moreover, our estimated Rt
797 range overlaps with the inferred age range for the retreating subduction of the Farallon slab (40-20
798 Ma ago), a processes, which may have triggered the injection of asthenospheric melts in the
799 lithospheric mantle and the generation of the Basin and Range province (Nieto-Samaniego et al.,
800 1999; Lee, 2005). If correct, our results would independently indicate that the last major geodynamic
801 modification in the lithospheric mantle underneath the JH occurred during the lower and mid-
802 Cenozoic. We argue that the refertilization event was able to increase the ^{3}He/^{4}He signature within
803 the MORB-like range, overprinting the pre-Cenozoic signature recorded by the Mexican lithospheric
804 mantle. Since then, the latter would have evolved in a similar way to that proposed by Gautheron and
805 Moreira (2002), i.e.i.e., in a steady state becoming slightly more radiogenic during the last ~20Ma
806 down to the measured ^{3}He/^{4}He values.

807 In conclusion, both the low production of ^{4}He and the relative lower Rt (compared to other areas)
808 could explain the high ^{3}He/^{4}He ratios measured in JH mantle xenoliths. However, we caution these
809 are local estimates; therefore, in order to minimize the effect generated by the area and possible
810 mantle heterogeneities, future work will target obtaining isotopic data for mantle xenoliths from other

811 localities of the Basin and Range extension in Mexico. This will allow a more realistic reconstruction
812 of the evolution of the Mexican lithosphere in terms of noble gases.

813

814 *6.25~~4~~.1 Mantle CO_2 fluxes*

815 We combine the ^{3}He flux estimated above with the $CO_2/^3$He ratios measured in the JH xenoliths (e.g.
816 Marty and Jambon, 1987; Tucker et al., 2018) to calculate the mantle-derived CO_2 fluxes in the area.
817 Taking U concentrations between 0.01 ppm and 0.03 ppm and a $CO_2/^3He_{(avg)}$ ~1.47 x 10^9, the
818 calculated CO_2 fluxes range from 3.93 x 10^7 mol/yr (1.02 x 10^{10} at/s/cm^2) to 1.18 x 10^8 mol/yr
819 (3.05x10^{10} at/s/cm^2; ~~(~~Figure 11C-11~~0~~BD). Our estimated fluxes are lower than previously estimated
820 for other continental rift localities (such as the EAR), consistent with the small area of the San Luis
821 Potosí volcanic filed (considered in the model), ~~ ~~and correspond to <0.1% of the MORB CO_2 fluxes;
822 similarly, our fluxes are lower than estimated for hot spot settings such as Hawaii or Canary Islands
823 (Hauri et al., 2019). Additional studies on noble gas and CO_2 isotopic data from other mantle
824 xenoliths locations in central and northwestern Mexico are required to further validate our results.

825
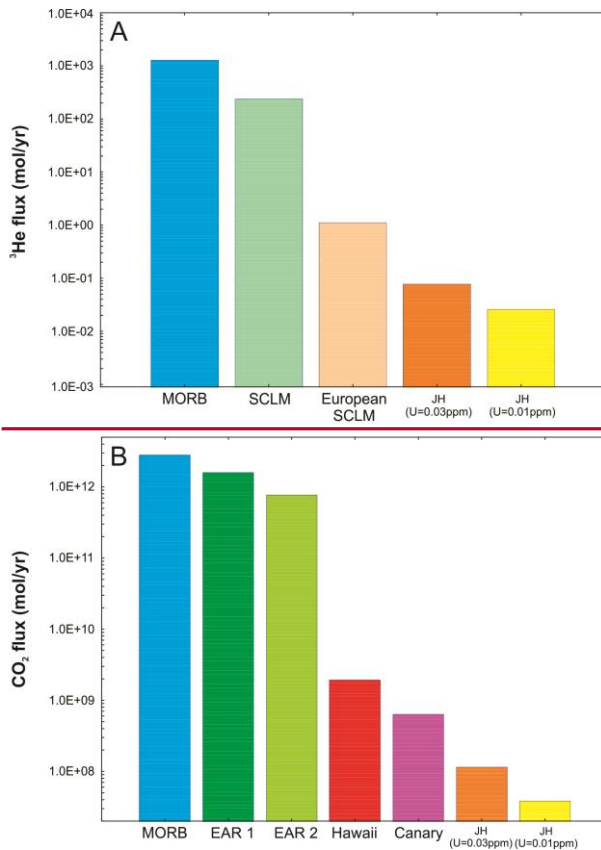
Figure 10. A) Comparison between ³He fluxes measured in central Mexico based on JH mantle xenoliths analysis (at U=0.01 and 0.03 ppm) and other localities; MORB value was built using data from Michael and Graham (2015) using a CO₂/³He ratio =2.2 x 10⁹ (Marty and Tolstikhin, 1998), SCLM value was taken from Gautheron and Moreira (2002), the European SCLM flux was calculated based on Gautheron et al. (2005). B) Associated CO₂ fluxes (mol/yr) for central Mexico compared with other tectonic localities. MORB CO₂ flux was calculated after Michael and Graham (2015); EAR1 and EAR2 values were taken from Lee et al. (2016) and Foley and Fischer (2017), respectively; Hawaii and Canary fluxes were obtained from Hauri et al. (2019).

826

827

828

6.5 36 Inferences on CO₂ origin.

In JH peridotites, fluids are dominated by CO_2 (Figure 6), as typically recorded by other worldwide mantle xenoliths (Andersen and Neumann, 2001; Deines, 2002; Frezzotti and Touret, 2014). (Deines, 2002; Andersen and Neumann, 2001, Frezzotti and Touret, 2014). Thus, the CO_2 isotopic composition can be used to constrain carbon origin. Our samples exhibit $\delta^{13}C$ ratios between −0.97 and −2.86‰ (Figure 11A12A); they are therefore isotopically more positive (^{13}C-rich) than found in

835 European mantle xenoliths in alkaline intra-plate and extensional contexts, such as in the Hyblean
836 plateau (southeast Sicily, Italy; ranging from-4 to -2‰; Correale et al., 2015) and Lower Silesia
837 (southwest Poland; ranging from -4.7 to -3.1‰; Rizzo et al., 2018).

838

839 The CO_2 isotopic composition in the JH peridotites is also well above the $\delta^{13}C$ MORB mantle range
840 ($-8‰ < \delta^{13}C < -4‰$; Sano and Marty, 1995). When $\delta^{13}C$ values are plotted against Rc/Ra and
841 $CO_2/^3He$ ratios (Figure ~~11B~~12B, ~~11C~~12C), our samples fall along a MORB-Limestone mixing line,
842 suggesting source mantle Carbon contamination by C-rich fluids with a crustal carbonate signature.

843 The crustal carbon component found in ~~FI~~ fluid inclusions of JH xenoliths may in principle derive
844 from two main distinct processes: (i) infiltration of CO_2 rich fluids derived by assimilation of
845 carbonates by host magmas during ascent through the continental crust, and (ii) mantle
846 metasomatism by CO_2-rich fluids and melts derived from subducted oceanic crust and sediments.

847 Infiltration of CO_2 fluids in mantle xenoliths outgassed during assimilation of carbonates in basanitic
848 magmas in the continental crust should be considered since JH maar formed on carbonate deposits
849 (the Valles-San Luis Potosí calcareous platform (PVSLP) and the Mesozoic Basin of central
850 Mexico). However, the relatively fast ascent rates of the host magma through the continental crust
851 (Luhr et al., 1989; Pier et al., 1989), and the lack of carbonate xenoliths in the host lava, argue against
852 a crustal component inherited ~~–~~during sin-eruptive magma ascent. Conversely, petrographic and
853 Raman evidence indicates pervasive infiltration of carbonate-bearing silicate melts and CO_2-fluids
854 in peridotites (Figure 4), strongly supporting deep carbon mobility during a metasomatic event in the
855 lithospheric mantle. We, therefore, conclude that the carbonate component identified in JH CO_2
856 fluids was trapped under mantle conditions and is related to CO_2 degassing of metasomatic
857 carbonate-rich silicate melts on reaction with mantle minerals. Metasomatic processes occurred well
858 before entrainment by the host magma and eruption (as proposed by Liang and Elthon, 1990).

859 As mentioned in the previous sections, northwestern Mexico's current tectonic configuration
860 indicates that the Cocos and Rivera plates do not directly affect the mantle under the Mesa Central,
861 making it difficult to consider involvement of present subduction (Figure 1). Moreover, some studies
862 suggest that the contribution of carbonate sediments from the subducting slab is minimal. The CO_2-
863 rich plume gases released by arc volcanoes (e.g., Popocatepetl) come from the assimilation of
864 limestone deposits, as evidenced by trace element analysis performed in mafic rocks and the presence
865 of carbonate xenoliths in volcanic deposits (Goff et al., 1998, 2001; Aiuppa et al., 2017). A low
866 contribution of subducted Carbon in fluids has also been proposed for other volcanic fields belonging
867 to the TMVB, such as the Sierra Chichinautzin Volcanic Field (SCVF; Verma, 2000) and the
868 Michoacan-Guanajuato Volcanic Field (MGVF; Verma and Hasenaka, 2004).

869 In contrast to present-day subduction being an unlikely driver, we emphasize a possible major role
870 played by older subduction of the Farallon underneath the northwestern margin of North America
871 during the Mesozoic and early Cenozoic (Atwater, 1989; Ferrari et al., 2012; Henry and Aranda-
872 Gomez, 1992; Sedlock, 2003). Several authors claim that the North American lithospheric mantle
873 could have been hydrated by fluids or melts released by flat subduction of the Farallon plate, as
874 evidenced by petrological studies of mantle xenoliths from the Sierra Nevada and the Colorado
875 Plateau (Smith et al., 1999; Lee, 2005; Li et al., 2008). "Farallon hydration" (Lee, 2005) is suggested
876 to have occurred during the late Cretaceous and early Cenozoic, and to have affected the lithospheric

877 mantle up to 800 km inboard of the trench (Li et al., 2008). This metasomatic event is also well
878 documented in Mexican xenoliths (Liang and Elthon, 1990; Dávalos-Elizondo et al., 2016; Levresse
879 et al., 2016). For example, Luhr and Aranda-Gómez (1997) interpreted the systematic east to west
880 oxygen fugacity increase in Cenozoic mantle xenoliths from central and northern Mexico as induced
881 by the progressive oxidation of the lithospheric mantle by fluids released by the Farallon oceanic
882 slab.

883 In light of the above, the interaction between subducted fluids delivered by the Farallon plate and the
884 Mexican lithospheric mantle could represent a feasible mechanism to explain the heavy $\delta^{13}C$
885 signatures of JH mantle fluids. We argue that the crustal carbon component identified in the ~~FI~~ fluid
886 inclusions would reflect a mantle feature induced by an old subduction-related carbonate component
887 inherited during the mid-Cenozoic before the Basin and Range extension (Middle Miocene; Henry
888 and Aranda-Gomez, 1992; Sedlock, 2003) and recycled in the local mantle.

889
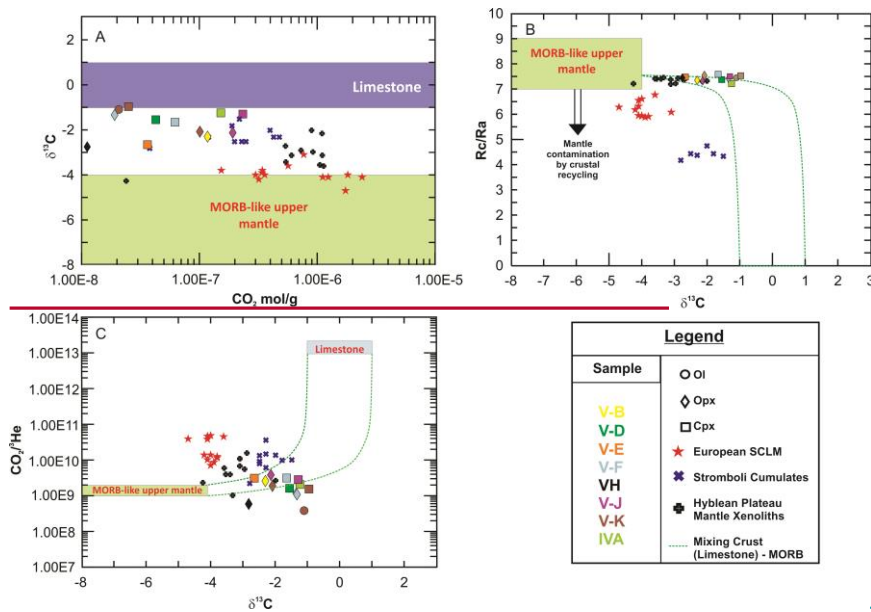
Figure 11. A) CO_2 vs $\delta^{13}C$. Hyblean, Stromboli and European SCLM data from Correale et al. (2015), Gennaro et al. (2017) and Rizzo et al. (2018), respectively. B) $\delta^{13}C$ vs $^3He/^4He$ corrected for air contamination (Rc/Ra). Dotted lines are binary mixing between two endmembers: 1) Limestone at $\delta^{13}C = 1, 1$ and Rc/Ra= 0.01 and 2) MORB like upper mantle at $\delta^{13}C = -4$ and Rc/Ra = 7.38. C) $\delta^{13}C$ vs $CO_2/^3He$. Dotted lines are binary mixing between two endmembers: 1) Limestone at $\delta^{13}C = 1, 1$ and $CO_2/^3He = 10^{13}$ and 2) MORB like upper mantle at $\delta^{13}C = -4$ and $CO_2/^3He = 1.00 \times 10^9, 2.00 \times 10^9$.

890 **7. CONCLUSIONS**

891 We investigate the petrography and noble gas-CO_2 composition of ~~FI~~ fluid inclusions in ultramafic
892 mantle xenoliths collected from JH, in central Mexico. Peridotites are classified as spinel-lherzolites

893 and harzburgites. Petrographic observations and Raman microspectroscopy analyses of fluid and
894 melt inclusions reveal the coexistence of glass/carbonate microveins and a CO_2 fluid phase
895 permeating the rocks, suggesting interaction between peridotites and degassing carbonate-rich
896 silicate melts at mantle depth.

897 The $^4He/^{40}Ar*$ range (0.14 - 3.11) partially overlaps that of fertile mantle (1-5), which could and
898 indicate eithers a low degree of partial melting and/or the occurrence of a
899 metasomatism/refertilization process by melts degassing fluids ultimately entrapped in the mantle as
900 secondary fluid inclusions.

901 Ne and Ar systematics reveal a mixing between atmospheric and MORB-like fluids, strongly
902 supporting the presence of an atmospheric component eventually recycled from the Farallon plate
903 subduction. Although, $(^{21}Ne/^{22}Ne)_{EX}$ ratios suggest the existence of plume-derived Neon in our fluid
904 inclusions, JH mantle xenoliths exhibit homogeneous $^3He/^4He$ signature (7.394 ±+ 0.2-14 Ra) that is
905 comparable to that of the MORB-like mantle and higher similar tothan other worldwide SCLM
906 localities (eg., Eastern Australia, N/S Kenya rifts and WARS). This isotopic signature results from a
907 low recycling of crustal components in the local mantle possibly overprinted by a
908 metasomatism/refertilization episode reasonably occurred after the subduction retreatingretreat of
909 the Farallon slab during the early and mid-Cenozoic.

910 Based on the "Steady-state" model proposed by Gautheron and Moreira (2002), we estimated a
911 helium residence time in the local SCLM between 20-60Ma, which overlaps the geodynamic
912 evolution of the area and the metasomatism/refertilization event. Since then, the lithospheric mantle
913 would have evolved in a steady state for helium (from a MORB signature ~8.5 Ra) becoming slightly
914 more radiogenic during the last ~20Ma. We also calculated ^3He fluxes between 0.027 - 0.080 mol/g,
915 ^4He production rates from 340 to 1000 mol/yr and mantle CO_2 fluxes from 3.93 x 10^7 mol/yr to
916 $1.18x10^8$ mol/yr represent less than the 0.1% of the MORB CO_2 fluxes.

917 He and Ne isotopic signatures argue against the presence of a mantle plume under central Mexico.

918 The $\delta^{13}C$ values measured in JH FI fluid inclusions reveal a binary mixing between a MORB-like
919 upper mantle and a crustal carbonate component (limestone). We propose that the crustal
920 CO_2/carbonate component identified in JH xenoliths was trapped under mantle conditions through
921 metasomatic reactions between peridotites ad C-bearing silicate melts. These would have acted as
922 carriers in the local mantle of a recycled carbon component inherited from the Mesozoic to early
923 Cenozoic Farallon subduction.

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937 **REFERENCES**
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TABLES

Table 1. *Modal composition of JH mantle xenoliths.*

Sample	Rock type	Ol (%)	Opx (%)	Cpx (%)	Sp (%)
VE	Lherzolite	54.47	28.96	14.37	2.2
VJ	Lherzolite	52.01	32.31	13.39	2.29
IVA	Lherzolite	72.48	15.86	10.45	1.21
VF	Lherzolite	52.08	33.97	11.93	2.02

VI	Lherzolite	53.41	23.48	19.79	3.32
VG	Harzburgite	68.14	30.04	1.26	0.56
VK	Lherzolite	61.27	24.59	13.69	0.44
VH	Harzburgite	62.08	31.26	4.47	2.18

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Sample (nodule)	Phase	Weight (g)	^{3}He	^{4}He	^{20}Ne	^{21}Ne	^{22}Ne	CO_2	^{40}Ar	^{36}Ar	^{40*}Ar	^{4}He/^{20}Ne	^{4}He/
V-A	Ol	0.95855	1.67E-17	1.65E-12	9.11E-16	2.72E-18	9.26E-17	2.80E-11	Formatted Table				
V-A	Opx	0.26388	4.74E-18	4.91E-13	8.90E-15	2.59E-17	9.00E-16	3.91E-10	3.61E-12	5.45E-15	2.00E-12	55.2	0.25
V-A	Cpx	0.21991	6.45E-18	6.57E-13	5.81E-16	2.62E-18	5.41E-17	6.23E-09	5.16E-12	1.55E-15	4.70E-12	1131.4	0.14
V-B	Ol	0.99706	2.53E-17	2.48E-12	1.84E-15	5.52E-18	1.88E-16	2.26E-10	3.70E-12	6.01E-15	1.92E-12	1349.7	1.29
V-B	Opx	0.4776	3.43E-17	3.36E-12	6.75E-15	1.97E-17	6.61E-16	4.88E-08	7.67E-12	7.95E-15	5.32E-12	497.5	0.63
V-B	Cpx	0.48584	4.67E-17	4.62E-12	4.41E-16	2.00E-18	3.61E-17	9.70E-08	1.12E-11	1.36E-15	1.08E-11	10483.3	0.43
V-C	Ol	0.59294	3.71E-18	3.74E-13	2.35E-16	n.a	2.61E-17	2.38E-10	Formatted Table				
V-C	Cpx	0.5587	8.55E-18	8.40E-13	5.73E-16	1.82E-18	5.87E-17	7.61E-10	2.57E-12	1.02E-15	2.27E-12	1466.6	0.37
V-D	Ol	1.02241	2.08E-17	2.08E-12	3.76E-16	1.25E-18	3.67E-17	9.18E-10	2.76E-12	1.27E-15	2.38E-12	5534.0	0.87
V-D	Opx	0.49922	9.46E-18	9.43E-13	2.33E-15	7.04E-18	2.39E-16	4.39E-09	2.07E-12	3.30E-15	1.09E-12	404.4	0.86
V-D	Cpx	0.47389	2.66E-17	2.59E-12	3.02E-16	1.23E-18	2.73E-17	3.25E-08	6.01E-12	7.58E-16	5.78E-12	8576.0	0.45
V-E	Ol	1.02916	2.51E-17	2.42E-12	1.22E-15	3.90E-18	1.19E-16	4.14E-09	Formatted Table				
V-E	Opx	0.51352	1.98E-17	1.90E-12	5.12E-15	1.56E-17	5.16E-16	2.74E-08	3.03E-12	2.11E-15	2.41E-12	371.6	0.79
V-E	Cpx	0.32954	3.96E-17	3.81E-12	3.93E-15	1.27E-17	3.81E-16	1.25E-07	7.06E-12	1.50E-15	6.62E-12	970.0	0.58
V-F	Ol	1.01203	2.57E-17	2.44E-12	3.49E-15	1.05E-17	3.55E-16	2.81E-09	2.50E-12	2.81E-15	1.67E-12	700.6	1.46
V-F	Opx	0.52681	1.66E-17	1.61E-12	4.91E-15	1.51E-17	4.98E-16	1.85E-08	2.37E-12	2.11E-15	1.75E-12	328.5	0.92
V-F	Cpx	0.31734	5.58E-17	5.29E-12	2.01E-14	6.07E-17	1.99E-15	1.78E-07	1.06E-11	1.24E-14	6.98E-12	262.9	0.76
V-G	Ol	1.00336	1.94E-17	1.81E-12	7.91E-16	2.44E-18	7.78E-17	3.91E-11	Formatted Table				
V-G	Opx	0.50526	1.29E-17	1.23E-12	3.20E-15	9.62E-18	3.26E-16	4.54E-09	1.47E-12	1.69E-15	9.68E-13	384.5	1.27
V-G	Cpx	0.32136	3.21E-17	3.15E-12	1.57E-15	5.55E-18	1.52E-16	2.24E-08	3.17E-12	9.41E-16	2.89E-12	2003.4	1.09
V-H	Ol	1.0181	4.21E-17	4.03E-12	4.72E-15	1.47E-17	4.66E-16	4.72E-09	6.44E-12	6.29E-15	4.58E-12	853.7	0.88
V-H	Opx	0.53853	1.95E-17	1.86E-12	4.01E-14	1.16E-16	3.94E-15	1.23E-08	1.52E-11	4.14E-14	2.93E-12	46.5	0.64
V-H	Cpx	0.30754	3.92E-17	3.73E-12	3.52E-15	1.13E-17	3.46E-16	5.09E-08	4.74E-12	1.93E-15	4.17E-12	1062.1	0.90
V-I	Ol	1.0437	8.62E-19	8.56E-14	1.42E-16	5.22E-19	1.39E-17	4.74E-11	2.25E-13	5.78E-16	5.37E-14	604.6	1.59
V-I	Opx	0.5057	5.02E-17	9.93E-14	1.55E-16	6.59E-19	1.34E-17	2.26E-10	3.77E-13	8.58E-16	1.23E-13	639.0	0.8
V-I	Cpx	0.49525	9.34E-19	1.23E-13	5.08E-14	1.46E-16	4.90E-15	n.a	3.72E-14	2.97E-13	n.a	2.4	0.41
V-I r*	Ol	1.01139	9.47E-19	9.25E-14	4.09E-16	1.32E-18	4.07E-17	7.54E-10	1.75E-13	4.48E-16	4.32E-14	226.0	2.14
V-I r*	Opx	0.50086	9.81E-19	1.15E-13	1.13E-14	3.37E-17	1.14E-15	1.31E-09	2.02E-12	5.94E-15	2.63E-13	10.1	0.44
V-I r*	Cpx	0.57112	7.37E-19	9.81E-14	9.68E-15	2.89E-17	9.72E-16	4.07E-10	5.64E-13	1.62E-15	8.59E-14	10.1	1.14
V-J	Ol	1.0333	3.63E-17	3.53E-12	3.77E-15	1.15E-17	3.76E-16	4.55E-09	5.30E-12	6.20E-15	3.47E-12	937.0	1.02
V-J	Opx	0.5061	5.02E-17	4.93E-12	7.60E-15	2.36E-17	7.58E-16	1.08E-07	1.02E-11	7.88E-15	7.87E-12	649.1	0.63
V-J	Cpx	0.30875	1.11E-16	1.07E-11	6.19E-15	2.02E-17	6.07E-16	3.23E-07	8.59E-12	2.87E-15	7.75E-12	1726.7	1.38
V-K	Ol	1.0225	5.42E-17	5.24E-12	4.99E-15	1.58E-17	4.99E-16	2.46E-08	7.72E-12	6.93E-15	5.67E-12	1049.9	0.92
V-K	Opx	0.52687	5.37E-17	5.13E-12	2.48E-14	7.37E-17	2.38E-15	1.05E-07	1.54E-11	2.07E-14	9.25E-12	206.6	0.55
V-K	Cpx	0.30567	7.40E-17	7.07E-12	4.08E-14	1.21E-16	4.11E-15	1.16E-07	1.06E-11	1.40E-14	6.47E-12	173.4	1.09
IV-A	Ol	1.03046	2.52E-17	2.43E-12	4.47E-15	1.29E-17	4.34E-16	1.47E-09	2.09E-12	3.40E-15	1.08E-12	543.9	2.24
IV-A	Opx	0.49715	3.04E-17	3.02E-12	1.05E-14	3.07E-17	1.03E-15	4.49E-08	5.48E-12	6.38E-15	3.59E-12	286.9	0.84
IV-A	Cpx	0.47966	1.29E-16	1.29E-11	1.25E-14	3.82E-17	1.22E-15	2.73E-07	1.20E-11	9.65E-15	9.11E-12	1033.2	1.42

Table 2. Continued.

