

# Helium isotope variations in mineral separates from Costa Rica and Nicaragua: Assessing crustal contributions, timescale variations and diffusion-related mechanisms

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## Abstract

We report new He abundance and isotope measurements of phenocryst phases in volcanic tephra and lavas from the Nicaragua-Costa Rica section of the Central American arc, where significant variations in crustal thickness have been inferred. Helium isotope values range from  $4.6R_A$  to  $7.5R_A$ , with no evidence for crustal thickness influencing measured  $^3\text{He}/^4\text{He}$  ratios. A comparison of He abundances and isotopes measured in mafic phenocrysts from tephra vs. lavas from two separate eruptions at Cerro Negro show that both sampling media preserve phenocrysts with high  $^3\text{He}/^4\text{He}$  values.  $^3\text{He}/^4\text{He}$  ratios measured in phenocryst phases show good agreement with He isotope values of geothermal fluids from the same volcanoes. However, we note that the pyroxenes tend to have lower  $^3\text{He}/^4\text{He}$  ratios ( $4.6\text{--}7.0R_A$ ) than the olivines ( $^3\text{He}/^4\text{He}=6.1\text{--}7.5R_A$ ) over a range of concentration values and are consistently lower in cogenetic phenocryst pairs at all locations sampled. In order to assess how this difference arises, we explore two alternative mechanisms: (1) diffusion-related isotopic fractionation, and (2) late-stage radiogenic  $^4\text{He}$  additions, preferentially influencing pyroxene grains. In the first case, we reject diffusion-related fractionation of He isotopes since lower  $^3\text{He}/^4\text{He}$  ratios are not accompanied by a decrease in He concentration values. The second scenario is evaluated on the basis of Mg numbers in cogenetic phenocryst pairs and by petrological modeling of the crystallization sequence. Mg numbers and modeling results at low pressure conditions ( $=1$  kbar) suggest that olivine crystallization preceded pyroxene crystallization. However, since lavas do not show evidence for extensive crustal contamination, we suggest that the best explanation for the lower  $^3\text{He}/^4\text{He}$  ratios in pyroxenes is related to the closure temperatures of the phenocryst phases. Given its lower closure temperatures and higher He diffusion rates, we suggest that pyroxenes would be more susceptible to late-stage He exchange with a low  $^3\text{He}/^4\text{He}$  source during ascent, presumably the surrounding crust.

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## 1. Introduction

He isotopes have proven to be a powerful means by which to assess crustal contributions to magmatic systems in arc-related settings (Gasparon et al., 1994; Graham et al., 1993; Hilton et al., 1993, 1992, 2000; Patterson et al., 1997; Poreda and Craig, 1989; van Soest et al., 2002). Crustal He is characterized by a  $^3\text{He}/^4\text{He}$  ratio which is significantly lower ( $\sim 0.01\text{--}0.05R_A$ , where  $R_A$  is the  $^3\text{He}/^4\text{He}$  ratio of air =  $1.4 \times 10^{-6}$ ; Ozima and Podosek, 1983) than upper mantle values (as sampled by MORB =  $8 \pm 1R_A$ ; Farley and Neroda, 1998). As magma ascends it will suffer He loss through degassing and thus with lowered intrinsic He concentrations even minor amounts of crustal interaction can be easily recognized.

To evaluate the He isotope systematics of arc-related magmatic systems, a common experimental approach is to target mafic minerals, such as olivine and clinopyroxene, which can trap mantle volatiles as fluid or melt inclusions during crystallization within a magma chamber. Although both minerals have been shown to successfully record mantle He isotope signatures (Gasparon et al., 1994; Hilton et al., 1999, 2000; Patterson et al., 1997; van Soest et al., 2002), previous studies have noted the tendency of pyroxenes to preserve lower  $^3\text{He}/^4\text{He}$  ratios than coexisting olivines (Hilton et al., 1995; Marty et al., 1994). This observation has been explained by continued diffusive exchange of He between the clinopyroxene crystal lattice and magma at temperatures where exchange involving olivine is too slow to have any discernible effect (Hilton et al., 1995; Marty et al., 1994).

In this study, we focus on the Nicaragua-Costa Rica section of the Central American arc (Fig. 1) to examine details of the crustal contamination process in mafic phenocrysts from volcanic tephra and lavas. We investigate how small differences in  $^3\text{He}/^4\text{He}$  between olivines and pyroxenes can arise, assessing the relative merits of isotopic fractionation by diffusion and contamination processes. We explore a new approach by using the petrologic modeling program, MELTS (Ghiorso and Sack, 1995), to calculate the crystallization temperatures of each phase under defined conditions, thereby assessing whether pyroxenes are more prone to late-stage radiogenic  $^4\text{He}$  additions. Our unique data set also allows us to address several related questions such as: (1) Do minerals preserved in volcanic samples with different cooling histories (lava vs. tephra) record differences in He isotope characteristics?; (2) Do mineral phases show better preservation of magmatic volatile signatures than geothermal fluids?; and (3) Do

we observe temporal variations in  $^3\text{He}/^4\text{He}$  at a given volcanic centre?

## 2. Geologic background and setting

Volcanoes in Costa Rica and Nicaragua form the southern portion of the Central American volcanic Arc and result from subduction of the Cocos Plate beneath the Caribbean Plate (Fig. 1). The crustal structure of Costa Rica is significantly different from Nicaragua. In Costa Rica most Tertiary and Quaternary volcanics are superimposed, resulting in a thick crust of intrusive and extrusive arc magmas accumulated over time — up to 45 km (Carr et al., 2003). In contrast, Nicaraguan volcanism shows progressive southwestward migration of arc front volcanoes (Ehrenborg, 1996). This geographical configuration coupled with an overall smaller volume of magmatism (Carr et al., 2003) results in relatively thin crust ( $\sim 34$  km). In addition, several volcanoes in Nicaragua are associated with N–S striking extensional structures which cross the volcanic front and it has been speculated that these features promote rapid transit of magmas through the crust (Carr et al., 2003). Therefore, we might anticipate lower degrees of crustal contamination in Nicaragua than along other segments of the arc.

Prior studies (Carr, 1984; Plank and Langmuir, 1988) have noted a correlation between crustal thickness and the major element chemistry of erupted lavas. However, subsequent work investigating the relationships between trace elements and physical subduction parameters (Carr et al., 1990; Patino et al., 2000; Walker et al., 2001) concluded that along-arc geochemical characteristics were most strongly influenced by the dip of the subducting plate, rather than crustal thickness. In Nicaragua, the steep dip of the incoming plate results in effective fluid release, leading to a higher degree of melting and more efficient recycling of slab components than at other localities along the arc. Patino et al. (2000) determined that geochemical variability along the arc was best explained by regional differences in the intensity of the slab signature and local differences in the composition of the slab input. Furthermore, it was argued that none of the lavas erupted throughout this region showed geochemical or isotopic evidence of crustal assimilation (Carr et al., 2003; Patino et al., 2000). Likewise, He isotope studies of geothermal fluids at volcanic centres in Costa Rica and Nicaragua (Shaw et al., 2003; Snyder et al., 2001) indicate minimal crustal volatiles in the volcanic output along the arc.

The major volcanic centres included in this study are shown in Fig. 1. Apart from Arenal volcano, all of the Costa Rican volcanoes that we sampled are



Fig. 1. Regional map of Nicaragua and Costa Rica showing sample localities.

stratovolcanoes. The volume of material produced from individual volcanic centres in Costa Rica is significantly higher (up to 326 km<sup>3</sup> at Barva and 227 km<sup>3</sup> at Irazu) as compared to volumes at Nicaraguan volcanoes — 3 km<sup>3</sup> at both Cerro Negro and Nejapa (Carr et al., 2003). The Nejapa volcanic region in Nicaragua consists of maars and cones erupted along an N–S trending lineament resulting from an extensional offset of the volcanic front (Siebert and Simkin, 2002). The most recent eruption from this region occurred at Cerro Motastepe less than 2500 years ago (Siebert and Simkin, 2002). Of the volcanic regions sampled, Arenal and Cerro Negro have been the most active in recent decades. Cerro Negro in northwestern Nicaragua (see Fig. 1) has undergone at least 23 eruptive phases over its 150-year history (McKnight and Williams, 1997), with the most recent eruption in 1999. Given its high level of activity, Cerro

Negro is an ideal site to investigate temporal variations in <sup>3</sup>He/<sup>4</sup>He. In addition, as the volcano has produced both lava and tephra deposits in its recent eruption history, we are able to compare which of these two types of volcanic sample better preserves magmatic volatile signatures.