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Sample	Phase	Rc/Ra	Total Error +/-	$^{40}Ar/^{36}Ar$	Error (%)	$^{38}Ar/^{36}Ar$	Error (%)	$^{20}Ne/^{22}Ne$	Error (%)	$^{21}Ne/^{22}Ne$	Error
V-A	Ol	7.26	0.062	1391.46	0.09	0.19251	0.19	9.93	0.06	0.0297	0.00135
V-A	Opx	6.94	0.130	662.11	0.14	0.18892	0.19	9.87	0.04	0.0288	0.00050
V-A	Cpx	7.06	0.126	3320.08	0.30	0.20543	0.21	n.a	n.a	n.a	n.a
V-B	Ol	7.33	0.058	614.85	0.06	0.18772	0.19	9.87	0.04	0.0296	0.00082
V-B	Opx	7.35	0.063	964.58	0.07	0.18291	0.18	9.97	0.03	0.0298	0.00045
V-B	Cpx	7.27	0.058	8231.50	0.17	0.20717	0.21	12.18	0.26	0.0553	0.00431
V-C	Ol	7.13	0.096	2518.41	0.52	0.22231	0.22	n.a	n.a	n.a	n.a
V-C	Cpx	7.33	0.073	2511.64	0.23	0.19747	0.20	n.a	n.a	n.a	n.a
V-D	Ol	7.19	0.058	2177.87	0.12	0.19317	0.19	10.57	0.16	0.0354	0.00227
V-D	Opx	7.22	0.079	626.23	0.10	0.18834	0.19	n.a	n.a	n.a	n.a
V-D	Cpx	7.37	0.066	7926.55	0.31	0.20644	0.21	11.03	0.39	0.0452	0.00650
V-E	Ol	7.47	0.069	2598.15	0.43	0.19010	0.19	10.37	0.07	0.0332	0.00107
V-E	Opx	7.50	0.072	1436.20	0.13	0.18305	0.18	10.00	0.04	0.0306	0.00046
V-E	Cpx	7.48	0.071	4719.85	0.33	0.18136	0.18	10.25	0.05	0.0338	0.00115
V-F	Ol	7.57	0.069	889.63	0.08	0.18730	0.19	9.87	0.04	0.0297	0.00064
V-F	Opx	7.42	0.077	1123.07	0.14	0.19054	0.19	9.93	0.04	0.0307	0.00072
V-F	Cpx	7.59	0.071	856.84	0.06	0.18382	0.18	10.12	0.03	0.0306	0.00045
V-G	Ol	7.68	0.071	690.44	0.10	0.18565	0.18	10.23	0.06	0.0316	0.00117
V-G	Opx	7.53	0.081	866.39	0.17	0.18036	0.18	9.85	0.04	0.0296	0.00067
V-G	Cpx	7.32	0.073	3371.87	0.43	0.18281	0.18	11.06	0.11	0.0390	0.00227
V-H	Ol	7.52	0.079	1023.71	0.06	0.18503	0.18	10.18	0.03	0.0317	0.00041
V-H	Opx	7.52	0.085	366.42	0.00	0.18303	0.18	10.11	0.02	0.0301	0.00027
V-H	Cpx	7.56	0.071	2457.00	0.27	0.19215	0.19	10.15	0.05	0.0326	0.00104
V-I	Ol	7.25	0.127	388.43	0.22	0.19569	0.20	n.a	n.a	n.a	n.a
V-I	Opx	7.19	0.154	439.10	0.34	0.19092	0.19	11.59	0.73	0.0492	0.01944
V-I	Cpx	5.46	0.139	303.48	0.05	0.18009	0.18	10.24	0.01	0.0323	0.00025
V-I r*	Ol	7.37	0.172	391.97	0.30	0.19246	0.20	10.39	0.16	0.0336	0.00251
V-I r*	Opx	6.15	0.079	339.74	0.08	0.18402	0.19	9.91	0.03	0.0296	0.00029
V-I r*	Cpx	5.40	0.144	348.57	0.16	0.18113	0.19	9.98	0.03	0.0298	0.00034
V-J	Ol	7.38	0.074	854.91	0.06	0.18694	0.19	10.05	0.03	0.0307	0.00053
V-J	Opx	7.33	0.077	1294.25	0.07	0.18590	0.19	10.08	0.03	0.0313	0.00056

V-J	Cpx	7.50	0.067	2993.26	0.19	0.19053	0.19	10.24	0.03	0.0335	0.00071	...4
V-K	Ol	7.45	0.076	1114.13	0.00	0.18660	0.19	10.07	0.03	0.0319	0.00049	...7
V-K	Opx	7.54	0.078	741.96	0.00	0.18186	0.18	10.32	0.02	0.0316	0.00031	...1
V-K	Cpx	7.53	0.070	756.34	0.07	0.18796	0.19	9.92	0.02	0.0296	0.00029	...0
IV-A	Ol	7.45	0.083	614.05	0.07	0.18144	0.19	10.14	0.04	0.0303	0.00050	
IV-A	Opx	7.23	0.096	858.77	0.06	0.18068	0.19	10.10	0.03	0.0298	0.00045	...6
IV-A	Cpx	7.21	0.065	1238.93	1.99	0.18113	0.19	10.25	0.03	0.0314	0.00047	...2

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Table 3. ^{4}He production rates, ^{3}He fluxes, helium residence time and CO_2 fluxes calculated for the lithospheric mantle beneath central Mexico. P*, F and Rt values were calculated based on mathematical formulations proposed y Gautheron and Moreira (2002).

U (ppm)	P* (ccSTP/g)	P* (mol/yr)	F (ccSTP/year)	F (mol/yr)	Rt (Ma)	CO₂
0.01	7.69E+06	3.43E+02	5.99E+02	0.027	61.17	3.93E
0.012	9.23E+06	4.12E+02	7.19E+02	0.032	50.97	4.72E
0.014	1.08E+07	4.81E+02	8.38E+02	0.037	43.69	5.50E
0.016	1.23E+07	5.49E+02	9.58E+02	0.043	38.23	6.29E
0.018	1.38E+07	6.18E+02	1.08E+03	0.048	33.98	7.07E
0.02	1.54E+07	6.87E+02	1.20E+03	0.053	30.58	7.86E
0.022	1.69E+07	7.55E+02	1.32E+03	0.059	27.80	8.65E
0.024	1.85E+07	8.24E+02	1.44E+03	0.064	25.49	9.43E
0.026	2.00E+07	8.93E+02	1.56E+03	0.070	23.53	1.02E
0.028	2.15E+07	9.62E+02	1.68E+03	0.075	21.84	1.10E
0.03	2.31E+07	1.03E+03	1.80E+03	0.080	20.39	1.18E

P*: ^{4}He production

F: ^{3}He flux

Rt: Helium residence time

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1616 **Figure Captions**

1617 **Figure 1**. Location of the Joya Honda maar (JH) and geodynamic setting. The map shows the Mexican part
1618 of the Basin and Range Province which has an extension of 9.4×10^5 km^2 (Henry and Aranda-Gomez, 1992);
1619 the image was adapted from Aranda-Gómez et al. (2000). The green area is the area used to estimate the ^{4}He
1620 production, the helium residence time and ^{3}He-CO$_2$ fluxes for the lithospheric mantle located under San Luis
1621 Potosí state (see subsections 6.5 and 6.5.1). The pink square represents the location of the Los Encinos Volcanic
1622 Field (LE); although this is a monogenetic volcanic field associated with the Basin and Range extension, this
1623 lacks mantle xenoliths. Contours of Sierra Madre Occidental, Sierra Madre Oriental, the Transmexican
1624 Volcanic Belt and Mesa Central provinces were build based on Gómez-Tuena et al. (2007). VESVF: Ventura
1625 Espiritu Santo Volcanic Field, SDVF: Santo Domingo Volcanic Field, PiVF: Pinacate Volcanic Field, PaVF:
1626 Las Palomas Volcanic Field, Po: Potrillo maar, CVF: the Camargo Volcanic Field, DVF: Durango Volcanic
1627 Field, SQVF: San Quintin Volcanic Field, II: Isla Isabel. Upper right image: Google Earth image (February
1628 20th, 2020) showing the Joya Honda maar morphology and sampling area.

1629 **Figure 2**. Ternary classification for ultramafic and mafic rocks, from Streckeisen (1976),

1630 **Figure 3.** Microphotographs of the JH mantle xenoliths in cross-polarized light (A, B, C, D, E, G, H) and
1631 transmitted plane-polarized light (F). Ol: olivine, Opx: orthopyroxene, Cpx: clinopyroxene, Sp: spinel. A) Ol
1632 porphyroclast with well-developed kink bands and glass-rich veins. B) Spongy rims developed in Opx crystals;
1633 C) Cpx and Opx crystals are almost and totally replaced by the spongy rim. D) Porphyroclastic texture; Opx
1634 crystal being cut by a glass-rich vein. E) Opx cluster. F) Opx cluster cut by a vein composed of light brown
1635 glass and some opaque minerals, note the presence of spongy rims in Opx. G) Cpx porphyroclast with
1636 development of spongy bands. H) Glass-rich veins around Opx porphyroclast.

1637 **Figure 4.** Microphotographs of inclusions identified in olivine. A) Melt and fluid inclusions originating from
1638 microveins. B) Intragranular trail of dendritic inclusions. C) Inclusions composed by glass and high
1639 birefringent mineral phases (cross-polarized light illumination). D) Opaque phases associated to fluid
1640 inclusions.

1641 **Figure 5:** Raman spectroscopy applied in olivine inclusions. A) Raman spectra of birefringent mineral phases
1642 (Mg-calcite) observed in Figure 4C. B) Raman spectra of pure CO$_2$ fluid inclusions identified in Figure 4D. C)

Raman spectra of dolomite contained in some inclusions of Figure 4B. D) Raman spectra of magnesite and pyrite contained in olivine inclusions.

Figure 6. ^{4}He, ^{40}Ar* and CO_2 contents measured in fluid inclusions hosted in JH mantle xenoliths. SCLM: Subcontinental Lithospheric Mantle. The West Antarctic Rift System (WARS) SCLM compositional range was built using fluid inclusions data measured by Broadley et al. (2016) and Correale et al. (2019). European SCLM range includes fluid inclusions values measured in mantle xenoliths from the Rhenish Massif (Germany), Pannonian basin, Massif Central (Central France), Tallante - Calatrava (Spain), Lower Silesia (Poland) and the Eastern Transylvanian Basin; data was taken from Buikin et al. (2005), Gautheron et al., (2005a), Martelli et al. (2011), Rizzo et al. (2018) and Faccini et al. (2020). Eastern Australia SCLM data was taken from Matsumoto et al. (1998, 2000) and Czuppon et al. (2009). Red sea region data from Hopp et al. (2004), Hopp et al. (2007a) and Halldórsson et al. (2014). Northern/Southern Kenya rifts data was taken from Hopp et al. (2007b) and Halldórsson et al. (2014). The Ethiopia (afar) field was designed after Halldórsson et al. (2014).

Figure 7. A) ^{4}He/^{20}Ne vs R/Ra diagram, the solid lines represent the binary mixing between air and an upper mantle source with R/Ra values between 7 and 8, B) ^{3}He/^{40}Ar vs ^{40}Ar/^{36}Ar diagram. C) ^{21}Ne/^{22}Ne vs. ^{20}Ne/^{22}Ne diagram in which the green line represents the binary mixing air-MORB mantle as defined by Sarda et al. (1988) and Moreira et al. (1998) at ^{21}Ne/^{22}Ne$_{air}$ = 0.029 and ^{20}Ne/^{22}Ne $_{air}$ = 9.8 and ^{21}Ne/^{22}Ne = 0.06 and ^{20}Ne/^{22}Ne = 12.5; the primordial neon composition is reported as Solar wind at ^{21}Ne/^{22}Ne = 0.0328 and ^{20}Ne/^{22}Ne = 13.8 (Heber et al., 2009); the crust endmember was plotted at ^{21}Ne/^{22}Ne = 0.6145 and ^{20}Ne/^{22}Ne = 0.3 (Kennedy et al., 1990). The WARS SCLM, European SCLM, Ethiopia (Afar), N/S Kenya rifts, Eastern Australia SCLM and Red sea compositional ranges were built using fluid inclusions data cited in Figure 6.

Figure 8. ^{4}He/^{40}Ar* vs ^{3}He/^{4}He corrected for air contamination (Rc/Ra) ratios of fluid inclusions from JH mantle xenoliths. MORB range is reported at Rc/Ra = 8 + 1 (Graham, 2002) and ^{4}He/^{40}Ar* from 1 to 5 (Yamamoto et al., 2009). The WARS SCLM, European SCLM, Ethiopia (Afar), N/S Kenya rifts, Eastern Australia SCLM and Red sea compositional ranges were built using fluid inclusions data cited in Figure 6. The diffusive fractionation path is modeled using the diffusion coefficient (D) of ^{3}He, ^{4}He, and ^{40}Ar* (D^{3}He/D^{4}He=1.15 and D^{4}He/D^{40}Ar=3.16 in solid mantle; Burnard, 2004; Yamamoto et al., 2009) (see supplementary material). Partial melting (see arrow) can lead to decreasing ^{4}He/^{40}Ar* (see supplementary materials).

Figure 9. A) ^{36}Ar vs ^{3}He concentration. Plotted values correspond to samples with ^{40}Ar/^{36}Ar > 500. B) ^{20}Ne/^{22}Ne vs ^{40}Ar/^{36}Ar. Mixing curves are the result of mass-balance and isotopic mass balance equations using the parameters reported in Table 3.

Figure 10. A) ^{21}Ne/^{22}Ne $_{EX}$ ratios vs ^{4}He/^{3}He ratios, adapted from Hopp et al. (2004) and Halldórsson et al. (2014). Values with 2σ uncertainties <10% are plotted. Dotted lines are binary mixing between three endmembers: 1) Plume, at 20Ra and ^{21}Ne/^{22}Ne $_{EX}$ = 0.034 ± 0.001, 2) MORB-like upper mantle at 8 Ra, 7 Ra and ^{21}Ne/^{22}Ne $_{EX}$ = 0.06 ± 0.001 and SCLM at 6.1 ± 0.9 Ra and ^{21}Ne/^{22}Ne $_{EX}$ = 0.07 ± 0.001. B) ^{3}He, C) ^{4}He and D) ^{40}Ar* vs ^{3}He/^{4}He corrected for air contamination (Rc/Ra). MORB range is report ed at Rc/Ra = 8 ± 1 (Graham, 2002).

Figure 11. A) Comparison between ^{3}He fluxes measured in central Mexico based on JH mantle xenoliths analysis (at U=0.01 and 0.03 ppm) and other localities. MORB value was estimated using data from Michael and Graham (2015) and based on CO_2/^{3}He ratio =2.2 x 10^9 (Marty and Tolstikhin, 1998); SCLM value was taken from Gautheron and Moreira (2002); the European SCLM flux was calculated based on Gautheron et al. (2005a). B) ^{3}He fluxes scaled to the surface area. See the text for more details. C) Associated CO_2 fluxes (mol/yr) for central Mexico compared with other tectonic localities. MORB CO_2 flux was calculated after Michael and Graham (2015); EAR1 and EAR2 values were taken from Lee et al. (2016) and Foley and Fischer (2017), respectively; Hawaii and Canary fluxes were obtained from Hauri et al. (2019). D) CO_2 fluxes scaled to the surface area.

Figure 12. A) CO_2 vs $\delta^{13}C$. Hyblean, Stromboli and European SCLM data from Correale et al. (2015), Gennaro et al. (2017) and Rizzo et al. (2018), respectively. B) $\delta^{13}C$ vs 3He/4He corrected for air contamination (Rc/Ra). Dotted lines are binary mixing between two endmembers: 1) Limestone at $\delta^{13}C$ =-1, 1 and Rc/Ra= 0.01 and 2) MORB-like upper mantle at $\delta^{13}C$ = -4 and Rc/Ra = 7.38. C) $\delta^{13}C$ vs $CO_2/^3He$. Dotted lines are binary mixing between two endmembers: 1) Limestone at $\delta^{13}C$ =-1, 1 and $CO_2/^3He$ = 10^{-13} and 2) MORB-like upper mantle at $\delta^{13}C$ = -4 and $CO_2/^3He$ = 1.00 x 10^{-9}, 2.00 x 10^{-9}.

TABLES

Table **1**. Modal composition of JH mantle xenoliths.

Sample	Rock type	OI (%)	Opx (%)	Cpx (%)	Sp (%)
VE	Lherzolite	54.47	28.96	14.37	2.2
VJ	Lherzolite	52.01	32.31	13.39	2.29
IVA	Lherzolite	72.48	15.86	10.45	1.21
VF	Lherzolite	52.08	33.97	11.93	2.02
VI	Lherzolite	53.41	23.48	19.79	3.32
VG	Harzburgite	68.14	30.04	1.26	0.56
VK	Lherzolite	61.27	24.59	13.69	0.44
VH	Harzburgite	62.08	31.26	4.47	2.18

Table 2. Fluid inclusions compositions from JH mantle xenoliths. Concentrations are reported in mol/g. r*: reply made in sample V-I.

Sample	Phase	Weight (g)	^{3}He	^{4}He	^{20}Ne	^{21}Ne	^{22}Ne	CO_2^{a}	^{40}Ar	^{36}Ar	$^{40*}Ar$	$^{4}He/^{20}Ne$	$^{4}He/^{40}Ar*$	$^{4}He/CO_2$	R/Ra	Rc/Ra	error
V-A	Ol	0.95855	1.67E-17	1.65E-12	9.11E-16	2.72E-18	9.26E-17	2.80E-11	2.09E-12	1.50E-15	1.65E-12	1814.0	1.00	0.05901	7.26	7.26	
V-A	Opx	0.26388	4.74E-18	4.91E-13	8.90E-16	2.59E-17	9.00E-16	3.91E-10	3.61E-12	5.45E-15	2.00E-12	55.2	0.25	0.00126	6.91	6.94	0.13
V-A	Cpx	0.21991	6.45E-18	6.57E-13	5.81E-16	2.62E-18	5.41E-17	6.23E-09	5.16E-12	1.55E-15	4.70E-12	1131.4	0.14	0.00011	7.06	7.06	0.13
V-B	Ol	0.99706	2.53E-17	2.48E-12	1.84E-15	5.52E-18	1.88E-16	2.26E-10	3.70E-12	6.01E-15	1.92E-12	1349.7	1.29	0.01100	7.32	7.33	0.06
V-B	Opx	0.4776	3.43E-17	3.36E-12	6.75E-15	1.97E-17	6.61E-16	4.88E-08	7.67E-12	7.95E-15	5.32E-12	497.5	0.63	0.00007	7.34	7.35	0.06
V-B	Cpx	0.48584	4.67E-17	4.62E-12	4.41E-16	2.00E-18	3.61E-17	9.70E-08	1.12E-11	1.36E-15	1.08E-11	10483.3	0.43	0.00005	7.27	7.27	0.06
V-C	Ol	0.59294	3.71E-18	3.74E-13	2.35E-16	n.a	2.61E-17	2.38E-10	8.96E-13	3.56E-16	7.91E-13	1593.9	0.47	0.00157	7.13	7.13	0.10
V-C	Cpx	0.5587	8.55E-18	8.40E-13	5.73E-16	1.82E-18	5.87E-17	7.61E-10	2.57E-12	1.02E-15	2.27E-12	1466.6	0.37	0.00110	7.32	7.33	0.07
V-D	Ol	1.02241	2.08E-17	2.08E-12	3.76E-16	1.25E-18	3.67E-17	9.18E-10	2.76E-12	1.27E-15	2.38E-12	5534.0	0.87	0.00227	7.19	7.19	0.06
V-D	Opx	0.49922	9.46E-18	9.43E-13	2.33E-15	7.04E-18	2.39E-16	4.39E-09	2.07E-12	3.30E-15	1.09E-12	404.4	0.86	0.00021	7.21	7.22	0.08
V-D	Cpx	0.47389	2.66E-17	2.59E-12	3.02E-16	1.23E-18	2.73E-17	3.25E-08	6.01E-12	7.58E-16	5.78E-12	8576.0	0.45	0.00008	7.37	7.37	0.07
V-E	Ol	1.02916	2.51E-17	2.42E-12	1.22E-15	3.90E-18	1.19E-16	4.11E-09	8.79E-13	3.38E-16	7.79E-13	1982.0	3.11	0.00059	7.47	7.47	0.07
V-E	Opx	0.51352	1.98E-17	1.90E-12	5.12E-15	1.56E-17	5.16E-16	2.74E-08	3.03E-12	2.11E-15	2.41E-12	371.6	0.79	0.00007	7.49	7.50	0.07
V-E	Cpx	0.32954	3.96E-17	3.81E-12	3.93E-15	1.27E-17	3.81E-16	1.25E-07	7.06E-12	1.50E-15	6.62E-12	970.0	0.58	0.00003	7.48	7.48	0.07
V-F	Ol	1.01203	2.57E-17	2.44E-12	3.49E-15	1.05E-17	3.55E-16	2.81E-09	2.50E-12	2.81E-15	1.67E-12	700.6	1.46	0.00087	7.57	7.57	0.07
V-F	Opx	0.52681	1.66E-17	1.61E-12	4.91E-15	1.51E-17	4.98E-16	1.85E-08	2.37E-12	2.11E-15	1.75E-12	328.5	0.92	0.00009	7.41	7.42	0.08
V-F	Cpx	0.31734	5.58E-17	5.29E-12	2.01E-14	6.07E-17	1.99E-15	1.78E-07	1.06E-11	1.24E-14	6.98E-12	262.9	0.76	0.00003	7.58	7.59	0.07
V-G	Ol	1.00336	1.94E-17	1.81E-12	7.91E-16	2.44E-18	7.78E-17	3.91E-11	1.19E-12	1.72E-15	6.81E-13	2292.1	2.66	0.04634	7.68	7.68	0.07
V-G	Opx	0.50526	1.29E-17	1.23E-12	3.20E-15	9.62E-18	3.26E-16	4.54E-09	1.47E-12	1.69E-15	9.68E-13	384.5	1.27	0.00027	7.53	7.53	0.08
V-G	Cpx	0.32136	3.21E-17	3.15E-12	1.57E-15	5.55E-18	1.52E-16	2.24E-08	3.17E-12	9.41E-16	2.89E-12	2003.4	1.09	0.00014	7.32	7.32	0.07
V-H	Ol	1.0181	4.21E-17	4.03E-12	4.72E-15	1.47E-17	4.66E-16	4.72E-09	6.44E-12	6.29E-15	4.58E-12	853.7	0.88	0.00085	7.51	7.52	0.08
V-H	Opx	0.53853	1.95E-17	1.86E-12	4.01E-14	1.16E-16	3.94E-15	1.23E-08	1.52E-11	4.14E-14	2.93E-12	46.5	0.64	0.00015	7.47	7.52	0.08
V-H	Cpx	0.30754	3.92E-17	3.73E-12	3.52E-15	1.13E-17	3.46E-16	5.09E-08	4.74E-12	1.93E-15	4.17E-12	1062.1	0.90	0.00007	7.56	7.56	0.07
V-I	Ol	1.0437	8.62E-19	8.56E-14	1.42E-16	5.22E-19	1.39E-17	4.74E-11	2.25E-13	5.78E-16	5.37E-14	604.6	1.59	0.00181	7.24	7.25	0.13
V-I	Opx	0.5057	9.92E-19	9.93E-14	1.55E-16	6.59E-19	1.34E-17	2.26E-10	3.77E-13	8.58E-16	1.23E-13	639.0	0.8	0.00044	7.18	7.19	0.15
V-I	Cpx	0.49525	9.34E-19	1.23E-13	5.08E-14	1.46E-16	4.90E-15	n.a	1.13E-11	3.72E-14	2.97E-13	2.4	0.41	n.a	4.84	5.46	0.14
V-I r*	Ol	1.01139	9.47E-19	9.25E-14	4.09E-16	1.32E-18	4.07E-17	7.54E-10	1.75E-13	4.48E-16	4.32E-14	226.0	2.14	0.00012	7.36	7.37	
V-I r*	Opx	0.50086	9.81E-19	1.15E-13	1.13E-14	3.37E-17	1.14E-15	1.31E-09	2.02E-12	5.94E-15	2.63E-13	10.1	0.44	0.00009	5.98	6.15	0.08
V-I r*	Cpx	0.57112	7.37E-19	9.81E-14	9.68E-15	2.89E-17	9.72E-16	4.07E-10	5.64E-13	1.62E-15	8.59E-14	10.1	1.14	0.00024	5.26	5.40	0.14
V-J	Ol	1.0333	3.63E-17	3.53E-12	3.77E-15	1.15E-17	3.76E-16	4.55E-09	5.30E-12	6.20E-15	3.47E-12	937.0	1.02	0.00078	7.38	7.38	0.07
V-J	Opx	0.5061	5.02E-17	4.93E-12	7.60E-15	2.36E-17	7.58E-16	1.08E-07	1.02E-11	7.88E-15	7.87E-12	649.1	0.63	0.00005	7.32	7.33	0.08
V-J	Cpx	0.30875	1.11E-16	1.07E-11	6.19E-15	2.02E-17	6.07E-16	3.23E-07	8.59E-12	2.87E-15	7.75E-12	1726.7	1.38	0.00003	7.50	7.50	0.07
V-K	Ol	1.0225	5.42E-17	5.24E-12	4.99E-15	1.58E-17	4.99E-16	2.46E-08	7.72E-12	6.93E-15	5.67E-12	1049.9	0.92	0.00021	7.45	7.45	
V-K	Opx	0.52687	5.37E-17	5.13E-12	2.48E-14	7.37E-17	2.38E-15	1.05E-07	1.54E-11	2.07E-14	9.25E-12	206.6	0.55	0.00005	7.53	7.54	0.08
V-K	Cpx	0.30567	7.40E-17	7.07E-12	4.08E-14	1.21E-16	4.11E-15	1.16E-07	1.06E-11	1.40E-14	6.47E-12	173.4	1.09	0.00006	7.52	7.53	0.07
IV A	Ol	1.03046	2.52E-17	2.43E-12	4.47E-15	1.29E-17	4.34E-16	1.47E-09	2.09E-12	3.40E-15	1.08E-12	543.9	2.24	0.00165	7.45	7.45	0.08
IV A	Opx	0.49715	3.04E-17	3.02E-12	1.05E-14	3.07E-17	1.03E-15	4.49E-08	5.48E-12	6.38E-15	3.59E-12	286.9	0.84	0.00007	7.23	7.23	0.10
IV A	Cpx	0.47966	1.29E-16	1.29E-11	1.25E-14	3.82E-17	1.22E-15	2.73E-07	1.20E-11	9.65E-15	9.11E-12	1033.2	1.42	0.00005	7.21	7.21	0.06

Table 2. Continued. [a] First estimation of CO_2 during noble gases analysis; [b] CO_2 measured from glass line.