### 3. Analytical methods

Lavas and ash samples were collected from various localities throughout Nicaragua and Costa Rica — see Fig. 1. Rock samples were crushed and sieved into appropriate size fractions, then handpicked for olivine and pyroxene crystals using a binocular microscope. Before loading samples into the crushing device, they were ultrasonically cleaned using an acetone/methanol mixture. Approximately 1 g of olivine or pyroxene phenocrysts (see Table 1) was loaded into the on-line

Table 1

Helium, Mg number and calculated crystallization temperatures for mafic phenocrysts from Nicaragua and Costa Rica

Volcanic centre	Sample ID <sup>a</sup>	Latitude (N)	Longitude (W)	Sample details	Phase	Weight (g)	<sup>3</sup> He/ <sup>4</sup> He ( $R_M/R_A$ ) <sup>b</sup>	$X^b$	<sup>3</sup> He/ <sup>4</sup> He ( $R_C/R_A$ ) <sup>b</sup>	[He] <sub>C</sub> (10 <sup>-9</sup> cm <sup>3</sup> STP/g) <sup>b</sup>	Mg number <sup>c</sup>	MELTS $T$ (°C)	MELTS $T$ (°C), 1 wt.% H <sub>2</sub> O	MELTS $T$ (°C), $P=5$ kbar
<i>Nicaragua</i>														
Cerro Negro	CN-92-1	12°29.581'	86°43.655'	1992 ash	ol	1.022	5.87	22.0	6.10±0.46	1.06±0.02	79.6±3.3	1214	1183	1180
					px	1.058	5.32	15.1	5.62±0.24	2.24±0.06	78.7±2.5	1194	1147	1258
	CN-95-1	12°30.407'	86°42.470'	1995 ash	ol	1.090	6.88	68.0	6.97±0.28	1.94±0.07	77.8±2.8	1201	1158	1154
					px	1.014	5.40	11.5	5.82±0.21	2.72±0.02	79.1±2.9	1185	1138	1247
	CN-95-2	12°30.546'	86°42.046'	1995 lava	ol	1.043	6.56	11.2	7.11±0.47	0.68±0.02	80.0±2.3	1200	1158	1149
					<i>ol<sup>d</sup></i>	<i>1.078</i>	<i>6.56</i>	<i>43.9</i>	<i>6.69±0.37</i>	<i>1.25±0.05</i>				
					px	1.009	5.54	4.6	6.79±0.18	4.24±0.03	79.6±2.8	1182	1134	1247
					<i>px<sup>d</sup></i>	<i>1.030</i>	<i>6.16</i>	<i>20.9</i>	<i>6.41±0.15</i>	<i>4.83±0.08</i>				
	CN-99-2	12°30.074'	86°42.063'	1999 ash	ol	1.051	6.48	30.2	6.67±0.34	2.97±0.11	79.3±2.9	1208	1164	na <sup>c</sup>
					px	0.988	4.62	31.8	4.73±0.13	7.18±0.07	78.3±3.0	1190	1136	na
	CN-99-1	12°30.074'	86°42.063'	1999 lava	ol	1.005	6.11	7.1	6.95±0.41	0.56±0.01	80.5±2.3	1204	1162	1163
					px	1.054	5.32	4.0	7.00±0.18	2.79±0.02	79.4±2.7	1190	1146	1253
Nejapa	Nejapa-2	12°7.303'	86°19.558'	wall lava	ol	0.99	6.84	21.1	7.14±0.39	0.88±0.02	84.8±2.2	1184	1146	1009
					px	1.088	4.85	9.1	5.32±0.38	0.79±0.02	85.6±2.1	1180	1134	1245
	Nejapa-1	12°7.187'	86°19.446'	pit lava	ol	1.062	7.18	162.6	7.22±0.19	1.94±0.01	86.5±1.3	1208	1189	1172
					px	0.986	6.33	13.3	6.76±0.40	0.84±0.03	86.7±2.5	1200	1159	1268
Nejapa-Motastepe	NE201* Motastepe	12°8.052' 12°7.827'	86°19.580' 86°19.393'	lava	ol	0.765	6.72	34.7	6.89±0.57	1.33±0.08	82.4±0.9			
					ol	1.048	7.10	980.3	7.10±0.14	4.29±0.02	87.4±0.6	1216	1206	1203
	px				ol	1.026	5.80	34.0	5.95±0.44	0.65±0.03	87.5±2.0	1218	1180	1286
					ol	0.973	6.78	20.1	7.10±0.28	1.24±0.03				
Nejapa-C.L. Martinez	C.L. Martinez	12°9.497'	86°18.905'	lava	ol	0.973	6.78	20.1	7.10±0.28	1.24±0.03				
Nejapa-Asuseca	Asuseca	12°7.978'	86°18.041'	lava	ol	0.945	7.45	147.9	7.49±0.21	8.51±0.14	84.2±0.7			
					px	nd <sup>c</sup>	nd	nd	nd	nd	82.7±1.6			
Concepcion	Concepcion-1	11°29.504'	85°41.202'	tephra	ol	1.037	nd	nd	nd	nd	79.5±2.2	1203	1123	na
					px	1.170	nd	nd	nd	nd	73.5±1.4	1071	1077	1173
<i>Costa Rica</i>														
Irazu	IZ-63F*	10°4.524'	84°6.563'	lava	px	1.008	4.21	9.6	4.58±0.20	1.50±0.02				
Turrialba	4.1.01-1 <sup>f</sup>	10°1.210'	83°45.837'	lava	ol	0.716	7.48	125.2	7.53±0.16	2.67±0.05				
Barva	B2*	9°59.029'	83°51.325'	lava	px	0.679	nd	4.9	nd	0.137±0.007				
Arenal	AR143*	n.a.	n.a.	lava	px	0.855	nd	1.6	nd	0.024±0.002				

<sup>a</sup> All samples were collected by the authors and located with a GPS, apart from those marked with an asterisk (\*) which are from Mike Carr's collection.

<sup>b</sup>  $R_M$  is the measured He isotope ratio;  $X = (^4\text{He}/^{20}\text{Ne})_M / (^4\text{He}/^{20}\text{Ne})_{\text{air}}$ ;  $R_C/R_A$  is the air-corrected He isotope ratio =  $[(R_M/R_A \times X) - 1] / (X - 1)$ ;  $[\text{He}]_C = ([\text{He}]_M \times (X - 1)) / X$ ; errors are reported at the 1 sigma level.

<sup>c</sup> Note that only cogenetic pairs were selected for electron microprobe analyses—the entire data set is available as an electronic supplement.

<sup>d</sup> Italicized numbers are duplicate measurements.

<sup>e</sup> nd—not determined; na—not available. In some cases, MELTS temperatures could not be calculated due to program failure for these compositions.

<sup>f</sup> He isotopes for this sample were previously reported in Fischer et al. (2005)—the reported value was incorrect (8.3±0.3) and here we give the correct value.

crushers (connected to the preparation line of the noble gas mass spectrometer) and pumped overnight to ultra-high vacuum. A blank of the entire system was measured prior to every sample run.

Effective crushing of the samples is achieved by externally accelerating a magnetised hardened-steel slug up and down within the crusher for 2 min at a frequency of 60–90 impacts per minute. The magnetised slug is driven by an intermittent current passed through a solenoid (for a detailed description of the crushers see Scarsi, 2000). The volatiles released upon crushing are purified in the mass spectrometer preparation line using a combination of charcoal traps (cooled at liquid nitrogen temperature and at <20 K using a He-refrigeration unit) and getters (titanium and Zr–Al alloy). Helium was separated from Ne prior to inlet into the mass spectrometer, and was analysed for abundance and isotope ratios on a MAP215 mass spectrometer using SIO air ( $=1R_A$ ) and/or Murdering Mudpots (Yellowstone) He ( $=16.45R_A$ ) as standards. The gas extracted using the crushing technique represents a composite sample derived from many individual mineral grains containing different types and sizes of inclusions.

Electron microprobe analyses were carried out on a subset of samples — those with cogenetic mineral pairs. For each sample,  $\sim 20$  grains of olivine and pyroxene were mounted, polished, carbon coated and analysed for their major element chemistry in order to calculate their Mg numbers ( $=\text{Mg}/(\text{Mg}+\text{Fe}^{2+}) \times 100$ ) — a measure of their evolutionary history. Individual grains were measured with a 5  $\mu\text{m}$  spot at an accelerating voltage of 15 kV and a beam current of  $\sim 13.5$  nA using the Cameca-MBX microprobe at SIO.

#### 4. Results

Helium abundance and isotope results obtained by crushing phenocryst phases from recent tephra and lavas from Costa Rica and Nicaragua, as well as Mg numbers for cogenetic mineral pairs, are given in Table 1. He isotope ratios are reported in the form of  $R_C/R_A$ , where  $R_C$  is the air-corrected  $^3\text{He}/^4\text{He}$  ratio of the sample, assessed on the basis of He/Ne ratios (e.g.,  $R_C/R_A = [(R_M/R_A \times X) - 1]/(X - 1)$  where M is the measured value and  $X = (^4\text{He}/^{20}\text{Ne})_M / (^4\text{He}/^{20}\text{Ne})_{\text{air}}$ ). All abundance data have been corrected for blank contributions, which in all cases represent less than 2% of the total gas, and for air contamination (where  $[\text{He}]_C = ([\text{He}]_M \times (X - 1))/X$ ). In the case of Cerro Negro, analyses were carried out on both olivine and pyroxene phases for the 1992, 1995 and 1999 eruptions, allowing for (1) assessment of He variations over decadal timescales, and

(2) comparison with geothermal fluid data (obtained in 1992 (Sano and Williams, 1996) and 2002 (Shaw et al., 2003)).

$^3\text{He}/^4\text{He}$  ratios of samples range from  $4.58R_A$  (Irazu) to  $7.53R_A$  (Turrialba), lying within the typical range found in arc-related volcanics and geothermal fluids worldwide ( $5.37 \pm 1.87R_A$  (Hilton et al., 2002)). The pyroxenes tend to have lower  $^3\text{He}/^4\text{He}$  ratios (4.6– $7.0R_A$ ) than the olivines ( $^3\text{He}/^4\text{He} = 6.1$ – $7.5R_A$ ) over a range of concentration values (see Fig. 2a). This point is further emphasized in Fig. 2b, where coexisting mineral pairs are considered. In all cases except one (CN-99-1), the pyroxene samples show lower  $^3\text{He}/^4\text{He}$  ratios than coexisting olivines (Fig. 2b). In addition, in all Cerro Negro samples, the pyroxenes have higher He concentrations than coexisting olivines (Fig. 2c).

Comparing the volatile contents of melt inclusions in olivines from the 1992 and 1995 eruptions of Cerro Negro, Roggensack et al. (1997) noted a correlation between eruption style and volatile concentrations. The explosive 1992 eruption was characterized by higher  $\text{CO}_2$  and  $\text{H}_2\text{O}$  concentrations as compared to volatiles preserved in melt inclusions from the effusive 1995 eruption. If we compare the He contents of the 1992 phenocrysts with those from 1995, we do not observe higher He contents in the 1992 samples as might be anticipated (He concentrations of the 1992 ash pyroxenes are lower than 1995 ash and lava pyroxenes; 1992 ash olivines are lower than 1995 ash olivines). We note, however, that He concentrations generally reflect the inclusion density and are not necessarily related to source contents.

In Fig. 3, we compare the  $^3\text{He}/^4\text{He}$  ratios of the olivines to values measured in geothermal fluid samples (Sano and Williams, 1996; Shaw et al., 2003) and pyroxenes at four different localities: Cerro Negro, Nejapa, Irazu and Turrialba. Considering the entire data set, we find that among the different localities,  $^3\text{He}/^4\text{He}$  ratios of pyroxenes show the widest range (4.6 to  $7.0R_A$ ), while values in olivines range from 6.1 to  $7.5R_A$  and those of geothermal fluids range from 6.8 to  $8.0R_A$ . We note that values measured in geothermal fluids and olivines from the same site fall within error of each other in all cases. This is a key observation that reinforces the notion that olivine phenocrysts and geothermal fluids are equally useful at preserving source He isotope characteristics (Hilton et al., 2000, 1997; van Soest et al., 2002).

Mg numbers for cogenetic minerals range from 73.5 to 87.5, within the typical range found at other arc volcanoes (Gasparon et al., 1994; Hilton et al., 2000; Schiano et al., 2000; van Soest et al., 2002). A comparison of values measured in olivines vs. cogenetic



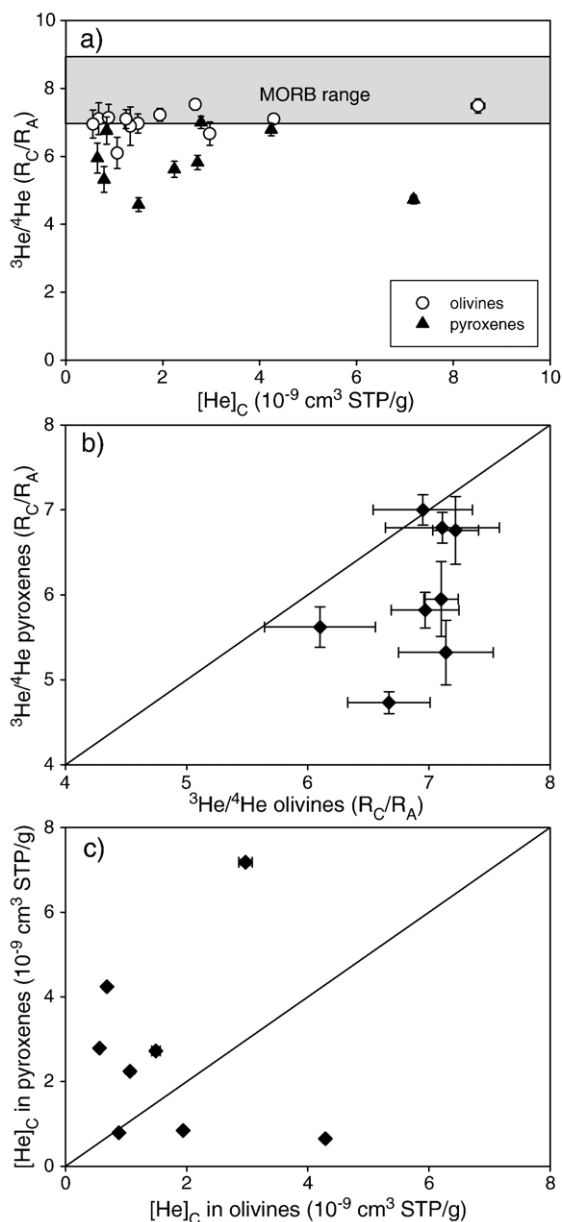


Fig. 2. He characteristics of mafic phenocrysts from Nicaragua and Costa Rica. (a)  $^3\text{He}/^4\text{He}$  ratios are plotted as a function of He concentrations in olivines and pyroxenes for the total data set. The shaded box shows the MORB range—note that only the highest values for each site are plotted. (b)  $^3\text{He}/^4\text{He}$  ratios of pyroxenes are plotted against ratios in their cogenetic olivines. The 1:1 line is shown for reference. The  $^3\text{He}/^4\text{He}$  ratios of olivines are consistently higher than cogenetic pyroxenes. (c) He concentrates of pyroxenes are plotted against concentrations in cogenetic olivines. The 1:1 line is shown for reference.

pyroxenes (Table 1; Fig. 4a) shows that Mg numbers of the different phases are essentially within error of each other.