Sample	Phase	$^{40}Ar/^{36}Ar$	error +/- (1σ)	$^{38}Ar/^{36}Ar$	error +/- (1σ)	$^{20}Ne/^{22}Ne$	error +/- (1σ)	$^{21}Ne/^{22}Ne$	error +/- (1σ)	$(^{21}Ne/^{22}Ne)$ EX to 12.5	error +/- (2σ)	$CO_2/^3He$	$^3He/^{36}Ar$	$CO_2/^3He$	CO_2^b
V-A	Ol	1391.46	1.24	0.19251	0.00037	9.93	0.06	0.0297	0.00135	0.043	0.003	1.68E+06	0.0111	n.a	n.a	n.a
V-A	Opx	662.11	0.93	0.18892	0.00036	9.87	0.04	0.0288	0.00050	n.a	n.a	8.24E+07	0.0009	n.a	n.a	n.a
V-A	Cpx	3320.08	9.83	0.20543	0.00042	n.a	n.a	n.a	n.a	n.a	n.a	9.66E+08	0.0041	n.a	n.a	n.a
V-B	Ol	614.85	0.37	0.18772	0.00035	9.87	0.04	0.0296	0.00082	0.053	0.003	8.93E+06	0.0042	n.a	n.a	n.a
V-B	Opx	964.58	0.65	0.18291	0.00033	9.97	0.03	0.0298	0.00045	0.041	0.001	1.42E+09	0.0043	2.58E+09	1.17E-07	-2.30
V-B	Cpx	8231.50	13.81	0.20717	0.00043	12.18	0.26	0.0553	0.00431	n.a	n.a	2.07E+09	0.0343	n.a	n.a	n.a
V-C	Ol	2518.41	13.00	0.22231	0.00049	n.a	n.a	n.a	n.a	n.a	n.a	6.43E+07	0.0104	n.a	n.a	n.a
V-C	Cpx	2511.64	5.81	0.19747	0.00039	n.a	n.a	n.a	n.a	n.a	n.a	8.90E+07	0.0084	n.a	n.a	n.a
V-D	Ol	2177.87	2.53	0.19317	0.00037	10.57	0.16	0.0354	0.00227	n.a	n.a	4.41E+07	0.0164	n.a	n.a	n.a
V-D	Opx	626.23	0.62	0.18834	0.00035	n.a	n.a	n.a	n.a	n.a	n.a	4.64E+08	0.0029	n.a	n.a	n.a
V-D	Cpx	7926.55	24.39	0.20644	0.00043	11.03	0.39	0.0452	0.00659	n.a	n.a	1.22E+09	0.0350	1.61E+09	4.27E-08	-1.55
V-E	Ol	2598.15	11.14	0.19010	0.00036	10.37	0.07	0.0332	0.00107	0.049	0.003	1.64E+08	0.0743	n.a	n.a	n.a
V-E	Opx	1436.20	1.91	0.18305	0.00033	10.00	0.04	0.0306	0.00046	0.050	0.002	1.39E+09	0.0094	n.a	n.a	n.a
V-E	Cpx	4719.85	15.56	0.18136	0.00033	10.25	0.05	0.0338	0.00115	0.058	0.004	3.16E+09	0.0265	9.17E+08	3.63E-08	-2.66
V-F	Ol	889.63	0.69	0.18730	0.00035	9.87	0.04	0.0297	0.00064	n.a	0.003	1.09E+08	0.0091	n.a	n.a	n.a
V-F	Opx	1123.07	1.53	0.19054	0.00036	9.93	0.04	0.0307	0.00072	0.063	0.003	1.11E+09	0.0079	1.15E+09	1.91E-08	-1.34
V-F	Cpx	856.84	0.53	0.18382	0.00034	10.12	0.03	0.0306	0.00045	0.042	0.001	3.18E+09	0.0045	1.12E+09	6.22E-08	-1.66
V-G	Ol	690.44	0.68	0.18565	0.00034	10.23	0.06	0.0316	0.00117	0.045	0.003	2.02E+06	0.0112	n.a	n.a	n.a
V-G	Opx	866.39	1.50	0.18036	0.00032	9.85	0.04	0.0296	0.00062	n.a	n.a	3.52E+08	0.0076	n.a	n.a	n.a
V-G	Cpx	3371.87	14.57	0.18281	0.00033	11.06	0.11	0.0390	0.00227	n.a	n.a	6.97E+08	0.0341	n.a	n.a	n.a
V-H	Ol	1023.71	0.63	0.18503	0.00034	10.18	0.03	0.0317	0.00041	0.048	0.001	1.12E+08	0.0067	n.a	n.a	n.a
V-H	Opx	366.42	0.00	0.18303	0.00033	10.11	0.02	0.0301	0.00027	0.039	0.001	6.33E+08	0.0005	n.a	n.a	n.a
V-H	Cpx	2457.00	6.70	0.19215	0.00037	10.15	0.05	0.0326	0.00104	0.056	0.004	1.30E+09	0.0203	n.a	n.a	n.a
V-I	Ol	388.43	0.86	0.19569	0.00038	n.a	n.a	n.a	n.a	n.a	n.a	5.50E+07	0.0015	n.a	n.a	n.a
V-I	Opx	439.10	1.49	0.19092	0.00036	11.59	0.73	0.0492	0.01944	n.a	n.a	2.28E+08	0.0586	n.a	n.a	n.a
V-I	Cpx	303.48	0.16	0.18009	0.00032	10.24	0.01	0.0323	0.00025	n.a	n.a	0.00E+00	0.0000	n.a	n.a	n.a
V-I r*	Ol	391.97	1.17	0.19246	0.00038	10.39	0.16	0.0336	0.00251	n.a	n.a	7.95E+08	0.0021	n.a	n.a	n.a
V-I r*	Opx	339.74	0.26	0.18402	0.00035	9.91	0.03	0.0296	0.00029	n.a	n.a	1.33E+09	0.0002	n.a	n.a	n.a
V-I r*	Cpx	348.57	0.56	0.18113	0.00034	9.98	0.03	0.0298	0.00034	n.a	n.a	5.52E+08	0.0005	n.a	n.a	n.a
V-J	Ol	854.91	0.48	0.18694	0.00035	10.05	0.03	0.0307	0.00053	0.047	0.002	1.25E+08	0.0058	n.a	n.a	n.a
V-J	Opx	1294.25	0.87	0.18590	0.00035	10.08	0.03	0.0313	0.00056	0.051	0.002	2.15E+09	0.0064	3.82E+09	1.92E-07	-2.13
V-J	Cpx	2993.26	5.58	0.19053	0.00036	10.24	0.03	0.0335	0.00071	0.056	0.002	2.90E+09	0.0388	2.10E+09	2.34E-07	-1.30
V-K	Ol	1114.13	0.00	0.18660	0.00035	10.07	0.03	0.0319	0.00049	0.058	0.002	4.54E+08	0.0078	3.82E+08	2.67E-08	
V-K	Opx	741.96	0.00	0.18186	0.00033	10.32	0.02	0.0316	0.00031	0.042	0.001	1.95E+09	0.0026	1.88E+09	1.01E-07	-2.08
V-K	Cpx	756.34	0.50	0.18796	0.00035	9.92	0.02	0.0296	0.00029	0.041	0.001	1.57E+09	0.0053	3.38E+08	2.50E-08	-0.97
IV A	Ol	614.05	0.43	0.18144	0.00034	10.14	0.04	0.0303	0.00050	0.039	0.001	5.84E+07	0.0074	n.a	n.a	n.a
IV A	Opx	858.77	0.49	0.18068	0.00033	10.10	0.03	0.0298	0.00045	n.a	n.a	1.48E+09	0.0048	2.22E+09	6.76E-08	-2.86
IV A	Cpx	1238.93	24.70	0.18113	0.00034	10.25	0.03	0.0314	0.00047	0.043	0.001	2.11E+09	0.0134	1.18E+09	1.52E-07	-1.25

Table 3. Expected noble gas isotopic ratios for the Mexican lithospheric mantle. $^{20}Ne/^{22}Ne_{air}$ $^{40}Ar/^{36}Ar_{air}$ ratios after Steiger and Jäger (1977) and Ozima and Podosek (2002).

R/Ra	$^4He/^{40}Ar*$	$^4He/^{20}Ne$	$^{36}Ar/^{22}Ne$	$^{40}Ar/^{36}Ar$	$^{20}Ne/^{22}Ne$	$^{20}Ne/^{22}Ne_{air}$	$^{40}Ar/^{36}Ar_{air}$
7.39 ± 0.14	0.14 - 3.11	11000	4.21 - 93.5	10500	12.5	9.8	295.5

Table 4. ^4He production rates, ^3He fluxes, helium residence time and CO_2 fluxes calculated for the lithospheric mantle beneath central Mexico. P*, F and Rt values were calculated based on mathematical formulations proposed y Gautheron and Moreira (2002). P*: ^4He production, F: ^3He flux, Rt: Helium residence time.

U (ppm)	P* (ccSTP/g)	P* (mol/yr)	F (ccSTP/year)	F (mol/yr)	Rt (Ma)	CO$_2$ flux (mol/yr)	CO$_2$ flux (g/yr)
0.01	7.69E+06	3.43E+02	5.99E+02	0.027	61.17	3.93E+07	1.73E+09
0.012	9.23E+06	4.12E+02	7.19E+02	0.032	50.97	4.72E+07	2.08E+09
0.014	1.08E+07	4.81E+02	8.38E+02	0.037	43.69	5.50E+07	2.42E+09
0.016	1.23E+07	5.49E+02	9.58E+02	0.043	38.23	6.29E+07	2.77E+09
0.018	1.38E+07	6.18E+02	1.08E+03	0.048	33.98	7.07E+07	3.11E+09
0.02	1.54E+07	6.87E+02	1.20E+03	0.053	30.58	7.86E+07	3.46E+09
0.022	1.69E+07	7.55E+02	1.32E+03	0.059	27.80	8.65E+07	3.80E+09
0.024	1.85E+07	8.24E+02	1.44E+03	0.064	25.49	9.43E+07	4.15E+09
0.026	2.00E+07	8.93E+02	1.56E+03	0.070	23.53	1.02E+08	4.50E+09
0.028	2.15E+07	9.62E+02	1.68E+03	0.075	21.84	1.10E+08	4.84E+09
0.03	2.31E+07	1.03E+03	1.80E+03	0.080	20.39	1.18E+08	5.19E+09

1   **THE COMPOSITION OF FLUIDS STORED IN THE CENTRAL MEXICAN**
2   **LITHOSPHERIC MANTLE: INFERENCES FROM NOBLE GASES AND CO_2 IN MANTLE**
3   **XENOLITHS**

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17   **ABSTRACT**

18   We present the first isotopic (noble gases and CO_2) characterization of fluid inclusions coupled to
19   Raman microspectroscopy analyses in mantle xenoliths from Central Mexico, a geodynamically
20   complex area where the Basin and Range extension was superimposed on the Farallon subduction
21   (terminated at 28 Ma). To characterize the isotopic signature of the Central Mexican lithospheric
22   mantle, we focus on fluid inclusions entrapped in mantle xenoliths found in deposits of the Joya
23   Honda maar (JH), a Quaternary monogenetic volcano belonging to the Ventura Espiritu Santo
24   Volcanic Field (VESVF) in the state of San Luis Potosí (central Mexico). Thirteen ultramafic
25   plagioclase-free xenoliths were selected, all exhibiting a paragenesis Ol> Opx> Cpx >> Sp, and being
26   classified as spinel-lherzolites and harzburgites. All xenoliths bring textural evidence of interstitial
27   glass veins bearing dendritic trails of secondary melt and fluid inclusions (composed of silicate glass
28   $\pm CO_2 \pm$ Mg-Ca carbonates $\pm$ pyrite). These are related to pervasive mantle metasomatism driven by
29   carbonate-rich silicate melt. The Ar and Ne systematics reflect mixing between MORB-like upper
30   mantle and atmospheric fluids, the latter interpreted as reflecting a recycled air component possibly
31   inherited from the Farallon plate subduction. The $^3He/^4He$ ratios vary between 7.13 and 7.68 Ra,
32   within the MORB range (7-9 Ra), and the $^4He/^{40}Ar^*$ ratios (0.4 - 3.11) are similarly close to the
33   expected range of the fertile mantle (1-5). Taken together, these pieces of evidence suggest that (i)
34   either the mantle He budget was scarcely modified by the Farallon plate subduction, and/or (ii) that
35   any (large) crustal contribution was masked by a later metasomatism/refertilization episode, possibly
36   during the subsequent Basin and Range extension. A silicate melt-driven
37   metasomatism/refertilization (revealed by the association between glass veins and fluid inclusions)
38   is consistent with calculated helium residence time for the Mexican lithospheric mantle (20 to 60Ma)

that overlaps the timing of the above geodynamic events. We propose that, after the refertilization event (e.g., over the last ~20Ma), the lithospheric mantle has evolved in a steady-state, becoming slightly more radiogenic. We also estimated ^{3}He fluxes (0.027 - 0.080 mol/g), ^{4}He production rates (340 - 1000 mol/yr), and mantle CO_2 fluxes (3.93 x 10^7 mol/yr to 1.18x10^8 mol/yr) using the helium isotopic values measured in JH mantle xenoliths. Finally, the JH xenoliths exhibit $CO_2/^3$He ratios comparable to those of the upper mantle (from 3.38 x 10^8 to 3.82x10^9) but more positive δ^{13}C values (between -1.0 and -2.7‰), supporting the involvement of a crustal carbonate component. We propose that the metasomatic silicate melts recycled a crustal carbonate component, inherited by the Farallon plate subduction.

Keywords: Mexican mantle xenoliths; fluid inclusions; noble gases; CO_2; mantle refertilization; carbonate recycling.

1. INTRODUCTION

The subduction of the Farallon oceanic slab under the North American plate, during the late Oligocene and Middle Miocene, has given rise to enormous changes in the tectonic configuration of the northwestern coast of Mexico. These include the transition from a compressive to a transform margin, and the beginning of a regional extension that produced the Basin and Range Province (Atwater, 1989; Ferrari et al., 2012; Henry and Aranda-Gomez, 1992; Sedlock, 2003).

The Basin and Range extension started about 30Ma and was accompanied by intraplate magmatism, which generated several volcanic fields north of the Transmexican Volcanic Belt (TMVB; Aranda-Gómez and Ortega-Gutiérrez, 1987; Luhr and Aranda-Gómez, 1997; Henry and Aranda-Gomez, 1992). These fields are typically monogenetic complexes associated with the eruption of alkaline basalts and basanites that have brought to the surface significant amounts of ultramafic xenoliths that now allow the composition of the local lithospheric mantle to be probed .

The Ventura Espiritu Santo Volcanic Field (VESVF), located in the San Luis Potosí state (central Mexico), is one of the best-known examples of this volcanism, and is characterized by spectacular volcanic structures like the Joya Honda maar (JH), and by frequent ultramafic nodules found in its deposits. Other mantle xenoliths-bearing alkali basalt localities are the Santo Domingo Volcanic Field (SDVF) also located in the San Luis Potosí state, the Pinacate Volcanic Field (PiVF), Las Palomas Volcanic Field (PaVF), the Potrillo maar (Po), the Camargo Volcanic Field (CVF), the Durango Volcanic Field (DVF), the San Quintin Volcanic Field (SQVF) and Isla Isabel (II; Figure 1; Basu, 1977; Gutmann, 1986; Aranda-Gómez and Ortega-Gutiérrez, 1987; Luhr et al., 1989; Pier et al., 1992; Luhr and Aranda-Gómez, 1997; Housh et al., 2010).

These volcanic structures in the central and NW portion of Mexico, and the textural and petrological characteristics of their ultramafic xenoliths, have already been discussed elsewhere (Aranda-Gómez and Ortega-Gutiérrez, 1987; Luhr and Aranda-Gómez, 1997; Henry and Aranda-Gomez, 1992). These previous studies have revealed a complex (multi-stage) history of deformation, melting and metasomatism, and opened new questions on the evolution of the Mexican lithospheric mantle. Debate exists, however, on the provenance of the metasomatic fluids, and if and to what extent subduction of the Farallon plate has modified mantle composition during the recent Mexican geological history (Pier et al., 1989; Luhr and Aranda-Gómez, 1997; Dávalos-Elizondo et al., 2016).

80   Addressing these questions requires information on the chemical features of metasomatic fluids
81   present in the lithospheric mantle. Fluid and melt inclusions preserved in mantle xenoliths are well
82   known for being valuable sources of information to study the evolution of volatile species trapped in
83   ultramafic mantle rocks, and to derive inferences about the local lithospheric mantle dynamics
84   (Roedder, 1984; Andersen and Neumann, 2001; Deines, 2002; Frezzotti et al., 2002a; Buikin et al.,
85   2005; Gautheron et al., 2005a; Martelli et al., 2011; Day et al., 2015; Broadley et al., 2016; Rizzo et
86   al., 2018; Correale et al., 2019; Faccini et al., 2020).

87   Here, we aim at filling this gap of knowledge on the volatile composition of the Mexican lithospheric
88   mantle, by reporting on the chemical and isotopic composition (He, Ne, Ar and CO_2) of fluid
89   inclusions entrapped in mantle xenoliths found in the JH. Noble gases are sensitive tracers that
90   provide insights on fluid origin, the composition and evolution of the mantle, and their relationship
91   with different tectonic processes such as subduction (Matsumoto et al., 2001; Hopp et al., 2007a;
92   Hopp and Ionov, 2011; Martelli et al., 2014; Broadley et al., 2016; Faccini et al., 2020) or mantle
93   plumes (Hopp et al., 2004, 2007a, 2007b; Buikin et al., 2005; Halldórsson et al., 2014; Boudoire et
94   al., 2018, 2020). In addition, studying CO_2 abundance and isotopic composition contribute to
95   assessing composition and provenance of metasomatic fluids that may have interacted with these
96   xenoliths (Sano and Marty, 1995; Correale et al., 2015; Gennaro et al., 2017; Rizzo et al., 2018), for
97   example revealing any addition to the mantle of carbonate-rich fluids delivered by sediments and
98   altered oceanic crust in the subducted slab (Plank and Manning, 2019).

99

100   **2. GEOLOGICAL SETTING**

101   The VESVF is located in the southern portion of the province known as the Mesa Central (Raisz,
102   1959; Nieto-Samaniego et al., 2005); very close to the Sierra Madre Oriental province (Figure 1).
103   The Mesa Central, located north of the TMVB, comprises a portion of continental crust that has a
104   thickness of 32 km and is delimited by regional faults (Fix, 1975; Nieto-Samaniego et al., 2005). The
105   oldest rocks found in this province are muscovite schists from the Paleozoic (252 Ma), superimposed
106   by turbiditic sequences of the Triassic and volcano-sedimentary sequences of continental origin
107   formed during the mid-late Jurassic (Barboza-Gudiño et al., 1999; Morán-Zenteno et al., 2005; Nieto-
108   Samaniego et al., 2005). The most abundant outcrops correspond to sequences of calcareous rocks
109   of marine origin, formed during a transgression episode during the end of the late Jurassic and the
110   Cretaceous (Carrillo-Bravo, 1971; López-Doncel, 2003; Nieto-Samaniego et al., 2005); these rocks
111   make up the so-called Valles-San Luis Potosí Platform (PVSLP) and the Mesozoic Basin of Central
112   Mexico whose thickness can reach 5 km and 6 km, respectively. Cenozoic rocks are mainly volcanic
113   and sedimentary (of continental origin), the most recent being the alkaline basalts of the VESVF,
114   SDVF and DVF whose origin is related to a melting zone located 34 km deep under the Mesa Central
115   (Fix, 1975).

116   The VESVF is formed by some isolated scoria cones and three maars among which is the JH
117   (Aranda-Gómez et al., 2007; Saucedo et al., 2017). The JH is located at the intersection between the
118   PVSLP and the Mesozoic Basin of central Mexico (22 ° 25'4.97 "N and 100 ° 47'15.62" W), and is
119   thought to have formed at about 311 ± 19 ka (Saucedo et al., 2017). This volcano is recognized as
120   one of the most spectacular volcanic structure of Mexico (Saucedo et al., 2017), with its elliptical
121   crater having vertical walls defining a 150 – 300 m deep depression (Figure 1). The maar formed
122   through a series of mixed magmatic and phreatomagmatic eruptions that emplaced a sequence of

123 pyroclastic falls and base surge deposits (having a maximum thickness of ~100 m). Magma–
124 groundwater interaction is thought to have occurred during magma ascent through of a NE-SW
125 normal fault system cutting folded limestones, calcareous mudstones, chert lenses and shales which
126 are part of the Cuesta del Cura (Albian-Cenomanian) and Tamaulipas (Aptian) Formations (Aranda-
127 Gómez and Luhr, 1996; Aranda Gómez et al., 2000; Saucedo et al., 2017). Saucedo et al. (2017)
128 identified 5 eruptive phases, the last two of which generated deposits rich in mantle xenoliths. The
129 erupted magmas are alkaline and mafic in composition (olivine-nepheline basanites and olivine
130 basalts), and their origin is thought to be associated with decompressional melting of the
131 asthenosphere and lithospheric mantle under la Mesa Central, as proposed for other volcanic fields
132 associated to the Basin and Range extension (Aranda-Gómez and Ortega-Gutiérrez, 1987; Luhr et
133 al., 1989; Lee, 2005; Aranda-Gómez et al., 2007).

134

135 **3. PETROLOGICAL BACKGROUND**

136 The JH mantle xenoliths have been previously studied and described as spinel lherzolites and
137 harzburgites (Aranda-Gómez and Ortega-Gutiérrez, 1987; Liang and Elthon, 1990; Luhr and Aranda-
138 Gómez, 1997). The modal composition indicates a relatively constant paragenesis: Ol is the most
139 abundant phase (55-88%), followed by Opx (17-32%), Cpx (1-17%) and Spinel (Sp; 0.3 - 5%); in
140 very few cases, the presence of phlogopite is also reported with percentages below 1% (Luhr and
141 Aranda-Gómez, 1997). Compositionally, Ol has a Mg# (Mg# = 100 x Mg/(Mg + $\sum$Fe)) ranging from
142 87.5 to 91, Opx from 88.6 to 91.2, Cpx from 87.7 to 91.4 and Sp from 75.5 to 82.5 (Liang and Elthon,
143 1990). These authors also report the development of Na-Al poor spongy rims on Opx, Cpx and spinel,
144 explained as due to variable degrees of partial melting that have affected the local upper mantle.

145 Liang and Elthon (1990) classified the xenoliths into two groups based on their modal and
146 geochemical compositions (groups Ia and Ib). Mantle xenoliths from group Ia are interpreted as
147 mantle residues generated by different degrees of partial melting and extraction of picritic melts in
148 the upper mantle; these authors calculated a degree of partial melting between 7% and 22% for Ia
149 xenoliths, using melting models based on bulk-rock MgO, Ni and Sc abundances. Group Ib
150 peridotites exhibit similar degrees of partial melting (1-20%) followed by metasomatic enrichment
151 (Liang and Elthon, 1990). One of the most important characteristic of Ib xenoliths is the extreme
152 core-to-rim chemical zoning (and LREE-enriched patterns; (La/Yb)N> 0.8) in clinopyroxene,
153 revealed by a decrease of of Al_2O_3 and Na_2O towards the rim, while Mg#, CaO, TiO_2 and Cr_2O_3 tend
154 to increase (Liang and Elthon, 1990). According to these authors, high FeO-Na_2O contents in the
155 cores of Ib minerals and LREE enrichment in Cpx crystals suggest interaction between silicate melts
156 (basanitic in composition) and a residual mantle similar to group Ia xenoliths. Additionally, they
157 explain the extreme core-to-rim chemical zoning, and reaction rims in Cpx, by the reaction with H_2O-
158 rich fluids depleting Cpx rims in Na_2O and Al_2O_3 (also increasing TiO_2 contents).

159

160 **4. SAMPLES AND METHODS**

161 Samples were collected from the eastern part of the JH (Figure 1), where units IV and V emerge
162 according to the stratigraphy described by Saucedo et al. (2017). These units are composed of
163 pyroclastic fall and flow deposits where the highest concentration of mantle xenoliths is found. The

164   nodules are usually dispersed within or hosted in basanitic lavas. Thirteen fresh nodules were selected
165   with diameters between 5 and 10 cm; additionally, a pyroxenite sample was studied (sample V-C)
166   and was only used for noble gas analysis due to its small diameter (<5 cm). Eight nodules were
167   selected for petrographic analysis on thin and polished sections. Petrographic analysis was performed
168   at the petrography laboratory of the University of Milano-Biccoca based on the textural classification
169   proposed by Mercier and Nicolas (1975); the modal composition was carried out by point counting
170   (from 4000 to 7000 points per section).

171   Two double-polished rock sections of about 130 μm thickness were selected for the Raman of fluid
172   inclusions. Analyzed fluid inclusions are located at 10 to 20 μm depth below the sample surface.
173   Analyses were performed using a Labram Evolution (Horiba Scientific, Japan) at the Dipartimento
174   di Scienze dell'Ambiente e della Terra, Università Milano Bicocca. The polarized Raman spectra
175   were excited using a green Ar-ion laser operating at 532 nm, with 50-70 mW emission power. Spectra
176   acquisition was performed with a backscattered geometry and a 600 g/mm diffraction grating. A
177   transmitted light Olympus B40 microscope with a $100 \times$ objective (Numerical aperture, N.A., $= 0.90$)
178   was used for all the acquisitions (spatial resolution $< = 1 \mu m$). Confocality was maintained with a
179   pinhole of 100 μm. Spectra were collected with variable acquisition times (from 20 to 30 sec). The
180   spectrometer was calibrated using a Silicon standard. To increase band attribution accuracy better
181   than 0.2 cm^{-1}, spectra were baseline corrected and processed by statistical analysis (Fityk software;
182   Wojdyr, 2010) using a Voigt Pseudo-function, a convolution of a Lorentzian with a Gaussian line
183   shape. Mineral and fluid identification has been based on our reference spectra database (Frezzotti et
184   al., 2012a).

185   Noble gas and CO_2 isotopic determinations were performed at the noble gas and stable isotopes
186   laboratories of INGV, Sezione di Palermo, following the preparation methods and analytical
187   procedures described in Gennaro et al. (2017), Rizzo et al. (2018) and Faccini et al. (2020). All
188   xenoliths were crushed and sieved with the aim of hand-picking crystals with diameters >0.5 mm.
189   Thirty-five aliquots (13 Ol, 11 Opx and 13 Cpx) of crystals (weights of 0.05 to 2 g) were selected for
190   noble gas isotopic analysis. Before analysis, samples were cleaned ultrasonically in 6.5% HNO_3 (for
191   CO_2 analysis samples were cleaned in HCl), deionized water and high-purity acetone. After drying,
192   samples were accurately weighed and loaded into an ultra-high-vacuum (UHV) crusher for noble gas
193   analyses that was pumped and backed for 48h at 120°C. As soon as the ultra-high-vacuum was
194   reached, fluid inclusions were released by single-step crushing at about 200 bar and room
195   temperature (21°C). Single step technique was used to minimize the addition of secondary helium
196   (cosmogenic ^{3}He and radiogenic ^{4}He) accumulated in the crystal lattice (Kurz, 1986; Graham, 2002,
197   Rizzo et al., 2018; Correale et al., 2019); this is supported by the homogeneity of the dataset (more
198   details about the effect of secondary helium in our samples are provided in supplementary material).
199   The moles of CO_2 were quantified by measuring the total pressure of gas (generally
200    $CO_2+N_2+O_2+$noble gases) released during crushing (by an IONIVAC Transmitters ITR90) in a
201   known volume of the system, then subtracting the residual pressure of N_2+O_2+noble gases after
202   removing CO_2 in a "cold finger" immersed in liquid nitrogen. For noble gas analysis, the residual
203   gas mixture was purified under Zr-Al getter pumps in a UHV stainless-steel preparation line. After
204   then, Ar (and Kr and Xe) was removed in a "cold finger" with active charcoal immersed in liquid
205   nitrogen. Finally, He and Ne were adsorbed in a cold head with active charcoal cooled at 10K and
206   then moved at 40 and 80K in order to release first He and then Ne, respectively. He and Ne isotopes
207   were analyzed using two different split-flight-tube mass spectrometers (Helix SFT-Thermo), while
208   Ar isotopes were analyzed by a multi-collector mass spectrometer (Argus, GVI). The measured

209    $^{3}He/^{4}He$ ratios are expressed as R/Ra (where R is the ratio of the sample and Ra the He isotopic ratio
210   of air = 1.39×10^{-6}); this ratio was corrected for atmospheric contamination based on the measured
211    $^{4}He/^{20}Ne$ ratio and the values are expressed as Rc/Ra (eq.1):

212                      $R_c/R_a = ((R_M/R_a)(He/Ne)_M - (He/Ne)_A)/((He/Ne)_M - (He/Ne)_A)$ eq.1

213   where R_M/R_a and $(He/Ne)_M$ are the measured values and $(He/Ne)_A$ refers to the atmospheric
214   theoretical value (0.318). ^{40}Ar values were also corrected for atmospheric contamination:

215              $^{40}Ar* = {}^{40}Ar_{sample} - ({}^{36}Ar_{sample} \cdot ({}^{40}Ar/{}^{36}Ar)_{air})$ eq.2

216   where $^{40}Ar*$ is the corrected ^{40}Ar, $^{40}Ar/^{36}Ar_{air}$ = 295.5 and $^{21}Ne/^{22}Ne_{air}$ = 0.029 (Steiger and Jäger,
217   1977; Ozima and Podosek, 2002). Values of ^{20}Ne, ^{21}Ne, ^{22}Ne, ^{36}Ar, and ^{38}Ar are also reported.
218   Analytical uncertainties (1σ) for $^{3}He/^{4}He$, $^{20}Ne/^{22}Ne$, $^{21}Ne/^{22}Ne$, $^{40}Ar/^{36}Ar$, and $^{38}Ar/^{36}Ar$ ratios are
219   <2.7%, <6.3%, <7.5%, <2.0%, and <1.7%, respectively. The $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios are
220   corrected for isobaric interferences at m/z values of 20 ($^{40}Ar^{2+}$) and 22 ($^{44}CO2^{+2}$) (Rizzo et al., 2018;
221   Faccini et al., 2020).