## 5. Discussion

Various processes have the potential to influence the He characteristics preserved in mineral phases. These include: (1) in situ post-eruptive in-growth, (2) addition of radiogenic  $^4\text{He}$  by crustal assimilation (Hilton et al., 1993, 2000; Marty et al., 1994; van Soest et al., 2002), (3) contamination as a result of magma ageing (Zindler and Hart, 1986), and (4) diffusion-controlled isotopic fractionation (Harrison et al., 2004; Trull and Kurz, 1993, 1999).

The first section of the discussion explores how post-eruptive processes could modify He isotopes and abundances. The following section focuses on evaluating the extent of crustal contamination observed in Central American lavas, assessing whether crustal thickness is a controlling factor, and determining how magma ageing may have influenced the He characteristics. The subsequent section addresses the fundamental question of whether He isotope characteristics change over time at a given volcanic centre. In order to assess this possibility, we first investigate whether values measured in tephra differ from those in lavas from the same eruption. We then evaluate how  $^3\text{He}/^4\text{He}$  ratios measured in phenocryst phases compare to those measured in geothermal fluids. Once we assess whether different sampling media exert an influence on measured values, we can determine whether temporal variations are observed. Finally, the last part of the discussion focuses on the observation of lower  $^3\text{He}/^4\text{He}$  ratios and higher He concentrations in the pyroxenes as compared to coexisting olivines. We explore two alternative processes that can explain this phenomenon:

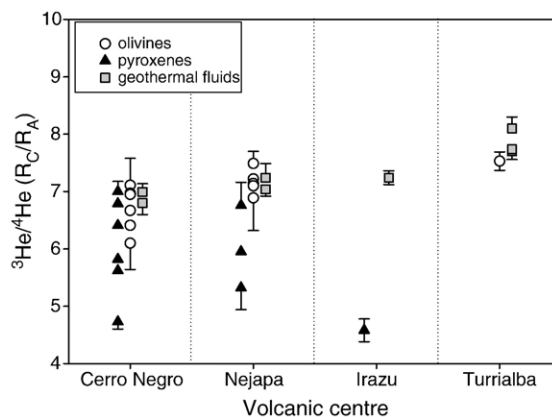


Fig. 3. A comparison of  $^3\text{He}/^4\text{He}$  ratios measured in olivines, pyroxenes and geothermal fluids at Cerro Negro, Nejapa, Irazu and Turrialba. The upper error bar limits for the highest  $^3\text{He}/^4\text{He}$  sample are shown for each site. Data is from this study, Sano and Williams (1996) and Shaw et al. (2003).

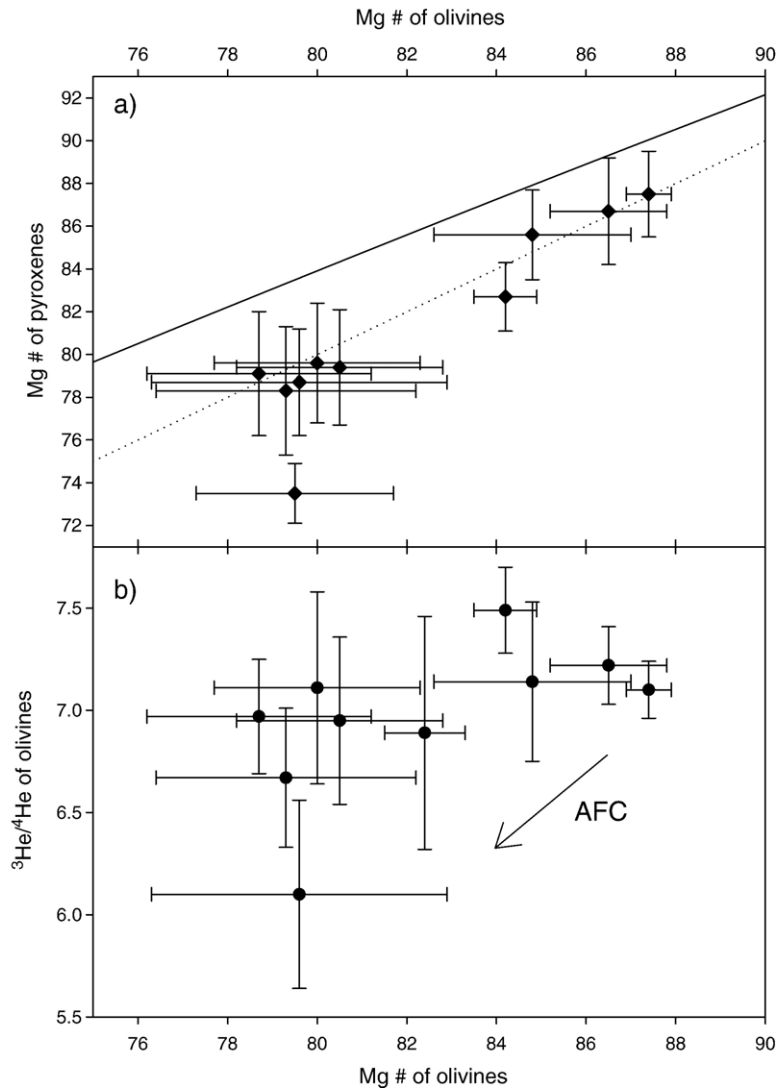


Fig. 4. (a) Comparison of Mg values for co-genetic mineral pairs. The 1:1 line (dotted) and the equilibrium line (solid) are shown for reference. (b)  $^3\text{He}/^4\text{He}$  ratios of olivines are plotted as a function of their measured Mg number. Note that lower  $^3\text{He}/^4\text{He}$  ratios correspond to lower Mg values, showing the influence of AFC processes.

(1) diffusion controlled mechanisms, and (2) relative timing of crystallization and contamination, assessed on the basis of Mg numbers and MELTS crystallization temperatures.

### 5.1. Post-eruptive modification

In the case of post-eruptive in-growth,  $^3\text{He}/^4\text{He}$  ratios could be modified by the addition of cosmogenic  $^3\text{He}$  or radiogenic in-growth of  $^4\text{He}$  due to U and Th decay. While the Cerro Negro samples are too young to have been modified by these processes, we assess this possibility for the other samples in this study. Taking a

conservative maximum age estimate of 10,000 years, a  $[\text{U}] = 0.175$  ppm (NE201 from Carr et al., 2003), a production ratio of  $2.15 \times 10^{-7}$   $\text{cm}^3$  STP/ppm U/My and  $\text{Th}/\text{U} = 3.3$  (Ozima and Podosek, 1983), an olivine/melt partition coefficient of 0.008 (Marty and Lussiez, 1993) and a pyroxene/melt partition coefficient of 0.04 (Henderson, 1982), we calculate maximum radiogenic  $^4\text{He}$  additions of  $3.4 \times 10^{-12}$   $\text{cm}^3$  STP/g (olivine) and  $1.5 \times 10^{-11}$   $\text{cm}^3$  STP/g (pyroxene), which are insignificant compared to measured concentrations. If samples with unknown ages were older than 400,000 years, then the radiogenic addition would represent only 10% of the lowest concentration pyroxene sample from Nejapa

( $0.65 \times 10^{-9}$  cm<sup>3</sup> He STP/g). Likewise, if we consider cosmogenic <sup>3</sup>He additions, we find that the change in the measured <sup>3</sup>He/<sup>4</sup>He ratios is negligible ( $< 5 \times 10^{-8} R_A$  for the lowest <sup>4</sup>He concentration sample) assuming a production rate of  $103 \pm 4$  atoms/g/year (Dunai, 2001) and a maximum age of 10,000 years. In addition, it should be noted that cosmogenic <sup>3</sup>He and radiogenic <sup>4</sup>He would likely be sited in the matrix of the phenocryst phases and using our limited-duration crushing technique (Hilton et al., 1993), we liberate gas dominantly from inclusions rather than matrix. Post-eruptive modification of measured <sup>3</sup>He/<sup>4</sup>He values is therefore discounted.

### 5.2. Crustal influences and magma ageing

The <sup>3</sup>He/<sup>4</sup>He ratios of phenocryst phases measured in lavas from the Central American arc are significantly higher than crustal values ( $0.05 R_A$ ) with most lying fairly close to the MORB range ( $8 \pm 1 R_A$ ): <sup>3</sup>He/<sup>4</sup>He values of olivines range from 6.1 to  $7.5 R_A$  and <sup>3</sup>He/<sup>4</sup>He values of pyroxenes range from 4.6 to  $7.0 R_A$  (Fig. 2a). This likely reflects the fact that the dominant source of He is from the mantle wedge (Craig et al., 1978), but with varying degrees of crustal interaction. Although the sediments on the subducting plate would be enriched in radiogenic <sup>4</sup>He, we discount the possibility that they could make a significant contribution to the volcanic output on the basis of the high diffusivity of He in sedimentary material. For example, based on diffusion experiments on interplanetary dust particles (Hiyagon,

1994) and theoretical calculations taking temperature and grain size into account (Hilton et al., 1992), He is not expected to be retained in subducting sediments beyond the fore-arc region. The arc crust through which the lavas erupt is a more likely candidate for the source of radiogenic <sup>4</sup>He. This is supported by the observation of lower <sup>3</sup>He/<sup>4</sup>He ratios measured in arcs with thick crust such as the Andes, Kamchatka and Taiwan (see discussion in Hilton et al., 2002).

Based on geophysical constraints relating Bouguer gravity to regional elevation, crustal thickness in southern Central America increases systematically from a minimum of 32 km in Nicaragua to 45 km in central Costa Rica (Carr et al., 1990, 2003). If crustal thickness was the dominant factor influencing <sup>3</sup>He/<sup>4</sup>He ratios, then we would anticipate lower values in Costa Rica. However, the highest <sup>3</sup>He/<sup>4</sup>He values come from Turrialba volcano in Costa Rica ( $7.53 \pm 0.16 R_A$ ), which erupts through crust thicker than at any of the other sites in this study. In Fig. 5 we plot <sup>3</sup>He/<sup>4</sup>He ratios and crustal thickness as a function of latitude for the entire data set. This figure illustrates the point that a simple correlation does not exist in southern Central America. In this case, the observed variation in <sup>3</sup>He/<sup>4</sup>He is likely related to other features affecting crust–mantle interaction.

Another test of the influence of crustal effects is to consider the relationship between <sup>3</sup>He/<sup>4</sup>He and Mg number. Prior arc-related phenocryst studies from the Sunda Arc in Indonesia (Gasparon et al., 1994) and the Lesser Antilles Arc (van Soest et al., 2002) report positive correlations between <sup>3</sup>He/<sup>4</sup>He ratios and Mg

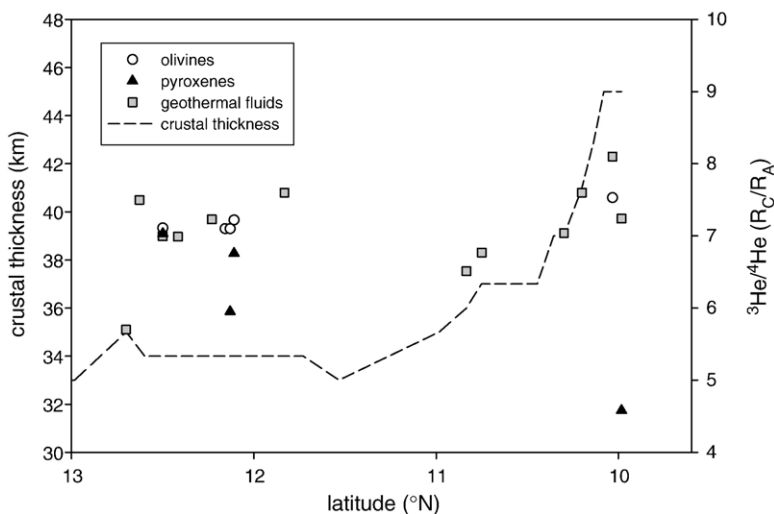


Fig. 5. He isotope data for olivines, pyroxenes and fumaroles (from Sano and Williams, 1996; Shaw et al., 2003 and this study) plotted as a function of latitude, superimposed on crustal thickness variations (from Carr et al., 2003). Only the highest values for each site are plotted. The important point to note is that high <sup>3</sup>He/<sup>4</sup>He are measured throughout Central America, even in regions where the crust is relatively thick.



number. This observation is attributed to the addition of crustally derived radiogenic  $^4\text{He}$  which would occur simultaneously with magma differentiation in the crust. Evolution to more evolved magma compositions would be traced by lower Mg numbers. Fig. 4b illustrates that this trend is observed throughout our study area, reinforcing the notion that AFC processes (Assimilation of crustal material and Fractional Crystallization of magma) are common to arc systems. However, in our data set we find no apparent relationship between the major element chemistry of host lavas (to be published elsewhere by Walker et al.) and He isotopes preserved in mafic phenocrysts. This would suggest that contamination does not occur by direct assimilation. However, if the assimilant was simply older plutons having the same chemical composition as the intruding magmas, the contaminant would not be apparent in the whole rock chemistry. Depending on the age of the earlier intrusions, this ‘auto-contamination’ process (Hilton et al., 2000) could influence the  $^3\text{He}/^4\text{He}$  ratios by adding radiogenic He. We note that the crust in Costa Rica is comprised of superimposed Tertiary and Quaternary volcanics, whereas in Nicaragua the volcanic front hosts only younger Quaternary intrusions (Ehrenborg, 1996). Thus, if age of the assimilant was the dominant controlling factor, we would expect lower  $^3\text{He}/^4\text{He}$  ratios in Costa Rica and this does not appear to be the case.

An alternative mechanism of reducing  $^3\text{He}/^4\text{He}$  ratios preserved in phenocrysts from typical upper mantle values is through magma ageing. In this case, a magma would develop a progressively lower He isotope signature with time through radiogenic  $^4\text{He}$  grow-in due to the decay of U and Th. Assuming that a magma’s composition was initially MORB-like ( $^3\text{He}/^4\text{He}=8R_A$  and  $[\text{He}]=15\times 10^{-6}\text{ cm}^3\text{ STP/g}$  (Hilton et al., 2000), and using the U contents and  $^4\text{He}$  production rate stated above (Section 5.1), we calculate that 116 and 250 million years would be required to decrease the He isotope ratio from  $8R_A$  to  $6.1R_A$  (the lowest value measured in olivines) and  $4.6R_A$  (the lowest value measured in pyroxenes), respectively. These grow-in times are completely implausible and unless extreme degrees of degassing prior to radiogenic in-growth are invoked (e.g., for a magma to reach  $4.6R_A$  in 100 years, >99.99995% of magmatic He would have to be lost prior to in-growth), magma ageing is not considered a viable means by which to modify  $^3\text{He}/^4\text{He}$  ratios.

In summary, our data set indicates that some level of radiogenic He additions have influenced  $^3\text{He}/^4\text{He}$  ratios throughout southern Central America since many samples lie below the typical upper mantle range of

$8\pm 1R_A$  and He isotope values decrease with decreasing Mg numbers. However, we find no clear relationship between He isotopes and crustal thickness or age of the crust through which the magmas erupt. Therefore, He characteristics are likely dominantly controlled by other factors such as the geometry of the magmatic plumbing system, its replenishment history and/or the eruptive frequency at a given volcanic centre. Degassing would lower intrinsic He contents and thereby increase the magma’s susceptibility to contamination.

### 5.3. Timescale variations in He isotopes

In order to assess timescale variations of He isotopes at a given volcanic centre, we first evaluate whether different sampling media show similar preservation of magmatic He signatures. Cerro Negro volcano was selected for this aspect of the study because it is highly active and has produced both lava and ash in recent eruptions.