222   Based on the results of the initial CO_2 measurements, twelve aliquots with the highest concentrations
223   were selected for isotopic CO_2 analysis. After crushing, the gas released was cleaned using a
224   purification line composed by two cryogenic traps and by a 626B Baratron® Absolute Capacitance
225   Manometer MKS (measuring range 10^{-3}–10 mbar) to remove H_2O and any atmospheric component,
226   and to quantify the gas released (Gennaro et al., 2017; Rizzo et al., 2018). The purified CO_2 was
227   condensed in a glass sampler (adjusted to atmospheric pressure by adding pure helium), and this was
228   transferred to the mass spectrometer. The $^{13}C/^{12}C$ isotope ratio was determined using a Thermo
229   (Finnigan) Delta Plus XP CF-IRMS connected to a Trace GC gas chromatograph and a Thermo
230   (Finnigan) GC/C III interface. The $^{13}C/^{12}C$ is expressed using the delta notation ($\delta^{13}C$) in per mil (‰)
231   relative to the V-PDB international standard.

232

233   **5. RESULTS**

234   **5.1 Petrography**

235   The suite of xenoliths exhibits the same mineralogy: Ol> Opx> Cpx >> Sp. All samples are
236   plagioclase-free and are classified as spinel lherzolites and harzburgites (Figure 2). Peridotites show
237   protogranular to porphyroclastic textures, in which two generations of Ol, Opx and Cpx crystals are
238   observed (Figure 3): the first generation corresponds to large, elongated and deformed crystals of
239   sizes greater than 3 mm (porphyroclasts); the second generation corresponds to smaller crystals with
240   polygonal shapes (neoblasts ≤ 3mm), which occur in the rock as a consequence of an intense
241   recrystallization process.

242   Olivines are present as translucent crystals without alteration. Ol porphyroclasts exhibit anhedral
243   forms (size <4.5 mm) with curved grain boundaries, kink bands and numerous fractures due to
244   deformation (Figure 3A); some crystals have Opx and Cpx inclusions (<1mm) with rounded shapes.
245   Most of the neoblasts are less than 2 mm long and are characterized by straight borders and subhedral
246   forms. Orthopyroxenes exhibit light brown colours without alteration; opx porphyroclasts are
247   characterized by anhedral and elongated forms with curved grain boundaries and diameters ≤ 4.5 mm

248   (Figure 3B, 3C and 3D). Neoblasts exhibit euhedral forms with well-developed straight boundaries
249   and sizes less than 2 mm; Opx tends to concentrate forming clusters of three or more crystals, where
250   vermicular spinel is commonly observed (Figure 3E and 3F); some Opx may contain small Cpx
251   inclusions (<0.2mm). Opx may exhibit a rough areas (especially over the rims) that resembles spongy
252   rims, which may expand over the entire crystal (Figure 3B, 3C and 3F). Cpx crystals are light green,
253   with subhedral to anhedral forms, sizes $\leq$ 2 mm (rare crystals with diameters greater than 4 mm are
254   present). Spongy textures along crystal rims in Cpx are very common and varies in thickness, this
255   texture sometimes develops as bands or affecting the entire crystal surface (Figure 3C and 3G).
256   Finally, spinel occurs as dark brown crystals with irregular shapes (anhedral forms with curved grain
257   borders), sizes $\leq$ 2 mm and develop as vermicular intergrowths in pyroxene clusters (Figure 3E and
258   3F).

259   Peridotites cut by glass veins that develop along the crystal borders, extending into single crystals as
260   micro-fractures. Veins have variable thicknesses, the largest being 0.3 mm thick (Figure 3D, 3F and
261   3H). Veins do not show a genetic relation with the host lava and are mainly formed by glass and may
262   contain relatively large ($\leq$0.25 mm) crystals of Cpx, tiny crystals with high birefringence, identified
263   as carbonates; and rare opaque minerals.

264

265   5.2 Fluid and melt inclusions

266   Olivine crystals contain abundant dendritic trails of secondary inclusions consisting of glass, mineral
267   phases, and a fluid phase. Dendritic inclusion trails are intragranular and typically originate from the
268   glass/carbonate microveins permeating the rocks (Figure 4A). Figure 4 shows this peculiar texture
269   resulting from the association of large (15-30 μm) irregularly-shaped inclusions containing silicate
270   glass (melt) with subordinate crystals and a fluid phase in variable proportions, along with smaller
271   (<20 μm) inclusions dominated by glass (melt) or fluid, $\pm$ crystals. Similar inclusion textures are
272   also observed in orthopyroxene and clinopyroxene, while fluid inclusions in the absence of glass,
273   generally observed in peridotites (Andersen and Neumann, 2001; Frezzotti and Touret, 2014), are
274   extremely rare. In inclusions, the silicate glass is colorless, isotropic, and does not show any
275   devitrification (Figure 4B). Mineral phases (< 30 μm) are high birefringent and texturally associated
276   with the glass (Figure 4C). The fluid is CO_2-rich, one or two phases (L, or L+V). Fluid-dominated
277   inclusions may contain tiny mineral grains, among which there is an opaque phase (Figure 4D).

278

279   5.3 Raman microspectroscopy

280   Raman microspectroscopy analyses of dendritic inclusions reveal that mineral phases texturally
281   associated with silicate glass are Mg-calcite (Figure 5A; vibrations at 1088, 714, 284, 158 cm^{-1}). The
282   fluid is pure CO_2 (Figure 5B; Fermi doublet at about 1282 -1387 cm^{-1}). Interestingly, in most CO_2
283   inclusions, Raman spectra also reveal the presence of dolomite (Figure 5C; vibrations at 1094-1096,
284   722-723, 299-300 cm^{-1}). Dolomite vibrations, however, are unexpectedly weak (likely linked to
285   disorder; Frezzotti et al., 2012a) and broad (full width at half maximum up to 15 cm^{-1}) (Figure 5C).
286   Also, the main vibration at 1098 cm^{-1} is downshifted from 2 to 4 cm^{-1}. These spectral characteristics
287   indicate a relevant order decrease in the crystalline structure as it occurs in decomposing carbonates
288   (Frezzotti and Peccerillo, 2007; Carteret et al., 2009; Frezzotti et al., 2012a).

289 The tiny mineral grains observed in a few CO_2 inclusions are magnesite (Figure 5D; vibrations at
290 1094, 723, 322, 202 cm^{-1}). An opaque mineral has been identified as pyrite (Figure 5D; vibrations at
291 342 and 377 cm^{-1}). The association of Mg-carbonate ± pyrite in CO_2-rich inclusions is suggestive of
292 fluid inclusion-host olivine reactions at low temperatures (Frezzotti et al., 2012b), probably during
293 host lava cooling at the surface.

294

295 **5.4 Elemental and Isotopic composition**

296 The elemental and isotopic composition of the crystal-hosted fluid inclusions in the JH mantle
297 xenoliths are reported in Table 2; reported errors are 1σ uncertainties, except for $^{21}Ne/^{22}Ne_{ext}$ ratios
298 whose errors are 2σ uncertainties. ^4He concentrations range between 8.56 x 10^{-14} and 1.29 x 10^{-11}
299 mol/g where the highest concentrations are observed in Cpx (~4.28 x 10^{-12} mol/g) followed by Ol
300 (~2.21 x 10^{-12} mol/g) and Opx (~2.06 x 10^{-12} mol/g). ^4He concentrations for the V-I crystals are
301 significantly lower than those measured in other nodules. $^{40}Ar*$ content ranges from 5.37 x 10^{-14} to
302 1.08 x 10^{-11} mol/g; in general, both $^{40}Ar*$ and ^4He values are similar to those previously reported in
303 mantle xenoliths from the European Subcontinental Lithospheric Mantle (European SCLM), the
304 West Antarctic Rift System (WARS), the Eastern Australia SCLM and some regions belonging the
305 East African Rift (Northern/Southern Kenya rifts and the Ethiopia-Afar region; Figure 6A;
306 Matsumoto et al., 1998, 2000; Hopp et al., 2004, 2007a, 2007b; Buikin et al., 2005; Gautheron et al.,
307 2005a; Czuppon et al., 2009; Martelli et al., 2011; Halldórsson et al., 2014; Broadley et al., 2016;
308 Rizzo et al., 2018; Correale et al., 2019; Faccini et al., 2020). ^{20}Ne, ^{21}Ne and ^{22}Ne values tend to be
309 high in Cpx and Opx; ^{20}Ne ranges from 1.42 x 10^{-16} to 5.08 x 10^{-14} mol/g, ^{21}Ne from 5.22 x 10^{-19} to
310 1.21 x 10^{-16} mol/g and ^{22}Ne from 1.34 x 10^{-17} to 4.90 x 10^{-15} mol/g. CO_2 is the most abundant gas, on
311 average its contents are higher in Cpx and Opx (1.02 x 10^{-7} and 3.18 x 10^{-8} mol/g, respectively) than
312 in Ol (3.43 x 10^{-9} mol/g); CO_2 contents are positively correlated with ^4He, $^{40}Ar*$, ^{20}Ne, ^{21}Ne and
313 ^{22}Ne, but are lower than those observed in European SCLM xenoliths (Figure 6B and 6C).

314 In detail, the Rc/Ra values vary as follows: Ol from 7.13 to 7.68 Ra, Opx from 6.15 to 7.54 Ra, and
315 Cpx from 5.40 to 7.59 Ra. The $^4He/^{40}Ar*$ ratios vary between 0.14 and 3.11 (Figure 8), which
316 overlaps in part the typical production ratio of the mantle ($^4He/^{40}Ar* = 1 - 5$; Yamamoto et al., 2009;
317 Marty, 2012); on average the highest values belong to Ol crystals (1.51 ± 0.76), compared to Opx
318 (0.72 ± 0.25) and Cpx (0.78 ± 0.40). $^4He/^{20}Ne$ values range from 2.4 to 10483; the highest values are
319 recorded in Cpx and Ol (on average 2223.2 ± 3196.8 and 1498.6 ± 1306.1, respectively), while Opx
320 exhibits considerably lower ratios (<639). This tendency is also observed for $^{40}Ar/^{36}Ar$ ratios that
321 vary from 303 to 8231 in Cpx, from 392 to 2518 in Ol, and from 340 to 1436 in Opx. It should be
322 noted that those samples with the lowest values of Rc/Ra, also are depleted in $^4He/Ar*$, $^{40}Ar/^{36}Ar$ and
323 $^4He/^{20}Ne$. On average $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios are 10.2 ± 0.50 and 0.0332 ± 0.0058,
324 respectively; in both cases, the values are slightly higher in Cpx compared to Ol and Opx. Finally,
325 the isotope composition of CO_2 expressed as δ^{13}C values (V-PDB) varies between -0.97 and -2.86‰
326 and does not exhibit a systematic variation between Ol, Opx and Cpx. The most negative value (-
327 2.86‰) was reported in IV-A Opx while the most positive values belong to two aliquots of the same
328 nodule: V-K Ol (-1.10) and V-K Opx (-0.97).

329

330

6. Discussion

Present textural and Raman spectroscopy observations indicate that the JH fluid inclusions are CO_2-dominated (Figure 5) and, even more importantly, that they are strictly associated with the pervasive infiltration of glass veins (Figures 3, 4). The inclusions typically exhibit the coexistence of glass, mineral phases, and a fluid phase, and form dendritic trails of fluid inclusions originating from the glass/carbonate microveins permeating the rocks (Figure 4A). The close association between glass and fluid inclusions, and their originating from the glass microveins, are strongly suggestive of trapping of fluids delivered by degassing of a carbonate-rich silicate melt at mantle depth. Textural observations and preliminary compositional information (indicating that glass veins contain 59±3 wt % SiO_2) clearly exclude that the glass veins are related to the basanitic to basaltic host magma.

In view of the above, and in line with previous work (Liang and Elthon, 1990; Luhr and Aranda-Gómez, 1997), we relate the fluid inclusions trapped in JH xenoliths to a melt-related metasomatic event deep in the source mantle. The overprinted textures in Cpx along crystal rims (named as spongy rims by Luhr and Aranda-Gómez, 1997) (see Figure 3) have also been associated to this metasomatic event (Liang and Elthon, 1990).

In the discussion below, we combined the above petrographic evidence and the isotopic signatures (noble gases and CO_2) of the JH fluid inclusions to constrain volatile origin and mantle characteristics. However, an initial screening of the dataset was necessary to filter out samples that have suffered from to secondary processes affecting fluid inclusion compositions (see Supplementary information). The filtered dataset is used below to infer volatile sources ad processes deep in the mantle.

6.1 Inferences on the noble gas signature of the JH source mantle

6.1.1 Interaction with atmospheric fluids and evidence for a recycled atmospheric component

In order to correctly interpret the noble gas data obtained in fluid inclusions from the JH mantle xenoliths, it is necessary to evaluate the interaction with atmospheric fluids. It is well known that Ar and Ne are more susceptible (relative to He) to contamination, due to their higher abundances in atmosphere relative to the mantle fluids. For this reason, tracers such as ^{40}Ar and ^{36}Ar, $^{4}He/^{20}Ne$, $^{20}Ne/^{22}Ne$, $^{21}Ne/^{22}Ne$, and $^{40}Ar/^{36}Ar$ are normally used to investigate the isotopic contribution from the atmosphere (Matsumoto et al., 2001; Gurenko et al., 2006; Hopp et al., 2004, 2007a, 2007b; Nuccio et al., 2008; Martelli et al., 2014; Oppenheimer et al., 2014; Rizzo et al., 2018).

He, Ne and Ar systematics suggest the existence of an atmospheric component in our samples (especially in nodule V-I). In general, the measured R/Ra and $^{4}He/^{20}Ne$ values fall along an air-MORB mixing curve, and overlap with those measured in mantle xenoliths from the European SCLM, the West Antarctic Rift System (WARS), Eastern Australia, Red sea region and N/S Kenya rifts (Figure 7A). The existence of such an atmospheric component is corroborated by $^{40}Ar/^{36}Ar$ and $^{20}Ne/^{22}Ne$ ratios significantly below the expected MORB values (44,000 and 12.5, respectively; Burnard, 1997; Moreira, 1998; Sarda, 2004). As shown in Figure 7B, $^{40}Ar/^{36}Ar$ and $^{3}He/^{36}Ar$ values also fall along a two-component mixing between a MORB-like upper mantle and atmosphere (He/Ar* ratios of 0.14 to 3.5 explain the whole data variability; see also Figure 9B). Likewise, samples fit the binary mixing air-MORB when using the three-isotope neon plot (Figure 7C), confirming the existence of atmospheric fluids in our inclusions. The atmospheric component is

especially notable in nodule V-I that exhibits an isotopic signature close to that of air with $^4He/^{20}Ne$ ratios below 10 (for Opx and Cpx) and $^{40}Ar/^{36}Ar$ values below 392. These compositions confirm that this nodule likely suffered secondary processes that modified its pristine mantle signature. This sample is therefore not considered representative of the local SCLM (and omitted from the following discussion).

The atmospheric component identified in the fluid inclusions may derive from two main possible processes, as summarized by Nuccio et al. (2008), Martelli et al. (2011), Correale et al. (2012), Rizzo et al. (2018), and Faccini et al. (2020): a) air entrapment in crystal fractures during or after eruption of transporting lava, and b) the interaction with subducted atmospheric fluids recycled in the upper mantle.

Although air entrapment in crystals microcracks cannot be totally discarded due to surface exposure of the xenoliths over the last 300 ky, the positive relation between ^3He and ^{36}Ar suggests a deep origin (Figure 9A), i.e., a recycled atmospheric component in the lithospheric mantle likely inherited from subduction (Matsumoto et al., 2001). In view of the above, and with the aim of constraining the $^{40}Ar/^{36}Ar$ signature expected for the local mantle, we also evaluate the relationship between $^{20}Ne/^{22}Ne$ and $^{40}Ar/^{36}Ar$ ratios (Figure 9B), using the approach used by Langmuir et al. (1978) and Hopp et al. (2007a). Considering an upper mantle $^{20}Ne/^{22}Ne$ equal to 12.5 (Sarda et al., 1988; Moreira et al., 1998), $^{36}Ar/^{22}Ne$ ratios between 4.21 and 93.5, a maximum $^4He/^{20}Ne$ ratio of 11,000 and $^4He/^{40}Ar*$ ratios between 0.14 and 3.11 (as observed in our samples; see Figures 7A and 8), we calculate a $^{40}Ar/^{36}Ar$ signature of about 10,500 for the local upper mantle (see Figure 9B and Table 3). Assuming a MORB-like $^{40}Ar/^{36}Ar$ signature of the pristine upper mantle (~44,000; Moreira et al.,1998), these calculations further support the existence of an atmospheric component in the Mexican lithospheric mantle, likely recycled during subduction events. Similar indications were observed in SCLM xenoliths from European localities, West Antarctic Rift System (WARS), Eastern Australia, Red sea region, N/S Kenya rifts and Ethiopia (Afar) (Matsumoto et al., 1998, 2000; Hopp et al., 2004, 2007a, 2007b; Buikin et al., 2005; Gautheron et al., 2005a; Czuppon et al., 2009; Martelli et al., 2011; Halldórsson et al., 2014; Broadley et al., 2016; Rizzo et al., 2018; Correale et al., 2019; Faccini et al., 2020).

Petrological evidence also highlights the interaction of the local upper mantle with metasomatic fluids possibly coming from the subducted oceanic crust (Pier et al., 1989; Luhr and Aranda-Gómez, 1997; Dávalos-Elizondo et al., 2016). Even though the present-day plate geometry in central and southern Mexico implies that the oceanic crust subduction terminates beneath the TMVB (Figure 1; Pardo and Suárez, 1995; Ferrari et al., 2012) i.e. 200 km south JH, subduction of the Farallon plate beneath the western part of North America during the Mesozoic and Paleogene could have potentially modified the Mexican lithospheric mantle directly below la Mesa Central (Pier et al., 1989; Bunge and Grand, 2000). Therefore, we consider realistic that the presence of an atmospheric component in fluid inclusions from JH is mostly attributable to a local SCLM feature.

6.1.2 Noble gas signature of the JH mantle source.

Ne isotopes can additionally be used, in combination with He isotopes, to resolve any potential influence of a mantle plume on the isotopic signature of the JH mantle xenoliths. To this aim, the relationship between the extrapolated neon isotope ratio (i.e. the air-free mantle $^{21}Ne/^{22}Ne$ ratio

415   expressed as $^{21}Ne/^{22}Ne_{EX}$) and the $^{3}He/^{4}He$ values was evaluated (e.g., Hopp et al., 2004, 2007b;
416   Halldórsson et al., 2014). The $^{21}Ne/^{22}Ne_{EX}$ values were calculated by extrapolating the measured
417    $^{21}Ne/^{22}Ne$ ratios to Neon-B ($^{20}Ne/^{22}Ne=12.5$) using the methodology proposed by Graham (2002)
418   and Halldórsson et al. (2014). Only those samples with $^{40}Ar/^{36}Ar$ ratios > 500 and $^{20}Ne/^{22}Ne$ ratios
419   distinguishable from air were selected. For comparison, the same calculation was made using the Ne
420   isotopes previously reported for the European SCLM (Buikin et al., 2005; Gautheron et al., 2005a;
421   Martelli et al., 2011; Rizzo et al., 2018; Faccini et al., 2020), the WARS (Broadley et al., 2016;
422   Correale et al., 2019), Eastern Australia SCLM (Matsumoto et al., 1998, 2000), Red sea region (Hopp
423   et al., 2004; Halldórsson et al., 2014), Ethiopia (Afar) region (Halldórsson et al., 2014) and N/S
424   Kenya rifts (Hopp et al., 2007b; Halldórsson et al., 2014); as a result, the graph reported in the Figure
425   10A was obtained.

426   As evidenced in Figure 10A, samples V-K/VF Ol, VF Opx and V-E/V-H Cpx exhibit ($^{21}Ne/^{22}Ne)_{EX}$
427   and $^{4}He/^{3}He$ ratios close to the theoretical value for a MORB-like upper mantle (as observed for some
428   mantle xenoliths from the Easter Australia SCLM and the Red sea region), the remaining values fall
429   along the MORB-Plume mixing line. When comparing our samples with other portions of SCLM on
430   Earth, we notice that JH nodules have similar ($^{21}Ne/^{22}Ne)_{EX}$ but lower $^{4}He/^{3}He$ values, confirming
431   the presence of a dominating MORB component. Instead, the Ethiopian xenoliths more clearly
432   exhibit both ($^{21}Ne/^{22}Ne)_{EX}$ and $^{4}He/^{3}He$ ratios close to the Plume endmember.

433   In the case of JH mantle xenoliths, ($^{21}Ne/^{22}Ne)_{EX}$ ratios <0.05 would suggest a deep-mantle
434   contribution of Neon (<10%). However, it must be taken into account that the samples less
435   contaminated by the atmospheric component fall within the AIR-MORB line when considering their
436   error bars (Figure 7C). In addition, the $^{3}He/^{4}He$ ratios reflect a homogeneous MORB-like signature.
437   Based on these evidences, we conclude that the upper mantle beneath JH is predominantly MORB-
438   like with a minimum contamination by a recycled crustal component, although we cannot totally
439   discard a deep-mantle contribution. This conclusion support the idea that the VESVF originates from
440   extension and melting of the lithospheric mantle under the Mesa Central province.

441   As discussed above, the relative invariance of the Rc/Ra values suggests that the upper mantle under
442   this portion of La Mesa Central is relatively homogeneous in terms of noble gases (Rc/Ra = 7.39 ±
443   0.14; Figure 10B - D). This $^{3}He/^{4}He$ signature is similar to that measured at the WARS (7.5 ± 0.5 Ra
444   and 7.1 ± 0.4 Ra; Broadley et al., 2016; Correale et al., 2019) and at the upper range of that inferred
445   at the N/S Kenya rifts and Red Sea region (6.6 ± 0.7 Ra and 7.0 ± 0.9 Ra, respectively; Hopp et al.,
446   2004, 2007b; Halldórsson et al., 2014), but manifestly less radiogenic than the European SCLM (6.1
447   ± 0.9; Gautheron and Moreira, 2002; Buikin et al., 2005; Gautheron et al., 2005a; Martelli et al.,
448   2011; Rizzo et al., 2018; Faccini et al., 2020).

449   The MORB-type $^{3}He/^{4}He$ signature at JH deserves some consideration in relation to the past
450   geodynamic history of the area. We envisage two possible scenarios.

451   In scenario 1, the relatively homogeneous (MORB-like) $^{3}He/^{4}He$ ratios for the JH mantle xenoliths
452   might be taken as indicative of a low-to-negligible recycling of crustal materials during the
453   subduction of Farallon plate (20-40 Ma). A limited input of U-Th-bearing crustal materials would in
454   fact explain well the low contribution of radiogenic ^{4}He in the local mantle. If this interpretation is
455   correct, then past subduction events would only have added a recycled atmospheric component into
456   the mantle (cfr 6.1.1). Alternatively, one may consider a scenario (scenario 2) in which any addition
457   of (subduction-related) materials during subduction of the Farallon plate was later (during the <20

Ma Basin and Range extensional phase) overprinted by an influx of MORB-like materials, rising from deeper (asthenospheric to deep SCL) mantle domains. This latter scenario is supported by the geodynamic reconstructions that indicate a metasomatism/refertilization of the lithospheric mantle during the Basin and Range extensional phase. Paleo-subduction reconstructions indicate that the Farallon plate subducted horizontally underneath Western North-America and Northern-Central Mexico between 74 - 40Ma, producing the Laramide orogeny in the United States and the mountain range known as the Sierra Madre Oriental (SMOr) east of the JH (Figure 1; Atwater, 1989; Cserna, 1989; Severinghaus and Atwater, 1990; Bunge and Grand, 2000; Eguiluz de Antuñano et al., 2000; Lee, 2005). This tectonic configuration would have changed at ~40-20Ma, however, when the retreat of the Farallon slab occurred, a commonly invoked cause for initiation of the Basin and Range extension (Leeman and Harry, 1993; Nieto-Samaniego et al., 1999, 2005; Lee, 2005; Sedlock, 2003). According to Nieto-Samaniego et al. (1999), retreating of the oceanic slab favored the influx of younger and hotter asthenospheric material that ultimately led to melt generation and extension at the base of the Mesa Central. Evidence of this process comes from the intense normal faulting in the Mesa Central registered 30Ma, 23-24Ma 12-13Ma ago, and from the transition from calc-alkaline volcanism (in the so-called Sierra Madre Occidental; SMO; Figure 1) to intraplate alkaline volcanism (Henry and Aranda-Gomez, 1992; Nieto-Samaniego et al., 1999; Aranda Gómez et al., 2000). Injection of ^{3}He-rich (MORB-like) asthenospheric melts during the mid-Cenozoic could well have caused re-fertilization/re-juvenation of the Mexican lithospheric mantle in a model similar to that proposed for the lithospheric mantle beneath the Yangtze craton and the WARS (Correale et al., 2016, 2019; Faccini et al., 2020). This scenario is possible if we assume that almost all ^{3}He comes from asthenospheric melts, as proposed by Gautheron and Moreira (2002) and Gautheron et al. (2005a) to explain the noble gases systematics of the European SCLM (a steady-state model).

Irrespective of subduction is considered to have (scenario 2) or have not (scenario 1) impacted the He mantle budget, there is unquestionable petrographic evidence (this study; Liang and Elthon, 1990; Luhr and Aranda-Gómez, 1997) for a melt-related metasomatic event affecting the JH, potentially during Basin and Range extensional phase (Nieto-Samaniego et al., 1999).

6.2 ^{3}He fluxes, ^{4}He production and the helium residence time for the Mexican lithospheric mantle

The MORB-type He signature of JH xenoliths can quantitatively be interpreted in light of the SCLM model of Gautheron and Moreira, (2002). According to the authors (see also (Griffin et al., 1999, 2009), the geochemical and isotopic characteristics of the SCLM are the ultimate result of any past interaction with fluids and melts coming from (i) deeper mantle sources and/or (2) recycled slab components that have alternated over geological time (Griffin et al., 1999). In terms of helium isotopes, Gautheron and Moreira (2002) argued that the SCLM is globally homogeneous (6.1±0.9 Ra). They based this inference on the study of suites of ultramafic xenoliths and alkali basalts collected from different continental settings (Europe, USA, Antarctic, Australia, and West Africa).

In order to explain its helium isotopic homogeneity, Gautheron and Moreira (2002) proposed the global lithospheric mantle is in steady state for helium. In their model, the global SCLM is continuously metasomatized by melts and fluids with a MORB-like helium signature coming from the asthenosphere (affecting the entire reservoir); eventually, this signature becomes more radiogenic due to U and Th decay resulting in lower ^{3}He/^{4}He ratios (e.g. 6.1 ± 0.9 Ra). Thus, the steady-state

501 model is based on the balance between the He flux from the asthenosphere and the in-situ production
502 in the lithosphere of radiogenic ^{4}He. From this model, it is possible to estimate the helium residence
503 time in the lithospheric mantle (Rt), the ^{3}He flux (F) and the ^{4}He production (P*). The model uses
504 the dimensions of the SCLM (thickness, surface and density) assuming a constant U + Th
505 concentration. These authors reported a Rt = ~200 Ma, F= 270 mol/yr and P* = 6.8×10^6 mol/yr for
506 the global SCLM, while Gautheron et al. (2005) obtained a Rt = 5-150 Ma, F= 3.5×10^4 at/m^2/s (~ 1
507 mol/yr) and P* ~ 3×10^4 mol/yr for the European SCLM.