#### 5.3.1. Do tephra show better preservation of magmatic He signatures than lavas?

It has been argued that material which is cooled rapidly, such as ash and other tephra deposits, shows better preservation of volatile signatures than lavas (Clocchiatti, 1975; Roedder, 1984; Wallace, 2005). This is based on the assumption that the cooling rate determines whether inclusions preserved in host minerals are glassy (Roedder, 1984; Shinohara et al., 2003). The slower cooling experienced by lavas may allow for melt inclusions to crystallize, leading to subsequent volatile loss by diffusion or cracking of the inclusion host (see discussion in Wallace, 2005). At surface pressures, a strong pressure gradient of hydrogen (and presumably other volatiles) exists between the inclusion and the external atmosphere which can lead to diffusional losses (Sobolev and Chaussidon, 1996). Such losses can be significant at high temperatures (Danyushevsky et al., 2002; Hauri, 2002). Because noble gases are sited in melt and fluid inclusions, such processes have the potential to modify intrinsic He characteristics.  $^3\text{He}/^4\text{He}$  values are theoretically more prone to respond to fractionation processes than other noble gas ratios due to the large mass difference between  $^3\text{He}$  and  $^4\text{He}$  and the theoretical relationship between mass and diffusion coefficients ( $D$  is inversely proportional to the square root of the atomic mass; see Craig and Lupton, 1976; Hart, 1984; Rama and Hart, 1965).

In Fig. 6, we show He results from Cerro Negro volcano, comparing isotope (Fig. 6a) and abundance

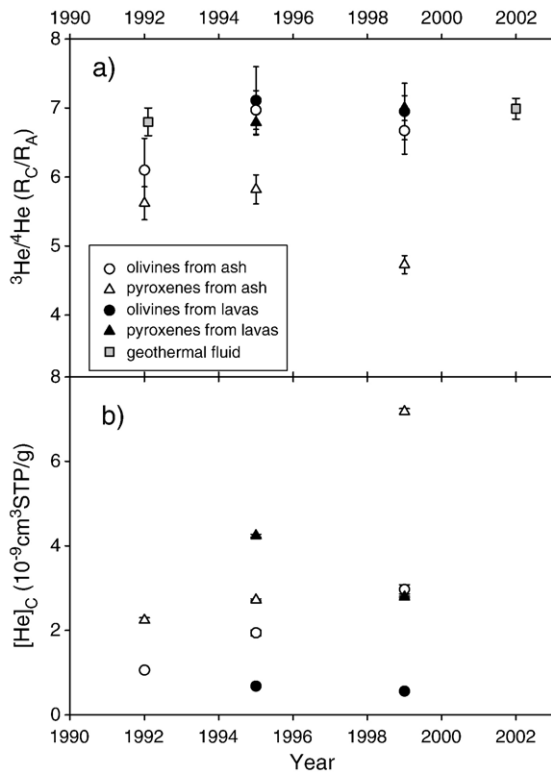


Fig. 6.  $^3\text{He}/^4\text{He}$  values (a) and He concentrations (b) in olivine (circles) and pyroxene (triangles) grains in separates from ash (open symbols) and lavas (filled symbols), as well as geothermal fluids (squares) from Cerro Negro volcano a function of time. Fumarole data is from Shaw et al. (2003) and Sano and Williams (1996).

(Fig. 6b) values in mineral phases from tephra to those measured in lavas, as well as  $^3\text{He}/^4\text{He}$  ratios of geothermal fluids. The principal point to note is that  $^3\text{He}/^4\text{He}$  values from the 1995 and 1999 eruptions do not show higher ratios in the ash samples as compared to lavas. Similarly, if we consider He abundances, there is no obvious consistent pattern of lower concentration values in the lava-hosted phenocrysts. However, as previously noted, He concentrations in minerals largely reflect the inclusion density and may not necessarily represent source composition. Therefore, based on these results, we find no evidence for preferential modification of  $^3\text{He}/^4\text{He}$  ratios in lava-hosted phenocrysts compared with tephra minerals.

### 5.3.2. Comparison to geothermal fluids

An important goal of this study is to critically assess whether phenocryst phases show better preservation of magmatic volatile signatures as compared to geothermal fluids. Geothermal systems could potentially be more susceptible to modification of intrinsic  $^3\text{He}/^4\text{He}$  ratios

due to shallow-level crustal processes which would add radiogenic He to fluids. This is particularly relevant for geothermal systems located far from the volcanic edifice (van Soest et al., 1998). Despite these potential problems, Hilton et al. (2000) measured higher ratios in geothermal fluids from La Palma (the Canary Islands) than in mafic phenocrysts from the same site and argued that geothermal fluids were less influenced by contamination effects than phenocryst phases. The authors advocated a model whereby the geothermal fluids directly sampled the exsolved volatile phase from the magmas (containing most of the He for a given magma batch), whereas the magmas would stall and degas in the Canarian uppermost mantle, allowing for contamination with radiogenic He from the surrounding wall rock. Likewise, a comparison of He isotopes in phenocrysts and geothermal fluids in the Tabar-Lihir-Tanga-Feni island arc (Patterson et al., 1997) shows that geothermal fluids have consistently high values, whereas values measured in mafic phenocrysts tend to show more variation.

In Fig. 3 we compare  $^3\text{He}/^4\text{He}$  ratios of mafic phenocrysts presented in this study to published geothermal fluid data from the same volcanoes (Sano and Williams, 1996; Shaw et al., 2003). We note that for these sites, the geothermal fluids have consistently high values and tend to show less variation than mafic mineral phases. However, the  $^3\text{He}/^4\text{He}$  ratios preserved in olivine grains are all within error of values measured in the geothermal fluids, with the exception of olivines from the 1992 ash at Cerro Negro, which have values within  $0.04R_A$  of error. We consider this to be a negligible difference (see discussion below) and thus conclude that in the case of southern Central America, the general correlation between He signatures preserved in olivine phenocrysts and geothermal fluids indicates that both phases can be used to reveal source characteristics. The close agreement between these two phases likely reflects the high level of activity of Central American volcanoes. For example, compared to La Palma (where geothermal  $^3\text{He}/^4\text{He} >$  olivine  $^3\text{He}/^4\text{He}$ ; Hilton et al., 2000) which has had 7 historic eruptions since it first erupted in 1585, Cerro Negro has had 23 eruptions in its  $\sim 150$  year history (Siebert and Simkin, 2002). The discrepancy between values measured in olivines and pyroxenes will be discussed in Section 5.4.

### 5.3.3. Do $^3\text{He}/^4\text{He}$ values at a given volcanic site vary over short timescales?

The question of whether magmatic systems show variations in  $^3\text{He}/^4\text{He}$  ratios over short timescales can be

addressed by considering data from the last three eruptions of Cerro Negro coupled with the recent geothermal fluid measurements. Roggensack et al. (1997) noted higher volatile contents preserved in melt inclusions from the explosive 1992 eruption as compared to those from the relatively effusive 1995 eruption. Comparing the He isotopes measured in olivines from these eruptions (Fig. 6a), we note that little variation has occurred over the time period 1992–1999. The values range from a minimum of  $6.10 \pm 0.46R_A$  in olivines from the 1992 eruption to a maximum of  $7.11 \pm 0.47R_A$  measured in olivines from the 1995 eruption, with intermediate values in the 1999 phases. This observation is corroborated by measurements of summit fumaroles from Cerro Negro's crater (Sano and Williams, 1996; Shaw et al., 2003), where the highest measured value ( $=6.99 \pm 0.14R_A$  sampled in 2002) is within error of the highest value measured in olivines. If we consider olivine phenocrysts from the 1992 eruption as compared to the fumarole measurements made just weeks after the eruption, we note that the fumarole emissions have  $^3\text{He}/^4\text{He}$  values which are slightly higher than in the olivines. This finding could lend support to the theory that geothermal fluids sample the magma source more directly than phenocryst phases (Hilton et al., 2000). However, given that this difference is small (to within  $0.04R_A$  of error), we conclude that  $^3\text{He}/^4\text{He}$  ratios in the Cerro Negro magmatic system do not vary significantly over short (decadal) timescales. Likewise,  $^3\text{He}/^4\text{He}$  measurements of fumaroles made over several months at Poas and Turrialba volcanoes in Costa Rica (Shaw et al., 2003) indicate negligible isotopic variation. In contrast, systematic monitoring of gas samples at Izu-Oshima Volcano, Japan, between 1986 and 1992, showed large He isotope variations (ranging from 1.71 to  $5.49R_A$ ) which were related to the associated volcanic activity (Sano et al., 1995). Likewise, Galeras volcano also showed increases in  $^3\text{He}/^4\text{He}$  ratios of crater fumaroles between 1988 ( $5.5R_A$ ) and 1995 ( $7.7R_A$ ), that spiked during 1992 (up to  $8.8R_A$ ), the year of intense eruptive activity and destruction of the lava dome (Sano et al., 1997).