508 However, some studies on noble gas systematics (including our results) support a more fertile
509 signature (^{3}He/^{4}He> 7.0 Ra) for some portions of the SCLM on Earth (e.g., Southern Australia and
510 West Antarctic Rift; Matsumoto et al., 1998; Broadley et al., 2016; Correale et al., 2019). Therefore,
511 we argue that the steady state model proposed by Gautheron and Moreira (2002) should be applied
512 in local portions of SCLM to eventually detail their interactions with the asthenosphere. Using this
513 steady-state model, and considering the ^{3}He/^{4}He signature of the JH mantle xenoliths, we estimated
514 the helium residence time, the ^{3}He flux and the ^{4}He production for the lithospheric mantle located
515 under the San Luis Potosí state (central Mexico):

516 $$F = \frac{P^*}{\left(\frac{^4He}{^3He}\right)_{SCLM} - \left(\frac{^4He}{^3He}\right)_{MORB}} \qquad \text{eq.3}$$

517 In eq. 3, F is the ^{3}He flux (cc STP/yr) and P* is the ^{4}He production (P*= 2.8×10^{-14} * (4.35+Th/U) *
518 U * M). U is the concentration of uranium in ppm and M is the mass of the subcontinental mantle.
519 The helium residence time Rt is defined as:

520 $$Rt = \frac{Total\ ^3He\ in\ the\ SCLM\ (cc\ STP)}{F} \qquad \text{eq.4}$$

521 The parameters used in the calculation are as follows: 1) the average of the ^{4}He/^{3}He ratios measured
522 in JH mantle xenoliths equal to 97,500 (7.38 Ra) and a MORB endmember equal to 84,600 (8.5 Ra).
523 The latter value is higher than that assumed by Gautheron and Moreira (2002) (8.0 Ra) because
524 preliminary results for mantle xenoliths from other localities in central Mexico yield Rc/Ra values
525 of $\leq$ 8.35 (unpublished data); 2) U contents between 0.01 and 0.03 ppm as previously reported for
526 mantle xenoliths from central Mexico (Dávalos-Elizondo et al., 2016) and a Th/U = 3 as assumed by
527 Gautheron and Moreira (2002); 3) A subcontinental mantle mass equal to 3.66×10^{21} g. This mass
528 was estimated assuming a thickness of the local lithospheric mantle of ~150km (density of 3.3×10^6
529 g/m^3; Gautheron and Moreira, 2002) and a surface of 7.4×10^9 m^2 that includes all the Cenozoic
530 intraplate monogenetic volcanic fields located in the San Luis Potosí state (VESVF, SDVF and Los
531 Encinos volcanic field; see Figure 1; Aranda-Gómez et al., 2007); 5) A upper mantle ^{4}He
532 concentration equal to 1×10^{-6} ccSTP/g (4.5×10^{-11} mol/g), which corresponds to the maximum value
533 identified for continental mantle xenoliths (Gautheron and Moreira, 2002); this value is equivalent
534 to a ^{3}He concentration =1.0×10^{-11} ccSTP/g (4.5×10^{-16} mol/g) assuming a Rc/Ra = 7.38; thus the
535 total ^{3}He estimated for the local SCLM is 1.64×10^6 mol (3.66×10^{10} cc STP). The results obtained are
536 reported in Table 4.

537 The calculated ^{3}He fluxes for the Mexican lithospheric mantle vary from 0.027 to 0.080 mol/g
538 (Figure 11A). These fluxes are very low if compared with the values reported for the global SCLM,
539 the European SCLM or MORB values (800-1300 mol/g; Marty and Jambon, 1987; Javoy et al., 1989;
540 Michael and Graham, 2015; Tucker et al., 2018). When scaled to the surface area (7.4×10^9 m^2) of
541 volcanism in the San Luis Potosí state, our specific fluxes vary between 6.9 and 20.7 at/s/cm^2 (Figure

542 11B) which are well above the MORB and the global SCLM values (4.8 at/s/cm^2 and 3.5 at/s/cm^2,
543 respectively; Craig et al., 1975; Gautheron and Moreira, 2002) confirming a high ^{3}He contribution
544 from the asthenosphere under central Mexico.

545 The associated Rt values range from 20 to 60 Ma. These estimates are lower if compared to the global
546 SCLM and would explain the less radiogenic character of the Mexican lithospheric mantle. In this
547 model, the Rt values do not depend on the area but have a close relationship with the average of the
548 ^{3}He/^{4}He ratios measured in the mantle xenoliths. It is reasonable to think that the smaller the ^{3}He/^{4}He
549 ratio measured in the xenoliths (7.38 Ra for JH xenoliths and 6.1Ra for the SCLM), the longer the
550 helium residence time in the lithospheric mantle should be. Therefore, low Rt values implies low ^{4}He
551 production and high ^{3}He/^{4}He ratios, as observed in JH mantle xenoliths. Moreover, our estimated Rt
552 range overlaps with the inferred age range for the retreating subduction of the Farallon slab (40-20
553 Ma ago) a processes, which may have triggered the injection of asthenospheric melts in the
554 lithospheric mantle and the generation of the Basin and Range province (Nieto-Samaniego et al.,
555 1999; Lee, 2005). If correct, our results would independently indicate that the last major geodynamic
556 modification in the lithospheric mantle underneath the JH occurred during the lower and mid-
557 Cenozoic. We argue that the refertilization event was able to increase the ^{3}He/^{4}He signature within
558 the MORB-like range, overprinting the pre-Cenozoic signature recorded by the Mexican lithospheric
559 mantle. Since then, the latter would have evolved in a similar way to that proposed by Gautheron and
560 Moreira (2002), i.e., in a steady state becoming slightly more radiogenic during the last ~20Ma down
561 to the measured ^{3}He/^{4}He values.

562 In conclusion, both the low production of ^{4}He and the relative lower Rt (compared to other areas)
563 could explain the high ^{3}He/^{4}He ratios measured in JH mantle xenoliths. However, we caution these
564 are local estimates; therefore, in order to minimize the effect generated by the area and possible
565 mantle heterogeneities, future work will target obtaining isotopic data for mantle xenoliths from other
566 localities of the Basin and Range extension in Mexico. This will allow a more realistic reconstruction
567 of the evolution of the Mexican lithosphere in terms of noble gases.

568

569 *6.2.1 Mantle CO$_2$ fluxes*

570 We combine the ^{3}He flux estimated above with the CO$_2$/^{3}He ratios measured in the JH xenoliths (e.g.
571 Marty and Jambon, 1987; Tucker et al., 2018) to calculate the mantle-derived CO$_2$ fluxes in the area.
572 Taking U concentrations between 0.01 ppm and 0.03 ppm and a CO$_2$/^{3}He$_{(avg)}$ ~1.47 x 10^9, the
573 calculated CO$_2$ fluxes range from 3.93 x 10^7 mol/yr (1.02 x 10^{10} at/s/cm^2) to 1.18 x 10^8 mol/yr
574 (3.05x10^{10} at/s/cm^2; Figure 11C-11D). Our estimated fluxes are lower than previously estimated for
575 other continental rift localities (such as the EAR), consistent with the small area of the San Luis
576 Potosí volcanic filed (considered in the model), and correspond to <0.1% of the MORB CO$_2$ fluxes;
577 similarly, our fluxes are lower than estimated for hot spot settings such as Hawaii or Canary Islands
578 (Hauri et al., 2019). Additional studies on noble gas and CO$_2$ isotopic data from other mantle
579 xenoliths locations in central and northwestern Mexico are required to further validate our results.

580

581

6.3 Inferences on CO₂ origin.

In JH peridotites, fluids are dominated by CO_2 (Figure 6), as typically recorded by other worldwide mantle xenoliths (Andersen and Neumann, 2001; Deines, 2002; Frezzotti and Touret, 2014). Thus, the CO_2 isotopic composition can be used to constrain carbon origin. Our samples exhibit $\delta^{13}C$ ratios between −0.97 and −2.86‰ (Figure 12A); they are therefore isotopically more positive (^{13}C-rich) than found in European mantle xenoliths in alkaline intra-plate and extensional contexts, such as in the Hyblean plateau (southeast Sicily, Italy; ranging from-4 to -2‰; Correale et al., 2015) and Lower Silesia (southwest Poland; ranging from -4.7 to -3.1‰; Rizzo et al., 2018).

The CO_2 isotopic composition in the JH peridotites is also well above the $\delta^{13}C$ MORB mantle range ($−8‰ < \delta^{13}C < −4‰$; Sano and Marty, 1995). When $\delta^{13}C$ values are plotted against Rc/Ra and CO_2/^{3}He ratios (Figure 12B, 12C), our samples fall along a MORB-Limestone mixing line, suggesting source mantle Carbon contamination by C-rich fluids with a crustal carbonate signature.

The crustal carbon component found in fluid inclusions of JH xenoliths may in principle derive from two main distinct processes: (i) infiltration of CO_2 rich fluids derived by assimilation of carbonates by host magmas during ascent through the continental crust, and (ii) mantle metasomatism by CO_2-rich fluids and melts derived from subducted oceanic crust and sediments.

Infiltration of CO_2 fluids in mantle xenoliths outgassed during assimilation of carbonates in basanitic magmas in the continental crust should be considered since JH maar formed on carbonate deposits (the Valles-San Luis Potosí calcareous platform (PVSLP) and the Mesozoic Basin of central Mexico). However, the relatively fast ascent rates of the host magma through the continental crust (Luhr et al., 1989; Pier et al., 1989), and the lack of carbonate xenoliths in the host lava, argue against a crustal component inherited during sin-eruptive magma ascent. Conversely, petrographic and Raman evidence indicates pervasive infiltration of carbonate-bearing silicate melts and CO_2-fluids in peridotites (Figure 4), strongly supporting deep carbon mobility during a metasomatic event in the lithospheric mantle. We, therefore, conclude that the carbonate component identified in JH CO_2 fluids was trapped under mantle conditions and is related to CO_2 degassing of metasomatic carbonate-rich silicate melts on reaction with mantle minerals. Metasomatic processes occurred well before entrainment by the host magma and eruption (as proposed by Liang and Elthon, 1990).

As mentioned in the previous sections, northwestern Mexico's current tectonic configuration indicates that the Cocos and Rivera plates do not directly affect the mantle under the Mesa Central, making it difficult to consider involvement of present subduction (Figure 1). Moreover, some studies suggest that the contribution of carbonate sediments from the subducting slab is minimal. The CO_2-rich plume gases released by arc volcanoes (e.g., Popocatepetl) come from the assimilation of limestone deposits, as evidenced by trace element analysis performed in mafic rocks and the presence of carbonate xenoliths in volcanic deposits (Goff et al., 1998, 2001; Aiuppa et al., 2017). A low contribution of subducted Carbon in fluids has also been proposed for other volcanic fields belonging to the TMVB, such as the Sierra Chichinautzin Volcanic Field (SCVF; Verma, 2000) and the Michoacan-Guanajuato Volcanic Field (MGVF; Verma and Hasenaka, 2004).

In contrast to present-day subduction being an unlikely driver, we emphasize a possible major role played by older subduction of the Farallon underneath the northwestern margin of North America during the Mesozoic and early Cenozoic (Atwater, 1989; Ferrari et al., 2012; Henry and Aranda-Gomez, 1992; Sedlock, 2003). Several authors claim that the North American lithospheric mantle

could have been hydrated by fluids or melts released by flat subduction of the Farallon plate, as evidenced by petrological studies of mantle xenoliths from the Sierra Nevada and the Colorado Plateau (Smith et al., 1999; Lee, 2005; Li et al., 2008). "Farallon hydration" (Lee, 2005) is suggested to have occurred during the late Cretaceous and early Cenozoic, and to have affected the lithospheric mantle up to 800 km inboard of the trench (Li et al., 2008). This metasomatic event is also well documented in Mexican xenoliths (Liang and Elthon, 1990; Dávalos-Elizondo et al., 2016; Levresse et al., 2016). For example, Luhr and Aranda-Gómez (1997) interpreted the systematic east to west oxygen fugacity increase in Cenozoic mantle xenoliths from central and northern Mexico as induced by the progressive oxidation of the lithospheric mantle by fluids released by the Farallon oceanic slab.

In light of the above, the interaction between subducted fluids delivered by the Farallon plate and the Mexican lithospheric mantle could represent a feasible mechanism to explain the heavy $\delta^{13}C$ signatures of JH mantle fluids. We argue that the crustal carbon component identified in the fluid inclusions would reflect a mantle feature induced by an old subduction-related carbonate component inherited during the mid-Cenozoic before the Basin and Range extension (Middle Miocene; Henry and Aranda-Gomez, 1992; Sedlock, 2003) and recycled in the local mantle.

7. CONCLUSIONS

We investigate the petrography and noble gas-CO_2 composition of fluid inclusions in ultramafic mantle xenoliths collected from JH, in central Mexico. Peridotites are classified as spinel-lherzolites and harzburgites. Petrographic observations and Raman microspectroscopy analyses of fluid and melt inclusions reveal the coexistence of glass/carbonate microveins and a CO_2 fluid phase permeating the rocks, suggesting interaction between peridotites and degassing carbonate-rich silicate melts at mantle depth.

The $^4He/^{40}Ar^*$ range (0.14 - 3.11) partially overlaps that of fertile mantle (1-5), which could indicate either a low degree of partial melting or the occurrence of a metasomatism/refertilization process by melts degassing fluids ultimately entrapped in the mantle as secondary fluid inclusions.

Ne and Ar systematics reveal a mixing between atmospheric and MORB-like fluids, strongly supporting the presence of an atmospheric component eventually recycled from the Farallon plate subduction. Although, $(^{21}Ne/^{22}Ne)_{EX}$ ratios suggest the existence of plume-derived Neon in our fluid inclusions, JH mantle xenoliths exhibit homogeneous $^3He/^4He$ signature (7.39 $\pm$ 0.14 Ra) that is comparable to that of the MORB-like mantle and similar to other worldwide SCLM localities (eg., Eastern Australia, N/S Kenya rifts and WARS). This isotopic signature results from a low recycling of crustal components in the local mantle possibly overprinted by a metasomatism/refertilization episode reasonably occurred after the retreat of the Farallon slab during the early and mid-Cenozoic.

Based on the "Steady-state" model proposed by Gautheron and Moreira (2002), we estimated a helium residence time in the local SCLM between 20-60Ma, which overlaps the geodynamic evolution of the area and the metasomatism/refertilization event. Since then, the lithospheric mantle would have evolved in a steady state for helium (from a MORB signature ~8.5 Ra) becoming slightly more radiogenic during the last ~20Ma. We also calculated ^3He fluxes between 0.027 - 0.080 mol/g,

664   [4]He production rates from 340 to 1000 mol/yr and mantle CO_2 fluxes from 3.93 x 10^7 mol/yr to
665   $1.18x10^8$ mol/yr represent less than the 0.1% of the MORB CO_2 fluxes.

666   The $\delta^{13}C$ values measured in JH fluid inclusions reveal a binary mixing between a MORB-like upper
667   mantle and a crustal carbonate component (limestone). We propose that the crustal CO_2/carbonate
668   component identified in JH xenoliths was trapped under mantle conditions through metasomatic
669   reactions between peridotites ad C-bearing silicate melts. These would have acted as carriers in the
670   local mantle of a recycled carbon component inherited from the Mesozoic to early Cenozoic Farallon
671   subduction.

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Figure Captions

Figure 1. Location of the Joya Honda maar (JH) and geodynamic setting. The map shows the Mexican part of the Basin and Range Province which has an extension of 9.4 x 10^5 km^2 (Henry and Aranda-Gomez, 1992); the image was adapted from Aranda-Gómez et al. (2000). The green area is the area used to estimate the ^{4}He production, the helium residence time and ^{3}He-CO_2 fluxes for the lithospheric mantle located under San Luis Potosí state (see subsections 6.5 and 6.5.1). The pink square represents the location of the Los Encinos Volcanic Field (LE); although this is a monogenetic volcanic field associated with the Basin and Range extension, this lacks mantle xenoliths. Contours of Sierra Madre Occidental, Sierra Madre Oriental, the Transmexican Volcanic Belt and Mesa Central provinces were build based on Gómez-Tuena et al. (2007). VESVF: Ventura Espiritu Santo Volcanic Field, SDVF: Santo Domingo Volcanic Field, PiVF: Pinacate Volcanic Field, PaVF: Las Palomas Volcanic Field, Po: Potrillo maar, CVF: the Camargo Volcanic Field, DVF: Durango Volcanic Field, SQVF: San Quintin Volcanic Field, II: Isla Isabel. Upper right image**:** Google Earth image (February 20th, 2020) showing the Joya Honda maar morphology and sampling area.

Figure 2. Ternary classification for ultramafic and mafic rocks, from Streckeisen (1976).

Figure 3. Microphotographs of the JH mantle xenoliths in cross-polarized light (A, B, C, D, E, G, H) and transmitted plane-polarized light (F). Ol: olivine, Opx: orthopyroxene, Cpx: clinopyroxene, Sp: spinel. A) Ol porphyroclast with well-developed kink bands and glass-rich veins. B) Spongy rims developed in Opx crystals; C) Cpx and Opx crystals are almost and totally replaced by the spongy rim. D) Porphyroclastic texture; Opx crystal being cut by a glass-rich vein. E) Opx cluster. F) Opx cluster cut by a vein composed of light brown glass and some opaque minerals, note the presence of spongy rims in Opx. G) Cpx porphyroclast with development of spongy bands. H) Glass-rich veins around Opx porphyroclast.

Figure 4. Microphotographs of inclusions identified in olivine. A) Melt and fluid inclusions originating from microveins. B) Intragranular trail of dendritic inclusions. C) Inclusions composed by glass and high birefringent mineral phases (cross-polarized light illumination). D) Opaque phases associated to fluid inclusions.

Figure 5: Raman spectroscopy applied in olivine inclusions. A) Raman spectra of birefringent mineral phases (Mg-calcite) observed in Figure 4C. B) Raman spectra of pure CO_2 fluid inclusions identified in Figure 4D. C) Raman spectra of dolomite contained in some inclusions of Figure 4B. D) Raman spectra of magnesite and pyrite contained in olivine inclusions.

Figure 6. ^{4}He, ^{40}Ar* and CO_2 contents measured in fluid inclusions hosted in JH mantle xenoliths. SCLM: Subcontinental Lithospheric Mantle. The West Antarctic Rift System (WARS) SCLM compositional range was built using fluid inclusions data measured by Broadley et al. (2016) and Correale et al. (2019). European SCLM range includes fluid inclusions values measured in mantle xenoliths from the Rhenish Massif (Germany), Pannonian basin, Massif Central (Central France), Tallante - Calatrava (Spain), Lower Silesia (Poland) and the Eastern Transylvanian Basin; data was taken from Buikin et al. (2005), Gautheron et al., (2005a), Martelli et al. (2011), Rizzo et al. (2018) and Faccini et al. (2020). Eastern Australia SCLM data was taken from Matsumoto et al. (1998, 2000) and Czuppon et al. (2009). Red sea region data from Hopp et al. (2004), Hopp et al. (2007a) and Halldórsson et al. (2014). Northern/Southern Kenya rifts data was taken from Hopp et al. (2007b) and Halldórsson et al. (2014). The Ethiopia (afar) field was designed after Halldórsson et al. (2014).

Figure 7. A) ^{4}He/^{20}Ne vs R/Ra diagram, the solid lines represent the binary mixing between air and an upper mantle source with R/Ra values between 7 and 8, B) ^{3}He/^{40}Ar vs ^{40}Ar/^{36}Ar diagram. C) ^{21}Ne/^{22}Ne vs. ^{20}Ne/^{22}Ne diagram in which the green line represents the binary mixing air-MORB mantle as defined by Sarda et al. (1988) and Moreira et al. (1998) at ^{21}Ne/^{22}Ne$_{air}$ = 0.029 and ^{20}Ne/^{22}Ne $_{air}$ = 9.8 and ^{21}Ne/^{22}Ne = 0.06 and ^{20}Ne/^{22}Ne = 12.5; the primordial neon composition is reported as Solar wind at ^{21}Ne/^{22}Ne = 0.0328 and ^{20}Ne/^{22}Ne = 13.8 (Heber et al., 2009); the crust endmember was plotted at ^{21}Ne/^{22}Ne = 0.6145 and ^{20}Ne/^{22}Ne =

1092   0.3 (Kennedy et al., 1990). The WARS SCLM, European SCLM, Ethiopia (Afar), N/S Kenya rifts, Eastern
1093   Australia SCLM and Red sea compositional ranges were built using fluid inclusions data cited in Figure 6.

1094   **Figure 8.** ^{4}He/^{40}Ar* vs ^{3}He/^{4}He corrected for air contamination (Rc/Ra) ratios of fluid inclusions from JH
1095   mantle xenoliths. MORB range is reported at Rc/Ra = 8 + 1 (Graham, 2002) and ^{4}He/^{40}Ar* from 1 to 5
1096   (Yamamoto et al., 2009). The WARS SCLM, European SCLM, Ethiopia (Afar), N/S Kenya rifts, Eastern
1097   Australia SCLM and Red sea compositional ranges were built using fluid inclusions data cited in Figure 6. The
1098   diffusive fractionation path is modeled using the diffusion coefficient (D) of ^{3}He, ^{4}He, and ^{40}Ar*
1099   (D^{3}He/D^{4}He=1.15 and D^{4}He/D^{40}Ar=3.16 in solid mantle; Burnard, 2004; Yamamoto et al., 2009) (see
1100   supplementary material). Partial melting (see arrow) can lead to decreasing ^{4}He/^{40}Ar* (see supplementary
1101   materials).

1102   **Figure 9.** A) ^{36}Ar vs ^{3}He concentration. Plotted values correspond to samples with ^{40}Ar/^{36}Ar > 500. B)
1103 ^{20}Ne/^{22}Ne vs ^{40}Ar/^{36}Ar. Mixing curves are the result of mass-balance and isotopic mass balance equations using
1104   the parameters reported in Table 3.

1105   **Figure 10**. A) ^{21}Ne/^{22}Ne $_{EX}$ ratios vs ^{4}He/^{3}He ratios, adapted from Hopp et al. (2004) and Halldórsson et al.
1106   (2014). Values with 2σ uncertainties <10% are plotted. Dotted lines are binary mixing between three
1107   endmembers: 1) Plume, at 20Ra and ^{21}Ne/^{22}Ne $_{EX}$ = 0.034 ± 0.001, 2) MORB-like upper mantle at 8 Ra, 7 Ra
1108   and ^{21}Ne/^{22}Ne $_{EX}$ = 0.06 ± 0.001 and SCLM at 6.1 ± 0.9 Ra and ^{21}Ne/^{22}Ne $_{EX}$ = 0.07 ± 0.001. B) ^{3}He, C) ^{4}He
1109   and D) ^{40}Ar* vs ^{3}He/^{4}He corrected for air contamination (Rc/Ra). MORB range is report ed at Rc/Ra = 8 ± 1
1110   (Graham, 2002).

1111   **Figure 11.** A) Comparison between ^{3}He fluxes measured in central Mexico based on JH mantle xenoliths
1112   analysis (at U=0.01 and 0.03 ppm) and other localities. MORB value was estimated using data from Michael
1113   and Graham (2015) and based on CO$_2$/^{3}He ratio =2.2 x 10^9 (Marty and Tolstikhin, 1998); SCLM value was
1114   taken from Gautheron and Moreira (2002); the European SCLM flux was calculated based on Gautheron et al.
1115   (2005a). B) ^{3}He fluxes scaled to the surface area. See the text for more details. C) Associated CO$_2$ fluxes
1116   (mol/yr) for central Mexico compared with other tectonic localities. MORB CO$_2$ flux was calculated after
1117   Michael and Graham (2015); EAR1 and EAR2 values were taken from Lee et al. (2016) and Foley and Fischer
1118   (2017), respectively; Hawaii and Canary fluxes were obtained from Hauri et al. (2019). D) CO$_2$ fluxes scaled
1119   to the surface area.

1120   **Figure 12.** A) CO$_2$ vs δ^{13}C. Hyblean, Stromboli and European SCLM data from Correale et al. (2015), Gennaro
1121   et al. (2017) and Rizzo et al. (2018), respectively. B) δ^{13}C vs 3He/4He corrected for air contamination (Rc/Ra).
1122   Dotted lines are binary mixing between two endmembers: 1) Limestone at δ^{13}C =-1, 1 and Rc/Ra= 0.01 and 2)
1123   MORB-like upper mantle at δ^{13}C = -4 and Rc/Ra = 7.38. C) δ^{13}C vs CO$_2$/^{3}He. Dotted lines are binary mixing
1124   between two endmembers: 1) Limestone at δ^{13}C =-1, 1 and CO$_2$/^{3}He = 10^{-13} and 2) MORB-like upper mantle
1125   at δ^{13}C = -4 and CO$_2$/^{3}He = 1.00 x 10^{-9}, 2.00 x 10^{-9}.

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TABLES

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Table 1. Modal composition of JH mantle xenoliths.

Sample	Rock type	Ol (%)	Opx (%)	Cpx (%)	Sp (%)
VE	Lherzolite	54.47	28.96	14.37	2.2
VJ	Lherzolite	52.01	32.31	13.39	2.29
IVA	Lherzolite	72.48	15.86	10.45	1.21
VF	Lherzolite	52.08	33.97	11.93	2.02
VI	Lherzolite	53.41	23.48	19.79	3.32
VG	Harzburgite	68.14	30.04	1.26	0.56
VK	Lherzolite	61.27	24.59	13.69	0.44
VH	Harzburgite	62.08	31.26	4.47	2.18

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Table 2. Fluid inclusions compositions from JH mantle xenoliths. Concentrations are reported in mol/g. r*: reply made in sample V-I.

Sample	Phase	Weight (g)	^{3}He	^{4}He	^{20}Ne	^{21}Ne	^{22}Ne	CO$_2$[a]	^{40}Ar	^{36}Ar	^{40*}Ar	^{4}He/^{20}Ne	^{4}He/^{40}Ar*	^{4}He/CO$_2$	R/Ra	Rc/Ra	error +/- (1σ)
V-A	Ol	0.95855	1.67E-17	1.65E-12	9.11E-16	2.72E-18	9.26E-17	2.80E-11	2.09E-12	1.50E-15	1.65E-12	1814.0	1.00	0.05901	7.26	7.26	0.06
V-A	Opx	0.26388	4.74E-18	4.91E-13	8.90E-15	2.59E-17	9.00E-16	3.91E-10	3.61E-12	5.45E-15	2.00E-12	55.2	0.25	0.00126	6.91	6.94	0.13
V-A	Cpx	0.21991	6.45E-18	6.57E-13	5.81E-16	2.62E-18	5.41E-17	6.23E-09	5.16E-12	1.55E-15	4.70E-12	1131.4	0.14	0.00011	7.06	7.06	0.13
V-B	Ol	0.99706	2.53E-17	2.48E-12	1.84E-15	5.52E-18	1.88E-16	2.26E-10	3.70E-12	6.01E-15	1.92E-12	1349.7	1.29	0.01100	7.32	7.33	0.06
V-B	Opx	0.4776	3.43E-17	3.36E-12	6.75E-15	1.97E-17	6.61E-16	4.88E-08	7.67E-12	7.95E-15	5.32E-12	497.5	0.63	0.00007	7.34	7.35	0.06
V-B	Cpx	0.48584	4.67E-17	4.62E-12	4.41E-16	2.00E-18	3.61E-17	9.70E-08	1.12E-11	1.36E-15	1.08E-11	10483.3	0.43	0.00005	7.27	7.27	0.06
V-C	Ol	0.59294	3.71E-18	3.74E-13	2.35E-16	n.a	2.61E-17	2.38E-10	8.96E-13	3.56E-16	7.91E-13	1593.9	0.47	0.00157	7.13	7.13	0.10
V-C	Cpx	0.5587	8.55E-18	8.40E-13	5.73E-16	1.82E-18	5.87E-17	7.61E-10	2.57E-12	1.02E-15	2.27E-12	1466.6	0.37	0.00110	7.32	7.33	0.07
V-D	Ol	1.02241	2.08E-17	2.08E-12	3.76E-16	1.25E-18	3.67E-17	9.18E-10	2.76E-12	1.27E-15	2.38E-12	5534.0	0.87	0.00227	7.19	7.19	0.06
V-D	Opx	0.49922	9.46E-18	9.43E-13	2.33E-15	7.04E-18	2.39E-16	4.39E-09	2.07E-12	3.30E-15	1.09E-12	404.4	0.86	0.00021	7.21	7.22	0.08
V-D	Cpx	0.47389	2.66E-17	2.59E-12	3.02E-16	1.23E-18	2.73E-17	3.25E-08	6.01E-12	7.58E-16	5.78E-12	8576.0	0.45	0.00008	7.37	7.37	0.07
V-E	Ol	1.02916	2.51E-17	2.42E-12	1.22E-15	3.90E-18	1.19E-16	4.11E-09	8.79E-13	3.38E-16	7.79E-13	1982.0	3.11	0.00059	7.47	7.47	0.07
V-E	Opx	0.51352	1.98E-17	1.90E-12	5.12E-15	1.56E-17	5.16E-16	2.74E-08	3.03E-12	2.11E-15	2.41E-12	371.6	0.79	0.00007	7.49	7.50	0.07
V-E	Cpx	0.32954	3.96E-17	3.81E-12	3.93E-15	1.27E-17	3.81E-16	1.25E-07	7.06E-12	1.50E-15	6.62E-12	970.0	0.58	0.00003	7.48	7.48	0.07
V-F	Ol	1.01203	2.57E-17	2.44E-12	3.49E-15	1.05E-17	3.55E-16	2.81E-09	2.50E-12	2.81E-15	1.67E-12	700.6	1.46	0.00087	7.57	7.57	0.07
V-F	Opx	0.52681	1.66E-17	1.61E-12	4.91E-15	1.51E-17	4.98E-16	1.85E-08	2.37E-12	2.11E-15	1.75E-12	328.5	0.92	0.00009	7.41	7.42	0.08
V-F	Cpx	0.31734	5.58E-17	5.29E-12	2.01E-14	6.07E-17	1.99E-15	1.78E-07	1.06E-11	1.24E-14	6.98E-12	262.9	0.76	0.00003	7.58	7.59	0.07
V-G	Ol	1.00336	1.94E-17	1.81E-12	7.91E-16	2.44E-18	7.78E-17	3.91E-11	1.19E-12	1.72E-15	6.81E-13	2292.1	2.66	0.04634	7.68	7.68	0.07
V-G	Opx	0.50526	1.29E-17	1.23E-12	3.20E-15	9.62E-18	3.26E-16	4.54E-09	1.47E-12	1.69E-15	9.68E-13	384.5	1.27	0.00027	7.53	7.53	0.08
V-G	Cpx	0.32136	3.21E-17	3.15E-12	1.57E-15	5.55E-18	1.52E-16	2.24E-08	3.17E-12	9.41E-16	2.89E-12	2003.4	1.09	0.00014	7.32	7.32	0.07
V-H	Ol	1.0181	4.21E-17	4.03E-12	4.72E-15	1.47E-17	4.66E-16	4.72E-09	6.44E-12	6.29E-15	4.58E-12	853.7	0.88	0.00085	7.51	7.52	0.08
V-H	Opx	0.53853	1.95E-17	1.86E-12	4.01E-14	1.16E-16	3.94E-15	1.23E-08	1.52E-11	4.14E-14	2.93E-12	46.5	0.64	0.00015	7.47	7.52	0.08
V-H	Cpx	0.30754	3.92E-17	3.73E-12	3.52E-15	1.13E-17	3.46E-16	5.09E-08	4.74E-12	1.93E-15	4.17E-12	1062.1	0.90	0.00007	7.56	7.56	0.07
V-I	Ol	1.0437	8.62E-19	8.56E-14	1.42E-16	5.22E-19	1.39E-17	4.74E-11	2.25E-13	5.78E-16	5.37E-14	604.6	1.59	0.00181	7.24	7.25	0.13
V-I	Opx	0.5057	9.92E-19	9.93E-14	1.55E-16	6.59E-19	1.34E-17	2.26E-10	3.77E-13	8.58E-16	1.23E-13	639.0	0.8	0.00044	7.18	7.19	0.15
V-I	Cpx	0.49525	9.34E-19	1.23E-13	5.08E-14	1.46E-16	4.90E-15	n.a	1.13E-11	3.72E-14	2.97E-13	2.4	0.41	n.a	4.84	5.46	0.14
V-I r*	Ol	1.01139	9.47E-19	9.25E-14	4.09E-16	1.32E-18	4.07E-17	7.54E-10	1.75E-13	4.48E-16	4.32E-14	226.0	2.14	0.00012	7.36	7.37	0.17
V-I r*	Opx	0.50086	9.81E-19	1.15E-13	1.13E-14	3.37E-17	1.14E-15	1.31E-09	2.02E-12	5.94E-15	2.63E-13	10.1	0.44	0.00009	5.98	6.15	0.08
V-I r*	Cpx	0.57112	7.37E-19	9.81E-14	9.68E-15	2.89E-17	9.72E-16	4.07E-10	5.64E-13	1.62E-15	8.59E-14	10.1	1.14	0.00024	5.26	5.40	0.14
V-J	Ol	1.0333	3.63E-17	3.53E-12	3.77E-15	1.15E-17	3.76E-16	4.55E-09	5.30E-12	6.20E-15	3.47E-12	937.0	1.02	0.00078	7.38	7.38	0.07
V-J	Opx	0.5061	5.02E-17	4.93E-12	7.60E-15	2.36E-17	7.58E-16	1.08E-07	1.02E-11	7.88E-15	7.87E-12	649.1	0.63	0.00005	7.32	7.33	0.08
V-J	Cpx	0.30875	1.11E-16	1.07E-11	6.19E-15	2.02E-17	6.07E-16	3.23E-07	8.59E-12	2.87E-15	7.75E-12	1726.7	1.38	0.00003	7.50	7.50	0.07
V-K	Ol	1.0225	5.42E-17	5.24E-12	4.99E-15	1.58E-17	4.99E-16	2.46E-08	7.72E-12	6.93E-15	5.67E-12	1049.9	0.92	0.00021	7.45	7.45	0.08
V-K	Opx	0.52687	5.37E-17	5.13E-12	2.48E-14	7.37E-17	2.38E-15	1.05E-07	1.54E-11	2.07E-14	9.25E-12	206.6	0.55	0.00005	7.53	7.54	0.08
V-K	Cpx	0.30567	7.40E-17	7.07E-12	4.08E-14	1.21E-16	4.11E-15	1.16E-07	1.06E-11	1.40E-14	6.47E-12	173.4	1.09	0.00006	7.52	7.53	0.07
IV A	Ol	1.03046	2.52E-17	2.43E-12	4.47E-15	1.29E-17	4.34E-16	1.47E-09	2.09E-12	3.40E-15	1.08E-12	543.9	2.24	0.00165	7.45	7.45	0.08
IV A	Opx	0.49715	3.04E-17	3.02E-12	1.05E-14	3.07E-17	1.03E-15	4.49E-08	5.48E-12	6.38E-15	3.59E-12	286.9	0.84	0.00007	7.23	7.23	0.10
IV A	Cpx	0.47966	1.29E-16	1.29E-11	1.25E-14	3.82E-17	1.22E-15	2.73E-07	1.20E-11	9.65E-15	9.11E-12	1033.2	1.42	0.00005	7.21	7.21	0.06

Table 2. Continued. [a.] First estimation of CO_2 during noble gases analysis; [b.] CO_2 measured from glass line.

Sample	Phase	$^{40}Ar/^{36}Ar$	error +/- (1σ)	$^{38}Ar/^{36}Ar$	error +/- (1σ)	$^{20}Ne/^{22}Ne$	error +/- (1σ)	$^{21}Ne/^{22}Ne$	error +/- (1σ)	$(^{21}Ne/^{22}Ne)$ EX to 12.5	error +/- (2σ)	$CO_2/^3He$	$^3He/^{36}Ar$	$CO_2/^3He$	CO_2^b	$δ^{13}C$
V-A	Ol	1391.46	1.24	0.19251	0.00037	9.93	0.06	0.0297	0.00135	0.043	0.003	1.68E+06	0.0111	n.a	n.a	n.a
V-A	Opx	662.11	0.93	0.18892	0.00036	9.87	0.04	0.0288	0.00050	n.a	n.a	8.24E+07	0.0009	n.a	n.a	n.a
V-A	Cpx	3320.08	9.83	0.20543	0.00042	n.a	n.a	n.a	n.a	n.a	n.a	9.66E+08	0.0041	n.a	n.a	n.a
V-B	Ol	614.85	0.37	0.18772	0.00035	9.87	0.04	0.0296	0.00082	0.053	0.003	8.93E+06	0.0042	n.a	n.a	n.a
V-B	Opx	964.58	0.65	0.18291	0.00033	9.97	0.03	0.0298	0.00045	0.041	0.001	1.42E+09	0.0043	2.58E+09	1.17E-07	-2.30
V-B	Cpx	8231.50	13.81	0.20717	0.00043	12.18	0.26	0.0553	0.00431	n.a	n.a	2.07E+09	0.0343	n.a	n.a	n.a
V-C	Ol	2518.41	13.00	0.22231	0.00049	n.a	n.a	n.a	n.a	n.a	n.a	6.43E+07	0.0104	n.a	n.a	n.a
V-C	Cpx	2511.64	5.81	0.19747	0.00039	n.a	n.a	n.a	n.a	n.a	n.a	8.90E+07	0.0084	n.a	n.a	n.a
V-D	Ol	2177.87	2.53	0.19317	0.00037	10.57	0.16	0.0354	0.00227	n.a	n.a	4.41E+07	0.0164	n.a	n.a	n.a
V-D	Opx	626.23	0.62	0.18834	0.00035	n.a	n.a	n.a	n.a	n.a	n.a	4.64E+08	0.0029	n.a	n.a	n.a
V-D	Cpx	7926.55	24.39	0.20644	0.00043	11.03	0.39	0.0452	0.00659	n.a	n.a	1.22E+09	0.0350	1.61E+09	4.27E-08	-1.55
V-E	Ol	2598.15	11.14	0.19010	0.00036	10.37	0.07	0.0332	0.00107	0.049	0.003	1.64E+08	0.0743	n.a	n.a	n.a
V-E	Opx	1436.20	1.91	0.18305	0.00033	10.00	0.04	0.0306	0.00046	0.050	0.002	1.39E+09	0.0094	n.a	n.a	n.a
V-E	Cpx	4719.85	15.56	0.18136	0.00033	10.25	0.05	0.0338	0.00115	0.058	0.004	3.16E+09	0.0265	9.17E+08	3.63E-08	-2.66
V-F	Ol	889.63	0.69	0.18730	0.00035	9.87	0.04	0.0297	0.00064	n.a	0.003	1.09E+08	0.0091	n.a	n.a	n.a
V-F	Opx	1123.07	1.53	0.19054	0.00036	9.93	0.04	0.0307	0.00072	0.063	0.003	1.11E+09	0.0079	1.15E+09	1.91E-08	-1.34
V-F	Cpx	856.84	0.53	0.18382	0.00034	10.12	0.03	0.0306	0.00045	0.042	0.001	3.18E+09	0.0045	1.12E+09	6.22E-08	-1.66
V-G	Ol	690.44	0.68	0.18565	0.00034	10.23	0.06	0.0316	0.00117	0.045	0.003	2.02E+06	0.0112	n.a	n.a	n.a
V-G	Opx	866.39	1.50	0.18036	0.00032	9.85	0.04	0.0296	0.00062	n.a	n.a	3.52E+08	0.0076	n.a	n.a	n.a
V-G	Cpx	3371.87	14.57	0.18281	0.00033	11.06	0.11	0.0390	0.00227	n.a	n.a	6.97E+08	0.0341	n.a	n.a	n.a
V-H	Ol	1023.71	0.63	0.18503	0.00034	10.18	0.03	0.0317	0.00041	0.048	0.001	1.12E+08	0.0067	n.a	n.a	n.a
V-H	Opx	366.42	0.00	0.18303	0.00033	10.11	0.02	0.0301	0.00027	0.039	0.001	6.33E+08	0.0005	n.a	n.a	n.a
V-H	Cpx	2457.00	6.70	0.19215	0.00037	10.15	0.05	0.0326	0.00104	0.056	0.004	1.30E+09	0.0203	n.a	n.a	n.a
V-I	Ol	388.43	0.86	0.19569	0.00038	n.a	n.a	n.a	n.a	n.a	n.a	5.50E+07	0.0015	n.a	n.a	n.a
V-I	Opx	439.10	1.49	0.19092	0.00036	11.59	0.73	0.0492	0.01944	n.a	n.a	2.28E+08	0.0586	n.a	n.a	n.a
V-I	Cpx	303.48	0.16	0.18009	0.00032	10.24	0.01	0.0323	0.00025	n.a	n.a	0.00E+00	0.0000	n.a	n.a	n.a
V-I r*	Ol	391.97	1.17	0.19246	0.00038	10.39	0.16	0.0336	0.00251	n.a	n.a	7.95E+08	0.0021	n.a	n.a	n.a
V-I r*	Opx	339.74	0.26	0.18402	0.00035	9.91	0.03	0.0296	0.00029	n.a	n.a	1.33E+09	0.0002	n.a	n.a	n.a
V-I r*	Cpx	348.57	0.56	0.18113	0.00034	9.98	0.03	0.0298	0.00034	n.a	n.a	5.52E+08	0.0005	n.a	n.a	n.a
V-J	Ol	854.91	0.48	0.18694	0.00035	10.05	0.03	0.0307	0.00053	0.047	0.002	1.25E+08	0.0058	n.a	n.a	n.a
V-J	Opx	1294.25	0.87	0.18590	0.00035	10.08	0.03	0.0313	0.00056	0.051	0.002	2.15E+09	0.0064	3.82E+09	1.92E-07	-2.13
V-J	Cpx	2993.26	5.58	0.19053	0.00036	10.24	0.03	0.0335	0.00071	0.056	0.002	2.90E+09	0.0388	2.10E+09	2.34E-07	-1.30
V-K	Ol	1114.13	0.00	0.18660	0.00035	10.07	0.03	0.0319	0.00049	0.058	0.002	4.54E+08	0.0078	3.82E+08	2.07E-08	-1.10
V-K	Opx	741.96	0.00	0.18186	0.00033	10.32	0.02	0.0316	0.00031	0.042	0.001	1.95E+09	0.0026	1.88E+09	1.01E-07	-2.08
V-K	Cpx	756.34	0.50	0.18796	0.00035	9.92	0.02	0.0296	0.00029	0.041	0.001	1.57E+09	0.0053	3.38E+08	2.50E-08	-0.97
IV A	Ol	614.05	0.43	0.18144	0.00034	10.14	0.04	0.0303	0.00050	0.039	0.001	5.84E+07	0.0074	n.a	n.a	n.a
IV A	Opx	858.77	0.49	0.18068	0.00033	10.10	0.03	0.0298	0.00045	n.a	n.a	1.48E+09	0.0048	2.22E+09	6.76E-08	-2.86
IV A	Cpx	1238.93	24.70	0.18113	0.00034	10.25	0.03	0.0314	0.00047	0.043	0.001	2.11E+09	0.0134	1.18E+09	1.52E-07	-1.25

Table 3. Expected noble gas isotopic ratios for the Mexican lithospheric mantle. $^{20}Ne/^{22}Ne_{air}$ $^{40}Ar/^{36}Ar_{air}$ ratios after Steiger and Jäger (1977) and Ozima and Podosek (2002).

R/Ra	$^4He/^{40}Ar*$	$^4He/^{20}Ne$	$^{36}Ar/^{22}Ne$	$^{40}Ar/^{36}Ar$	$^{20}Ne/^{22}Ne$	$^{20}Ne/^{22}Ne$ air	$^{40}Ar/^{36}Ar$ air
7.39 ± 0.14	0.14 - 3.11	11000	4.21 - 93.5	10500	12.5	9.8	295.5

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Table 4. ^4He production rates, ^3He fluxes, helium residence time and CO_2 fluxes calculated for the lithospheric mantle beneath central Mexico. P*, F and Rt values were calculated based on mathematical formulations proposed y Gautheron and Moreira (2002). P*: ^4He production, F: ^3He flux, Rt: Helium residence time.

U (ppm)	P* (ccSTP/g)	P* (mol/yr)	F (ccSTP/year)	F (mol/yr)	Rt (Ma)	CO_2 flux (mol/yr)	CO_2 flux (g/yr)
0.01	7.69E+06	3.43E+02	5.99E+02	0.027	61.17	3.93E+07	1.73E+09
0.012	9.23E+06	4.12E+02	7.19E+02	0.032	50.97	4.72E+07	2.08E+09
0.014	1.08E+07	4.81E+02	8.38E+02	0.037	43.69	5.50E+07	2.42E+09
0.016	1.23E+07	5.49E+02	9.58E+02	0.043	38.23	6.29E+07	2.77E+09
0.018	1.38E+07	6.18E+02	1.08E+03	0.048	33.98	7.07E+07	3.11E+09
0.02	1.54E+07	6.87E+02	1.20E+03	0.053	30.58	7.86E+07	3.46E+09
0.022	1.69E+07	7.55E+02	1.32E+03	0.059	27.80	8.65E+07	3.80E+09
0.024	1.85E+07	8.24E+02	1.44E+03	0.064	25.49	9.43E+07	4.15E+09
0.026	2.00E+07	8.93E+02	1.56E+03	0.070	23.53	1.02E+08	4.50E+09
0.028	2.15E+07	9.62E+02	1.68E+03	0.075	21.84	1.10E+08	4.84E+09
0.03	2.31E+07	1.03E+03	1.80E+03	0.080	20.39	1.18E+08	5.19E+09

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1   **SUPPLEMENTARY MATERIAL**

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3   **THE COMPOSITION OF FLUIDS STORED IN THE CENTRAL MEXICAN LITHOSPHERIC**
4   **MANTLE: INFERENCES FROM NOBLE GASES AND CO₂ IN MANTLE XENOLITHS**

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19   **1. Premise**

20   We discuss here the possible role played by secondary processes that may have concurred to determine the
21   noble gas isotope composition of the fluid inclusions. Our attempt is to show that these secondary processes
22   have overall played little role (with a few exceptions noted), and that therefore the fluid inclusions are well
23   representative of the source mantle. The few samples that have to some extent suffered from secondary
24   processes are filtered out from further discussion (see main text) on volatile origin and processing in the mantle
25   source.

26   **2. Exposure to cosmic rays**

27   Several studies have shown that rocks exposed to cosmic rays (i.e. after eruption) favor the accumulation of
28   ^{3}He in the crystal lattices shifting the original ^{3}He/^{4}He ratios to higher values (Kurz, 1986; Lal, 1987; Dunai
29   and Baur, 1995; Dunai, 2010; Broadley et al., 2016; Nesterenok and Yakubovich, 2016; Correale et al., 2019).
30   According to e.g. Dunai and Baur (1995) and Correale et al. (2019 and references therein), crystals with low
31   He concentrations are more prone to changes due to the diffusion of ^{3}He from lattices into the fluid inclusions.
32   However, in the case of the JH mantle xenoliths, the aliquots with the lowest He contents (^{3}He $<10^{-17}$ and ^{4}He
33      $< 10^{-12}$; Figure 9A, 9B) generally show an opposite effect, that is a decrease in ^{3}He/^{4}He compared to the samples
34   with the highest helium concentrations that we interpreted as the result of diffusive fractionation. The eruption
35   time of JH xenoliths (311 ± 19 ka; Saucedo et al., 2017) limits the exposure time to cosmic rays. Finally, the
36   single step crushing method prevents the contribution of secondary He accumulated in the crystal lattice
37   (cosmogenic ^{3}He and radiogenic ^{4}He), as evidenced by other authors (Kurz, 1986; Graham, 2002; Rizzo et al.,
38   2018; Correale et al., 2019; Faccini et al., 2020). We therefore conclude that the effect of cosmogenic ^{3}He in
39   our samples is negligible.

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3. Diffusive Fractionation

As shown in Figure 6, the lowest noble gas concentrations (especially helium) were measured in V-I crystals and, to a minor extent, in V-A and V-C (^{4}He<10^{-12} mol/g). Some CO_2 depletion is also evident in sample V-I (Figure 6C). When plotting ^{3}He, ^{4}He, ^{40}Ar*, and ^{4}He/^{40}Ar* vs. Rc/Ra (Figures 8 and 10B-10D), we find that in sample V-I the He and Ar depletion is also accompanied by ^{3}He/^{4}He <6.15 Ra, which are sensibly lower than the dataset average (7.39 ± 0.14 Ra). In samples V-A and V-C, the ^{3}He/^{4}He decrease is less important. It is worth noting that the lower Rc/Ra values mostly correspond to pyroxenes (Opx and Cpx) from the same nodule, while Ol crystals are less or not modified. Indeed, Ol from V-I show ^{3}He/^{4}He values (7.25 – 7.37 Ra) that are within the above reported average of the dataset.

Following Burnard et al. (1998), Burnard (2004), and Yamamoto et al. (2009), this data variability can be interpreted as due to preferential loss of He (relative to Ar and CO_2) due to diffusive fractionation. In fact, in case of radiogenic ^{4}He in-growth or addition to fluid inclusions, an increase of ^{4}He concentration with decreasing ^{3}He/^{4}He values should be expected, without any relative decrease of ^{3}He, ^{40}Ar*, and ^{4}He/^{40}Ar*. We highlight that He diffusion into the fast flowing melt-filled dissolution channels cutting the mantle is commonly invoked during partial melting (Burnard, 2004; Yamamoto et al., 2009; Faccini et al., 2020) and/or metasomatism of solid mantle that prevalently affects pyroxene crystals. Previous studies suggest that the ^{4}He diffusion coefficient is considerably higher than that of ^{40}Ar (D_{4He}/D_{40Ar} = 3.16 in solid mantle; Burnard, 2004; Yamamoto et al., 2009); this is fundamentally based on the assumption that the difference in the atomic masses of the two elements are the key controls of their different diffusion coefficients. Likewise, the difference in mass between ^{3}He and ^{4}He implies important differences in their diffusivities (D_{3He}/D_{4He} = 1.15; Trull and Kurz, 1993; Burnard, 2004; Yamamoto et al., 2009). Hence, in case of diffusive loss of He, a decrease in ^{3}He/^{4}He and ^{4}He/^{40}Ar* is expected, as observed in V-A and V-I pyroxenes. Because the clearest evidence of diffusive fractionation is observed in pyroxenes, we exclude V-C because Ol from this sample show ^{3}He/^{4}He values (7.13 Ra) comparable to Opx (7.33 Ra) from the same nodule (although Ol have lower He concentrations). In any case, in order to properly interpret the origin of the He in the following sections of the discussion, pyroxenes from V-I and V-A nodules will not be discussed further.

To support the hypothesis of a diffusive fractionation, in Figures 8 and 10B-C-D we model this process based on the approach proposed by Burnard et al. (1998), Burnard (2004), Yamamoto et al. (2009), and already applied in Boudoire et al. (2020) and Faccini et al. (2020). We consider a starting mantle composition of ^{3}He = 1.56 x 10^{-17} mol/g, ^{4}He = 1.5 x 10^{-12} mol/g, and ^{40}Ar*= 6 x 10^{-13} mol/g, which corresponds to the lowest concentrations of these species in nodules not evidently modified by diffusion. We additionally use a starting ^{4}He/^{40}Ar* = 2.5 (the average mantle production ratio), and a ^{3}He/^{4}He = 7.5 Ra, which is within the Rc/Ra variability of the dataset. According to our modeling, diffusive fractionation is able to justify the data variability observed in pyroxene from V-A and V-I samples, which will not be discussed anymore.

4. Effects on fluid inclusions by mantle melting and/or fluid-melt partitioning

It has been previously inferred that the noble gas signature of mantle xenoliths can depend to some extent on the melting history of the mantle source, and that the ^{4}He/^{40}Ar* ratio is a useful tracer to recognize relative variations of partial melting degree in mantle xenoliths (Graham, 2002; Burnard, 2004; Yamamoto et al., 2009; Correale et al., 2012, 2016, 2019; Rizzo et al., 2018; Faccini et al., 2020). The utility of ^{4}He/^{40}Ar* stands on the different mineral/melt partition coefficients of the two elements (e.g., olivine, DHe =0.00017 and DAr =0.0011; Herber et al., 2007). In detail, it is suggested that, even considering the wide uncertainties in the derived partition coefficients (Heber et al., 2007), He is more incompatible than Ar, and can thus escape the mantle more effectively during partial melting, ultimately causing a ^{4}He/^{40}Ar* decrease in the mantle residuum

85 (Burnard, 2004; Heber et al., 2007; Yamamoto et al., 2009). This possible mantle partial melting trend is
86 indicated in Figure 8.

87 In the JH nodules, the majority of Ol crystals have $^4He/^{40}Ar^*$ values within the typical production ratio of a
88 fertile mantle ($^4He/^{40}Ar^* = 1\text{-}5$; Marty, 2012), while Opx and Cpx crystals exhibit slightly lower $^4He/^{40}Ar^*$
89 ratios, from 0.4 to 1.4. In general, the $^4He/^{40}Ar^*$ population of our samples could imply that mantle melting
90 may have to some extent impacted the Opx and Cpx noble gas signature, but not that of Ol, ultimately
91 suggesting a low degree of partial melting. However, any detailed consideration on this process is prevented
92 by the lack of mineral chemistry in our samples to be compared to the composition of fluid inclusions. In
93 addition, we stress that the degrees of partial melting are not well constrained on petrological basis for the JH
94 spinel lherzolites, as a wide range (7-22%) has been proposed in previous work (Liang and Elthon, 1990).