A significant implication of constant  $^3\text{He}/^4\text{He}$  ratios in Cerro Negro's volcanic output is that the proportions of mantle and crustal He components in the mixture of sampled He remains constant over short timescales, i.e., the source is relatively homogeneous in its He isotope characteristics. Prior work on historical lavas from Cerro Negro (Walker and Carr, 1986) suggests that the magma feeding these eruptions was relatively homogeneous. An obvious way to homogenize volatiles is to have a large magma chamber, where the composition is buffered by

periodic re-injection of magma from below. However, in the case of Cerro Negro, it has been argued that the eruptions are fed by ephemeral dikes rather than a large magma chamber. This is based on melt inclusion studies (Roggensack, 2001; Roggensack et al., 1997), where large variations in calculated volatile saturation pressures were observed (1.0 up to 6.4 kbar corresponding to depths of 3 to 19 km). The authors acknowledge the possibility that a deep magma chamber may ultimately be the source of magmas, but that much of the compositional variation observed in olivine-hosted melt inclusions is due to interaction between ascending magma and more evolved magmas within the interior of the dikes. The finding of phenocryst phases out of equilibrium with host lavas suggests that much of their crystal growth may have occurred during ascent (Walker and Carr, 1986). However, based on measured  $^3\text{He}/^4\text{He}$  ratios, the olivines do not appear to have had significant interaction with the crust during ascent. This possibility is considered in more detail in the following section where we discuss the discrepancy between He characteristics preserved in cogenetic pyroxene and olivine phases.

#### 5.4. $^3\text{He}/^4\text{He}$ ratios: olivines vs. pyroxenes

The clear distinction between helium isotope characteristics of olivines and pyroxenes (see Fig. 2b) can either be explained by (1) diffusion-related mechanisms, or (2) late-stage crustal interaction. In the first case, we explore the likelihood of diffusion controlled isotope fractionation as well as the possibility of preferential He diffusion in pyroxenes vs. olivines. The second possibility is considered in terms of magma chamber processes, the relative timing of mineral crystallization and magma contamination. If the olivines crystallized from a magma before the pyroxenes, and if the subsequent pyroxene crystallization was accompanied by crustal assimilation during magma evolution, lower  $^3\text{He}/^4\text{He}$  ratios would be anticipated in the pyroxenes (see Hilton et al., 1993, 2000; Marty et al., 1994). This hypothesis has been evaluated using two independent methods: (1) electron microprobe analyses of cogenetic mineral pairs to determine Mg numbers, and (2) modeling the sequence of crystallization using the MELTS petrological modeling program (Ghiorso and Sack, 1995).

##### 5.4.1. Diffusion-related isotopic fractionation

Since the relative mass difference of  $^3\text{He}$  and  $^4\text{He}$  is large, predicted differences in their diffusivities can also be large (Kurz and Jenkins, 1981; Trull and Kurz, 1993,

1999). Theoretical calculations based on Graham's Law predict that  $^3\text{He}$  could diffuse up to 15% faster than  $^4\text{He}$ , where the relative diffusion rates are proportional to the inverse square roots of the atomic masses (Craig and Lupton, 1976; Rama and Hart, 1965). Thus, if the grains are sufficiently small, significant decreases in  $^3\text{He}/^4\text{He}$  ratios in residual He could be achieved over relatively short time periods. For example, Harrison et al. (2004) calculated that the  $^3\text{He}/^4\text{He}$  ratio of 5 mm phenocrysts could drop from  $8R_A$  to  $4R_A$  in as few as 60 years, where the fraction of He lost from the grain would be greater than 0.98. In order for diffusion to occur, a concentration gradient would need to exist where the He would diffuse from a region of high concentration to low concentration. As magma degassed, He from the phenocrysts could potentially diffuse from the phenocrysts into the magma at a rate determined by temperature (Trull and Kurz, 1999). Harrison et al. (2004) call upon diffusion to explain He isotope variations in phenocrysts from a suite of Siberian lavas. They find a concomitant decrease in  $^3\text{He}/^4\text{He}$  ratios with decreasing He concentrations which would be consistent with mass-dependent fractionation associated with diffusion. If we consider samples from Cerro Negro volcano only, where we would anticipate similar initial source compositions, we note that the samples having the lowest  $^3\text{He}/^4\text{He}$  ratios, the pyroxenes, do not show a systematic decrease in  $^3\text{He}/^4\text{He}$  ratios with decreasing He concentrations. Thus, we discount simple diffusion as a method by which to modify He isotope characteristics. An alternative mechanism of lowering  $^3\text{He}/^4\text{He}$  ratios in pyroxenes is preferential diffusive exchange of magmatic He in pyroxenes relative to olivines. The diffusivity of He is 10 times greater in pyroxene than it is in olivines (Trull and Kurz, 1993), thus the pyroxenes could exchange He with an evolving magma more readily than olivines. This possibility will be further discussed in Section 5.4.3.

#### 5.4.2. Mg numbers

As discussed previously, Mg numbers of phenocrysts are useful indicators of magma evolution (where higher values indicate crystallization from a more primitive melt). In order to test whether olivines are more primitive than their coexisting pyroxenes, we measured Fe and Mg contents of the phenocryst pairs. Fig. 4a shows that pyroxenes have Mg numbers that are essentially indistinguishable from the olivines. However, these values cannot be compared directly since olivine and pyroxene have different partition coefficients for Fe and Mg in equilibrium with a melt ( $K_D = (X_{\text{Mg}}/X_{\text{Fe}})_{\text{liquid}} / (X_{\text{Mg}}/X_{\text{Fe}})_{\text{mineral}}$ ). Estimates of  $K_D$  values

for olivine and pyroxene are 0.3 and 0.23, respectively (Roeder and Emslie, 1970). The relationship between Mg numbers of these minerals in equilibrium with the same melt composition was calculated and is plotted as a solid line in Fig. 4a. We note that the Mg numbers of the olivines are much higher than the pyroxenes with which they would be in equilibrium. Our data set is thus consistent with a scenario where olivines record a more primitive magma signature than their coexisting pyroxenes. In addition, based on modeling of olivine-liquid equilibrium and Fe–Mg diffusion rates, it has been suggested that olivines crystals can be prone to significant Fe and Mg exchange with the melt as it evolves (see Gaetani and Watson, 2000, 2002; Jurewicz and Watson, 1988). If this is the case, then our Mg numbers would represent minimum values and the olivines could have been even more primitive when the volatiles were trapped.

#### 5.4.3. MELTS modeling

If we invoke a model where the lower  $^3\text{He}/^4\text{He}$  ratios found in the pyroxenes indicate radiogenic He additions, due to crustal assimilation occurring after olivine crystallization, then we need to estimate the relative timing of crystallization for each phase. Using the MELTS program (Ghiorso and Sack, 1995), we can calculate the crystallization temperatures of mineral phases in equilibrium with melt of a given composition, under a defined set of conditions. If we assume that the bulk composition of the lavas is representative of the original melt composition, then the crystallization temperatures of olivine and pyroxene can be calculated. Using a simple cooling model, we can then estimate the time interval that elapses between the crystallization of olivine and pyroxene. We calculate crystallization temperatures for each phase using three different sets of conditions: (1) a simple case where we assume an isobaric system at 1 kbar cooling from 1300 to 1000 in  $2^\circ$  intervals, (2) an isobaric system at 1 kbar cooling from 1300 to 1000 in  $2^\circ$  intervals with 1 wt.%  $\text{H}_2\text{O}$  added to compositions — to test how water affects the relative timing of crystallization, and (3) an isobaric system at 5 kbar cooling from 1300 to 1000 in  $2^\circ$  intervals — to examine the effect of pressure on phase crystallization. Results of this modeling are given in Table 1.

If we compare the first two cases, we note that the effect of adding water is to lower the crystallization temperature, although the relative temperature difference between olivine and pyroxene crystallization is essentially the same in both cases. We note that in all cases—in either wet or dry magma scenarios—but one



(Nejapa-Motastepe), the olivines crystallized at higher temperatures than their cogenetic pyroxenes. Mostly, the absolute temperature difference is not large — generally crystallization of each phase occurs within 30° of each other. Although it is possible that cooling rates could be sufficiently slow to allow olivine crystallization to occur before the onset of pyroxene crystallization, it is unlikely that this small temperature difference (and consequent short time interval) could account for the observed He characteristics. For example, if we consider a typical magma chamber cooling rate of 0.1 °C/year (based on estimates at Kilauea volcano (Cooper et al., 2001) and model values (Phillips and Woods, 2002) and assume a maximum 30 °C temperature difference, we calculate that the onset of pyroxene crystallization would occur at most 300 years after olivine crystallization. Based on typical U and Th compositions, 300 years is insufficient time for a radiogenic <sup>4</sup>He signature to grow in, and likely insufficient time for extensive assimilation of <sup>4</sup>He-rich crust. Without prior knowledge of the dynamics of each volcanic system, it is difficult to constrain the amount of assimilation that could occur over this time period.

In the case of Cerro Negro, melt inclusion studies have revealed insight to crystallization and magma processes (Roggensack, 2001). Based on crystal size distribution (CSD) analysis and assumed crystal growth rates, Roggensack estimates a residence time for Cerro Negro olivine crystals of ~0.9 years — much less than 300 years. The young ages of these olivines coupled with the assumption that olivine crystallization preceded that of pyroxene reinforces the conclusion that radiogenic in-growth is incapable of producing the requisite <sup>3</sup>He/<sup>4</sup>He ratios observed in the pyroxenes. Roggensack noted enhanced K<sub>2</sub>O in melt inclusions of later-formed olivines, which could indicate late-stage crustal additions and thus provide a source of radiogenic <sup>4</sup>He. However, based on the observation of a correlation between K<sub>2</sub>O and trace elements in the melt inclusions he suggested that much of the variability can be ascribed to fractional crystallization. We note that a crustal signature associated with direct crustal assimilation is not apparent in the radiogenic isotopes and trace element chemistry of any of the lavas erupted in Nicaragua (Carr et al., 1990; Patino et al., 2000; Walker et al., 2001).

If we consider the third case, where crystallization occurs at a pressure of 5 kbar (= 15 km depth) consistent with high equilibrium pressures calculated from water contents of melt inclusions at Cerro Negro (Roggensack et al., 1997), we note that pyroxene would begin crystallizing long before olivine (the minimum temperature difference is 78 °C). While this crystallization

sequence is not typical for arc systems, we cannot discount this possibility. If this scenario is correct, we would need to invoke a different method by which to produce the observed He characteristics since the earliest formed crystals — pyroxene, in this case — would be expected to trap higher (less radiogenically modified) He isotope signatures and our data show that they do not. An alternative explanation for our observations is diffusional He exchange, which is explored in the following section.

#### 5.4.4. Diffusional He exchange with surrounding crust

Magmatic plumbing systems can be modeled by mush zones whereby magma passes through various interconnected chambers (Marsh, 1995, 1998; Sinton and Detrick, 1992). As magma ascends to the surface, it experiences rapid cooling at its margins, where it is in contact with the surrounding crust and the semi-solidified mush zones (Danyushevsky et al., 2004). This rapid cooling facilitates crystallization and thus newly formed phenocrysts will lie in close proximity to the crust — a source of radiogenic <sup>4</sup>He. Although crust in Nicaragua is relatively young (Carr et al., 2003), any radiogenic He signature that it may have acquired could be exchanged with mineral phases via diffusion.

Rather than considering the onset of crystallization as discussed above, a more appropriate consideration may be the effective closure temperatures of the mineral phases. The concept of closure temperatures was first defined by Dodson (1973) to relate cooling rates to diffusion parameters for a given species. The idea that the mobility of a species (via diffusion) would cease at a given temperature has been applied to He (Marty et al., 1994; Hilton et al., 1995; van Soest et al., 2002) where it has been suggested that olivine closure temperatures are higher than those of pyroxenes. A lower closure temperature of pyroxenes would allow for diffusive He exchange between the pyroxenes and the magma (and/or surrounding crust) to persist after the olivines had been closed. In this way, pyroxenes would be susceptible to late stage contributions of radiogenic <sup>4</sup>He from the crust and its associated fluids. Based on experimental measurements, He diffuses 10 times faster in pyroxenes than in olivines (Trull and Kurz, 1993), lending support to this hypothesis.

Thus, we conclude that the most viable explanation of the lower <sup>3</sup>He/<sup>4</sup>He ratios observed in the pyroxenes is diffusive exchange with radiogenic He from the surrounding crust (and associated fluids) occurring after olivines were closed. This agrees with findings of others (Marty et al., 1994; Hilton et al., 1995; van Soest et al., 2002) and underscores the sensitivity of

He in identifying and assessing crustal contamination processes.

## 6. Conclusions

The Nicaragua-Costa Rica segment of the Central American arc is a well-studied region and thus offers the possibility of testing various hypotheses regarding how He isotopes are sampled and potentially modified in arc systems. In this contribution, we have explored several issues including whether or not a relationship exists between crustal thickness and He characteristics, if certain types of material (ash vs. lava vs. fumarole gases) or mineral phases (olivine vs. pyroxenes) show better preservation of primitive volatile signatures and whether short-term variations in He characteristics can be discerned. Finally, we examined the roles of diffusion and crustal contamination in generating observed isotope characteristics. Major findings of our study are listed below.

- (1) There is no apparent relationship between measured He isotope ratios and crustal thickness or age of the crust through which magmas erupt. This may be related to the high degree of volcanic activity in Central America, which does not allow significant interaction between magma and the crust to take place. Despite this, it is clear that AFC processes have had some influence on He isotope characteristics, since  $^3\text{He}/^4\text{He}$  ratios show a positive trend with Mg numbers (in olivines).
- (2) Despite faster cooling rates, tephra deposits do not show better preservation of volatile signatures than lavas — at least for helium.
- (3) The observation of uniform  $^3\text{He}/^4\text{He}$  ratios over the last 3 eruptive phases of Cerro Negro volcano as well as in fumarole measurements during passive degassing periods suggests that the volatile composition of the magma source feeding the volcano has been relatively homogeneous over the last decade.
- (4) Lower  $^3\text{He}/^4\text{He}$  ratios observed in pyroxenes relative to cogenetic olivines indicate that the pyroxenes could have crystallized after the olivines from a melt that was influenced by crustal He. Mg numbers recorded in mineral phases and MELTS modeling of the crystallization sequence lend support to this hypothesis. We note, however, that the MELTS-calculated temperature difference is small and direct crustal assimilation is not corroborated by radiogenic isotopes and trace element ratios of associated

lavas. A more likely scenario is that the lower closure temperature of the pyroxenes has allowed for diffusive He exchange with crustal He.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemgeo.2005.12.003](https://doi.org/10.1016/j.chemgeo.2005.12.003).

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