95 The mentioned behavior of $^4He/^{40}Ar^*$ in relation to partial melting is valid if fluid inclusions trapped in mantle
96 minerals represent a residuum rather than inclusions degassed from melt(s) percolating and metasomatizing
97 the local mantle. Nevertheless, our suite of samples exhibits textural evidence of interstitial glass veins bearing
98 dendritic trails of secondary melt and fluid inclusions related to pervasive mantle metasomatism driven by
99 carbonate-rich silicate melt. This suggests that the composition of fluid inclusions (e.g., $^4He/^{40}Ar^*$) could also,
100 or alternatively (to mantle melting), be influenced by fluid-melt partitioning from the metasomatizing melt. In
101 fact, assuming a mantle with $^4He/^{40}Ar^*=1$, and considering the olivine/melt partition coefficient proposed by
102 Heber et al. (2007), the first melt should have $^4He/^{40}Ar^*=6.5$ while the first gas exsolved from the melt should
103 have $^4He/^{40}Ar^*=0.92$ (assuming a solubility ratio $S_{He}/S_{Ar}\sim7$; Lux, 1987). This implies, that a metasomatizing
104 melt poorly or slightly degassed would equally fit most of the dataset. According to the petrographic evidence,
105 metasomatic melt degassing seems the most reasonable process to explain most of our fluid inclusions
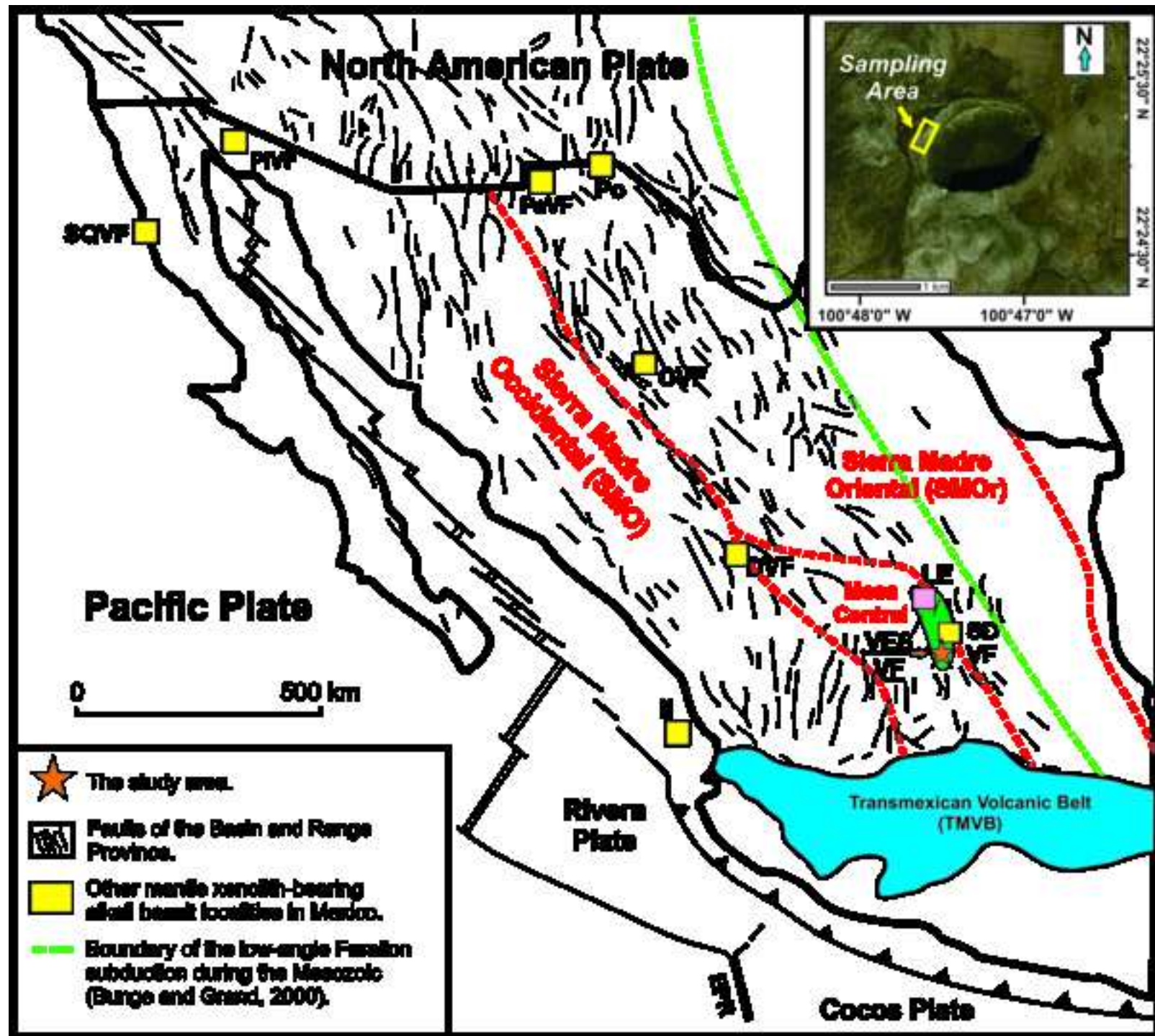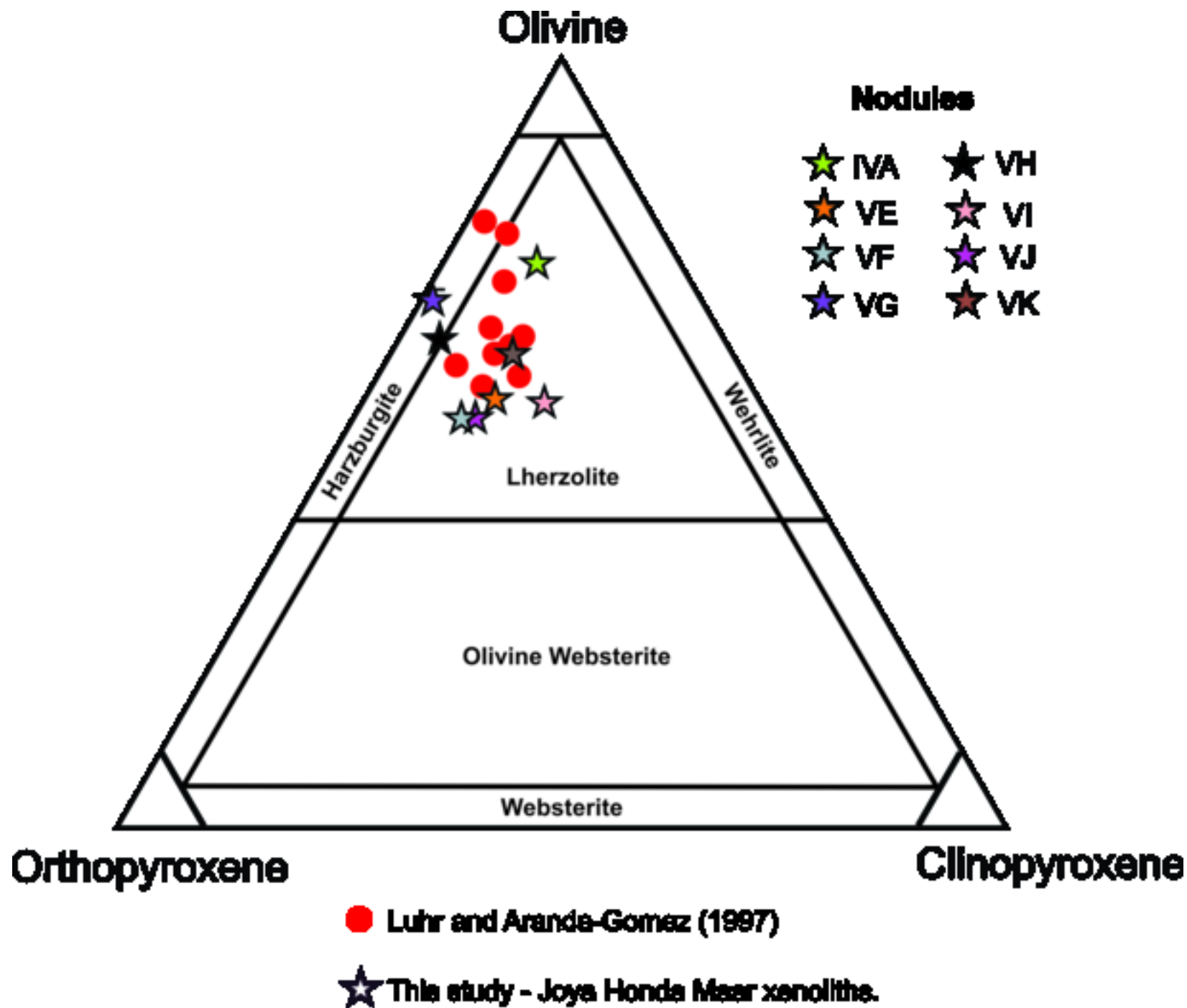106 compositional variability.
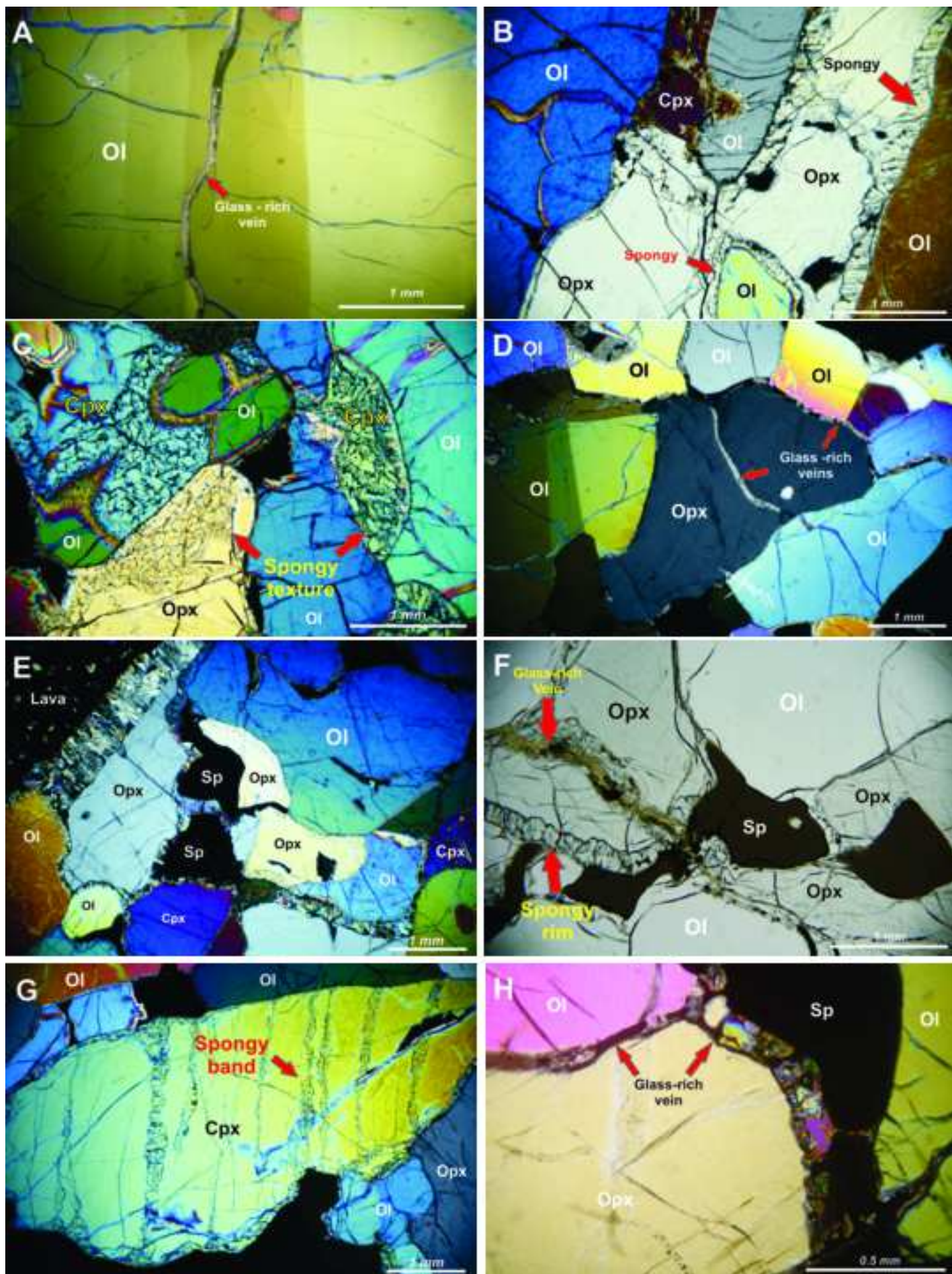
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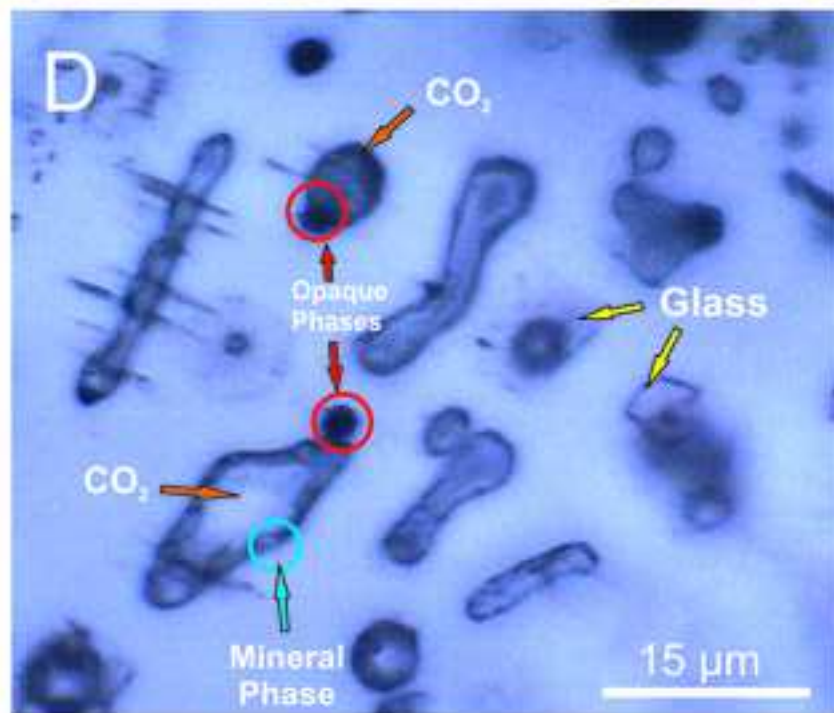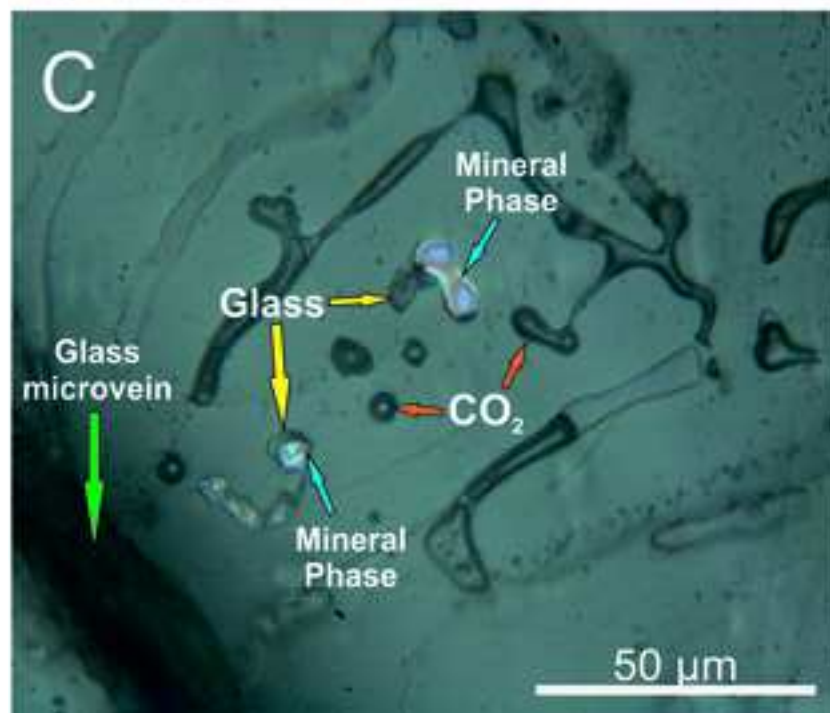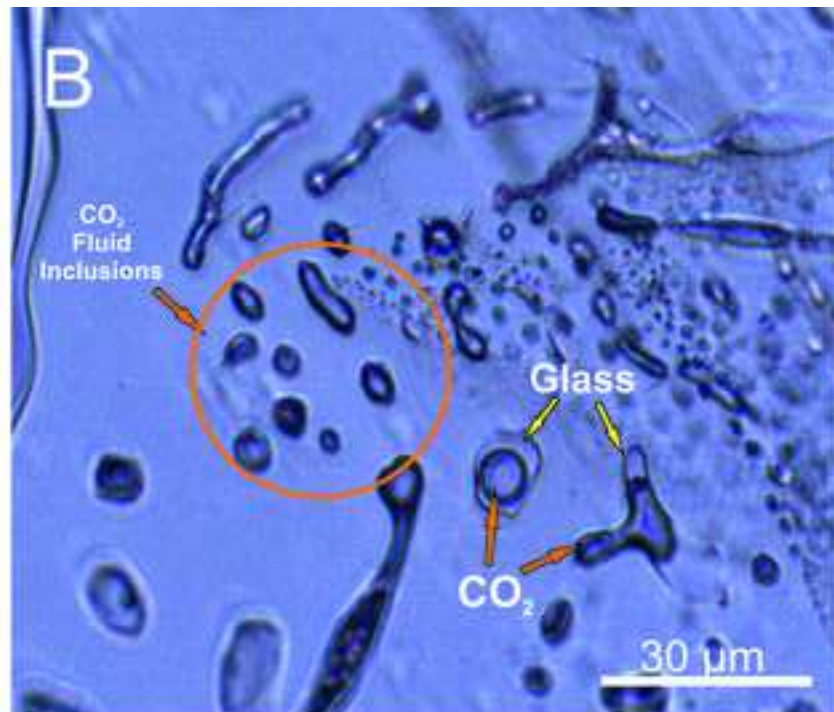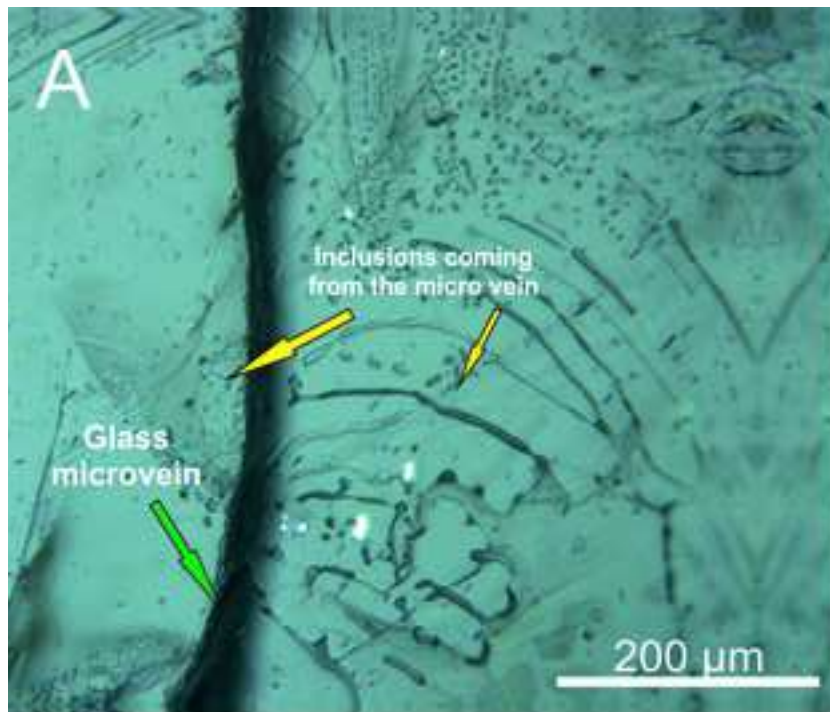130   Geology 524, 104–118. https://doi.org/10.1016/j.chemgeo.2019.06.020

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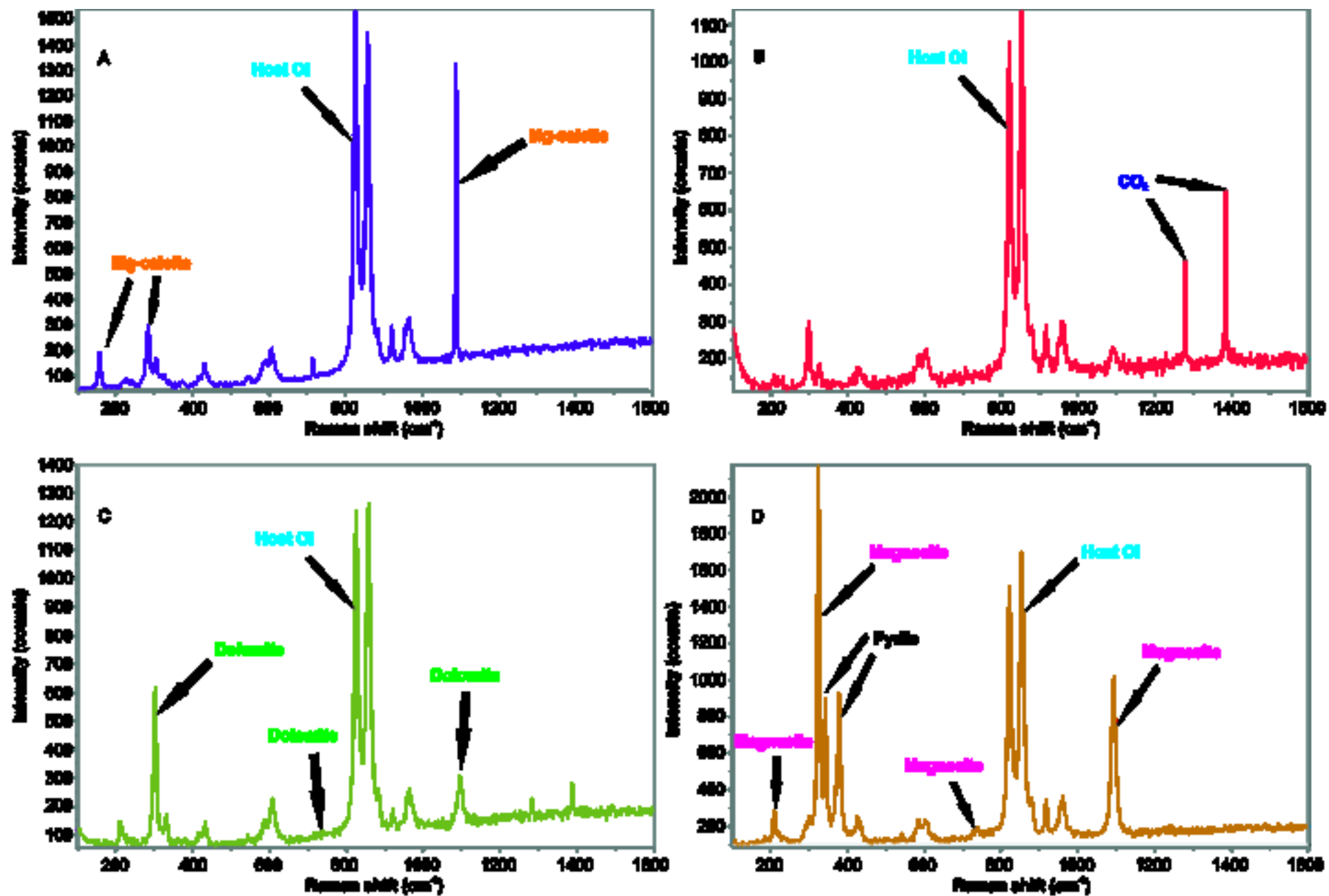176   Bergonzoni, G., 2018. Geochemistry of Noble Gases and CO2 in Fluid Inclusions From Lithospheric

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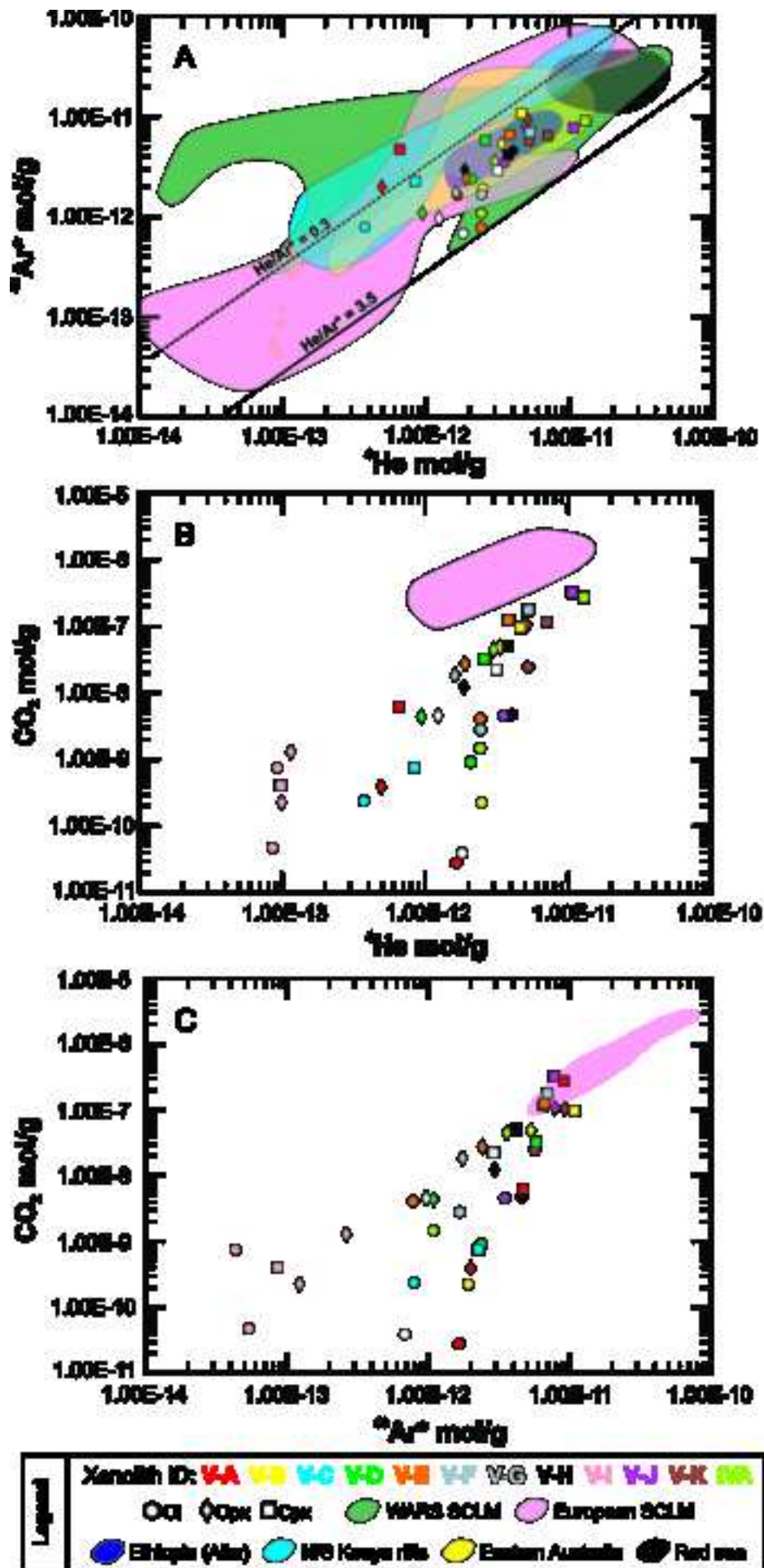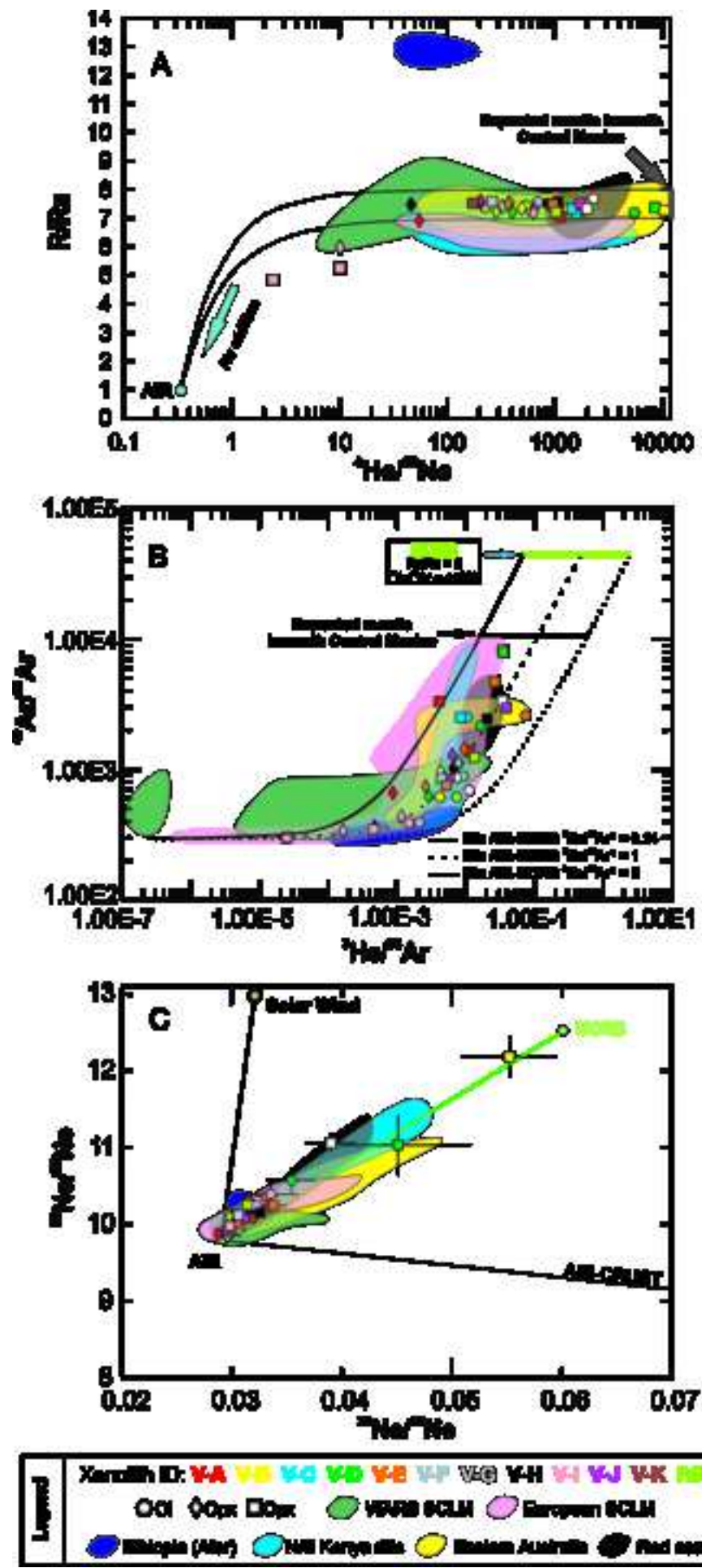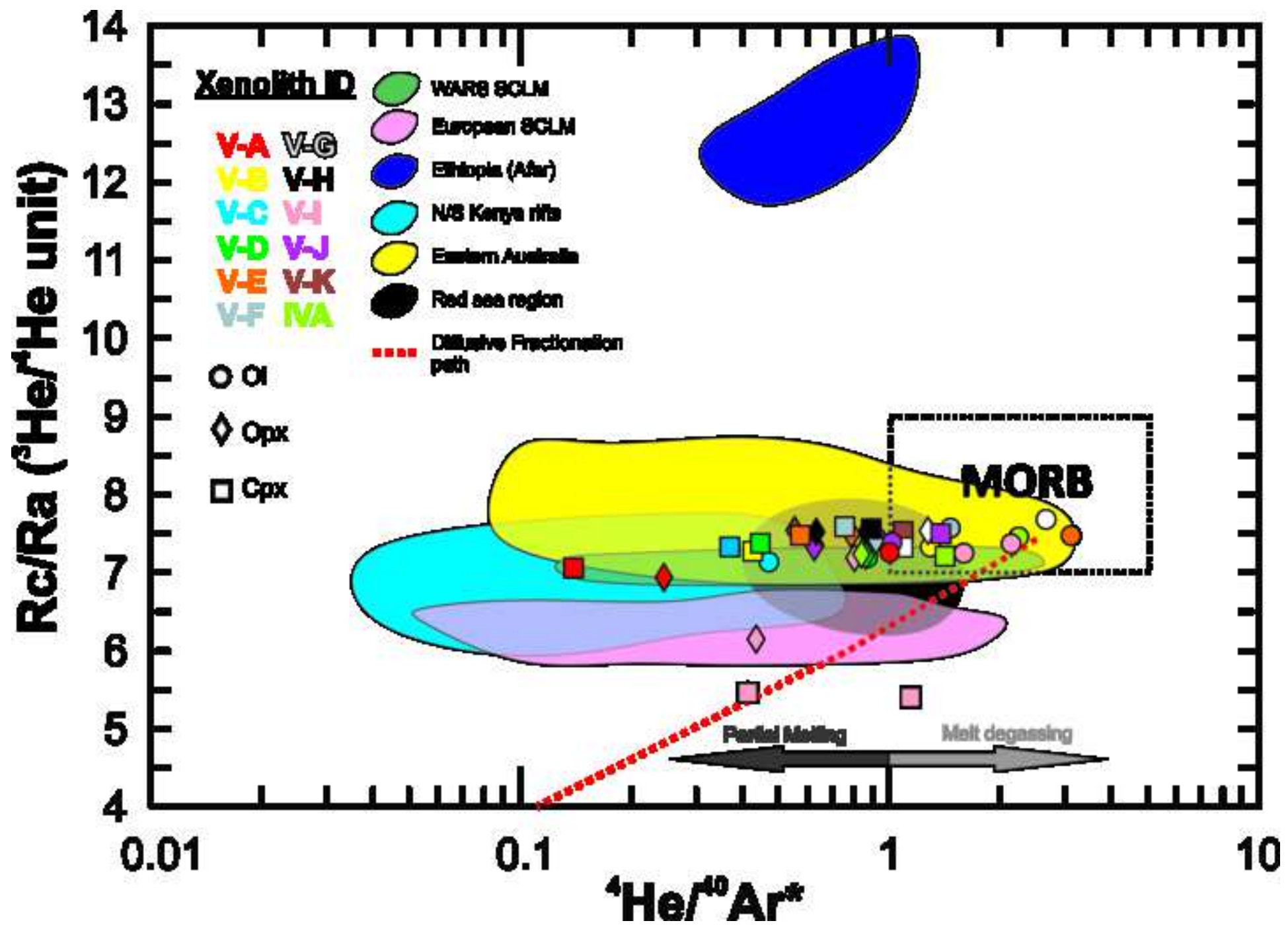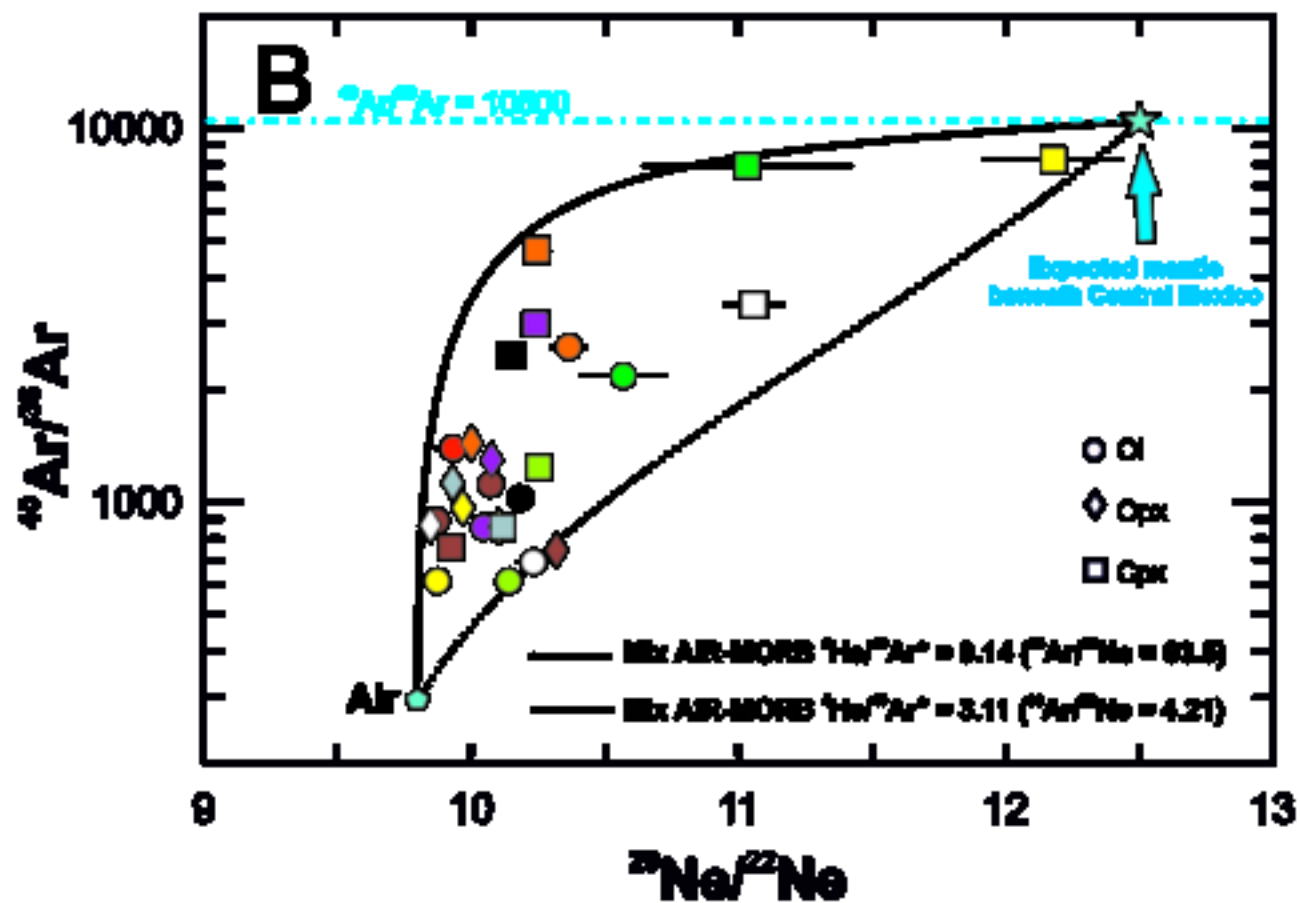193

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

Figure 2   Click here to access/download;Figure;Figure 2.tif

Olivine

Orthopyroxene

Clinopyroxene

Harzburgite

Lherzolite

Wehrlite

Olivine Websterite

Websterite

Nodules

★ IVA   ★ VH
★ VE   ★ VI
★ VF   ★ VJ
★ VG   ★ VK

● Luhr and Arande-Gomez (1997)

☆ This study – Joya Honda Maar xenoliths.

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

Figure 4

Figure 5

Figure 6

Figure 7   Click here to access/download;Figure;Figure 7.tif
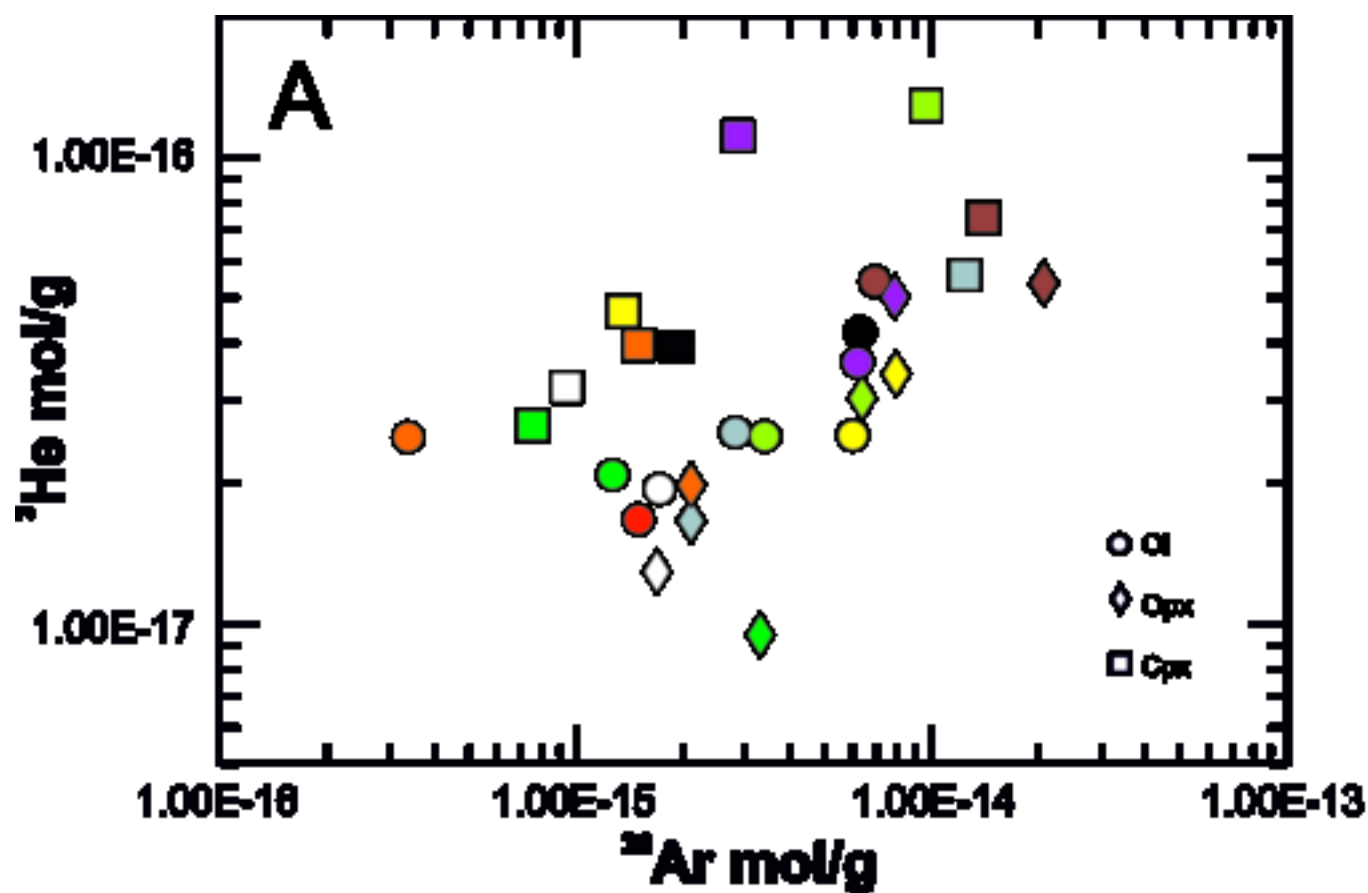
Figure 8   Click here to access/download;Figure;Figure 8.tif ⬇

Xenolith ID: V-A V-B V-D V-E V-F V-G V-H V-I V-J V-K IVA

Figure 10

Figure 10

Figure 11

Figure 12

Figure 12
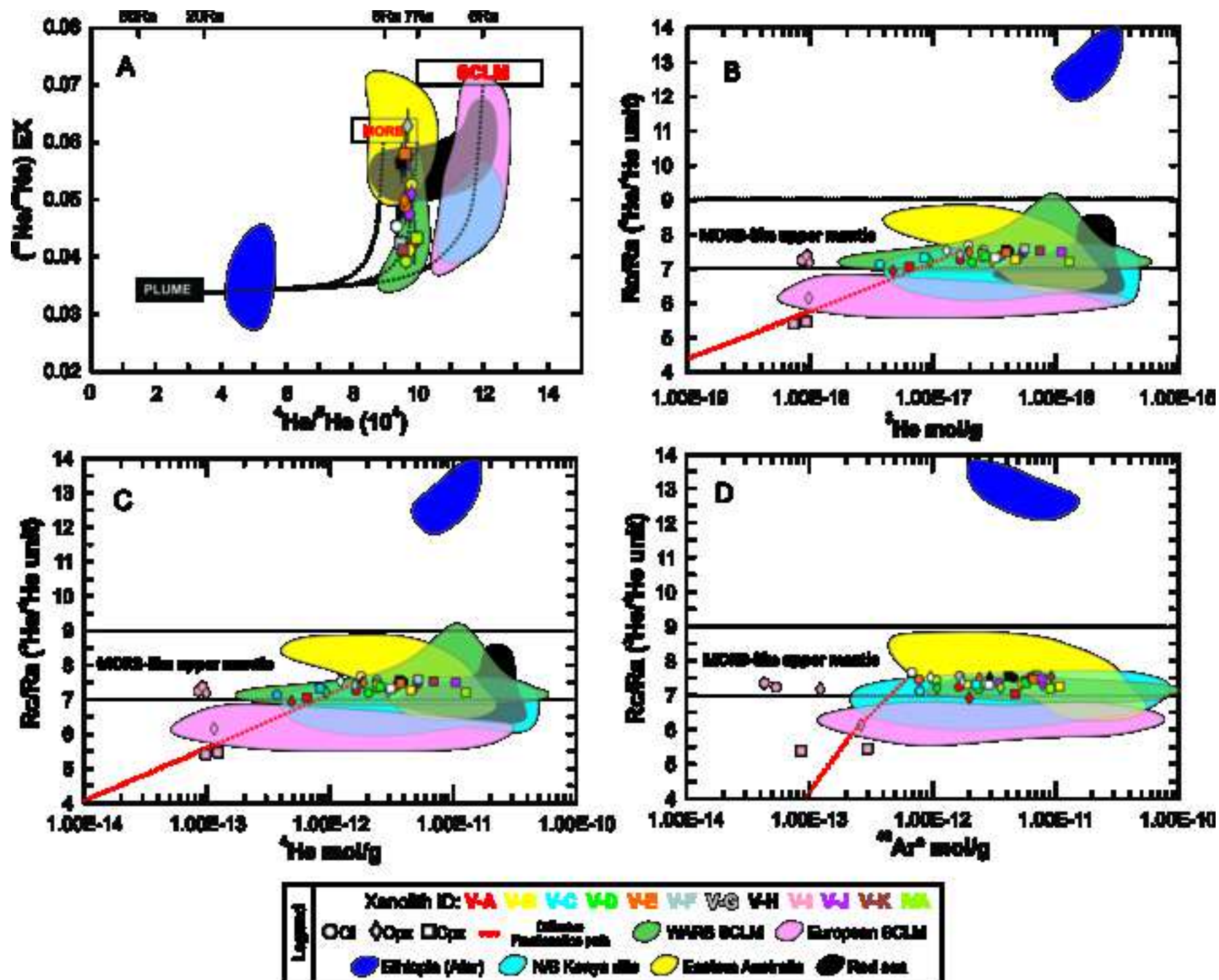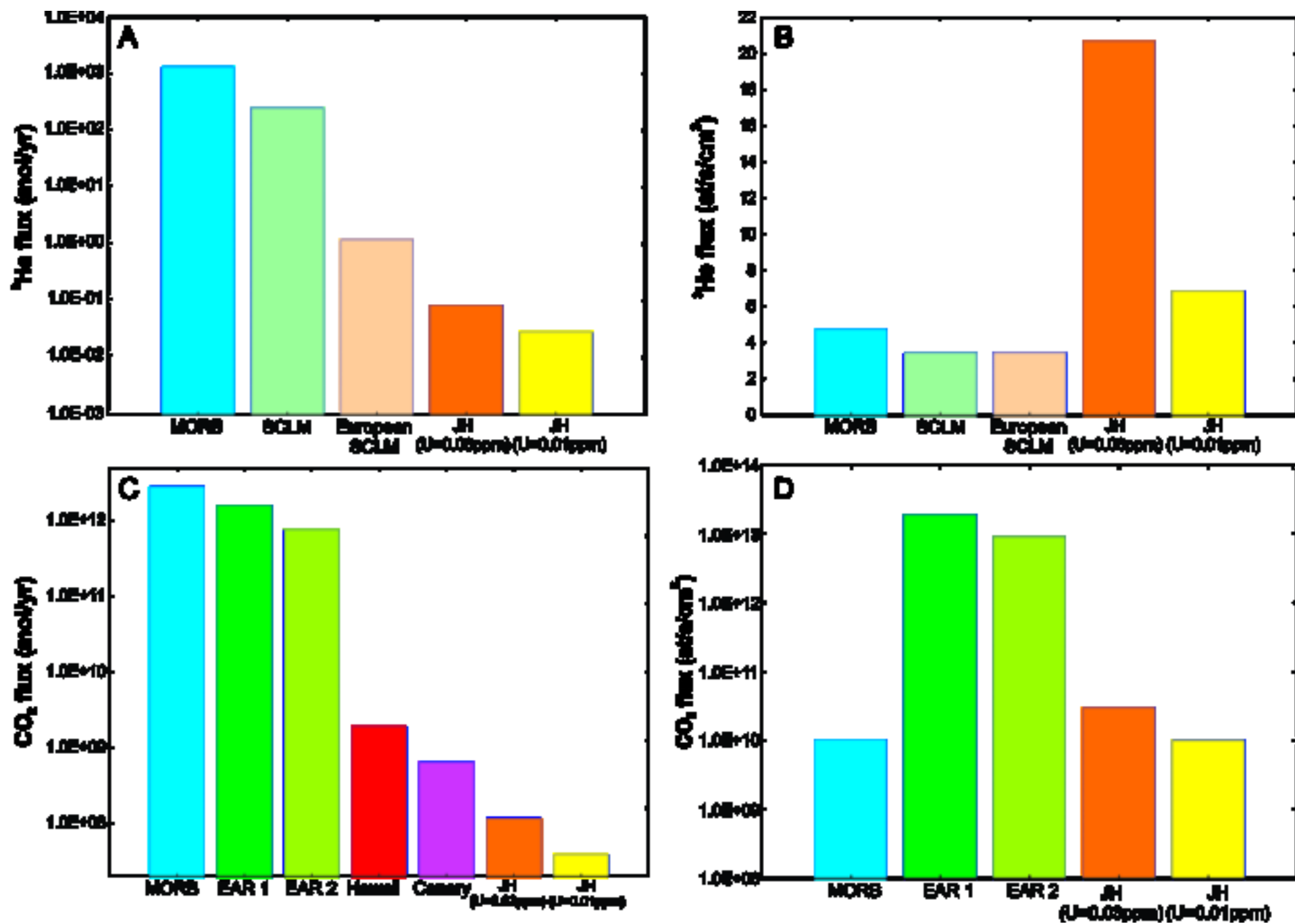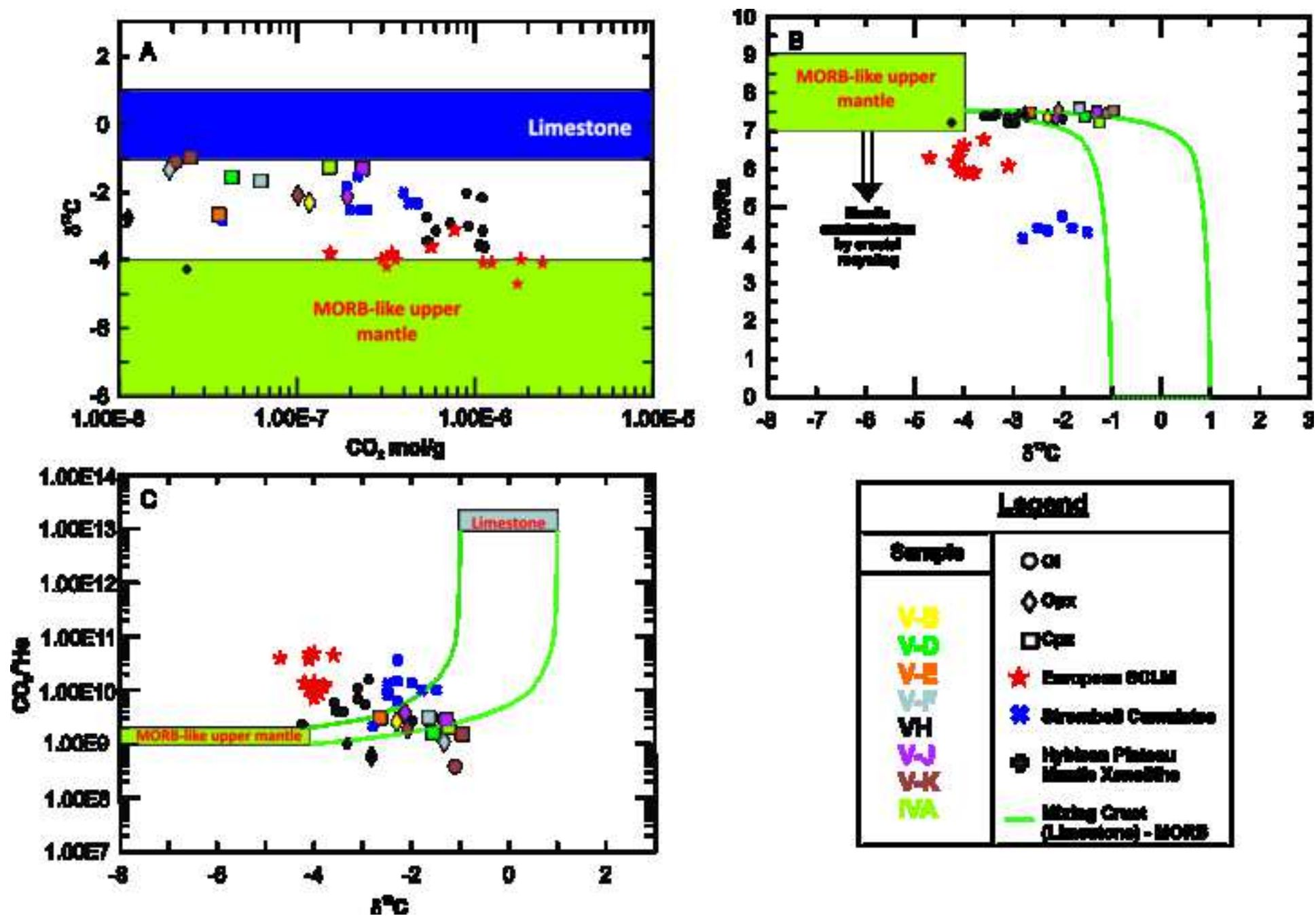
Declaration of interests

☒ 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: