Discussion

Helium isotopes in historical lavas from Mount Vesuvius Comment on 'Noble gas isotopic ratios from historical lavas and fumaroles at Mount Vesuvius' by D. Tedesco et al.

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1. Introduction

Helium isotope results recently published by Tedesco et al. [1] appear to show a decrease in $^3He/^4He$ since 1631 AD at Mount Vesuvius. The authors proposed that this change is the result of a residual magma with a fractionated (low) $^3He/^4He$ ratio, produced by preferential degassing of ^3He during historical time. If such a process generally occurred in nature, it would seriously hinder our ability to characterize the $^3He/^4He$ ratio of mantle source regions. In proposing their model, Tedesco et al. [1] disregarded the previously published data of Graham et al. [2] which showed no change in $^3He/^4He$ with time at Vesuvius and implied that differences between the two studies result from different methods of gas extraction. In response, we have reanalyzed several of the critical samples by fusion. These new results are in complete agreement with our original analyses performed by crushing [2] and are completely at odds with any measurable change in the $^3He/^4He$ ratio of Vesuvius lavas since 1631 AD.

2. Results

Helium isotope results from our laboratory are reported in Table 1. The $^3He/^4He$ ratio has been measured in separated olivine and clinopyroxene crystals, both by crushing in vacuum and by fusion in a high temperature furnace following methods described previously [3]. Helium isotope ratios obtained by fusion agree within analytical uncertainty with values measured earlier by crushing [2] (Table 1), as expected for well-preserved, young lavas in which radiogenic or cosmogenic helium additions are negligible.

3. Discussion

The $^3He/^4He$ ratio vs. eruption age is shown for Mount Vesuvius lavas in Fig. 1. Fig. 1 illustrates that, for the older part of the historical record, there is clear disagreement between the results of Tedesco et al. [1] and those obtained in our lab. Significantly, in this part of the record, one of our samples (V4) is from the same 1631 AD lava analyzed by Tedesco et al. [1] and another (V17) is the same sample of the 1714 AD lava. There is also a systematic offset between our data set and that of Tedesco et al. in the younger samples. From 1886 to 1944, the data of Tedesco et al.

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Table 1
Helium isotopes in historical lavas of Mount Vesuvius

Sample	Date/location	Phase	Crushed			Melted		
			$^3He/^4He$ (R/R$_A$)	2σ$_m$	[He] (10^{-9} cm^3 STP/g)	$^3He/^4He$ (R/R$_A$)	2σ$_m$	[He] (10^{-9} cm^3 STP/g)
V4	1631 Torre del Greco	ol	2.42	0.06	76.7	–	–	–
		cpx	2.23	0.08	9.23	2.30	0.07	32.4
V17	1714 Massa del Carceriere	cpx	2.72	0.10	8.87	2.61	0.07	15.2
V74	1855	ol	–	–	–	2.46	0.40	14.9
	S. Sebastiano	cpx	2.48	0.18	1.68	–	–	–
V150	1906 Molara	cpx	2.60	0.08	17.7	–	–	–
V135b	1944 main flow	cpx	2.42	0.14	4.89	2.43	0.12	8.68
VN1	1944 Atrio del Cavallo	cpx	2.65	0.04	92.9	–	–	–

VN1 is a cumulate nodule: all other samples are lava flows. Crushing results are from Graham et al. [2]. Melting results are for mineral separates in the 0.25–0.85 mm size fraction.

show five of seven samples with $^3He/^4He \geq 2.9$ R$_A$ and no duplicate analyses were performed. In contrast, we have performed three duplicate analyses (clinopyroxene from 1631, 1714 and 1944) and all agree within analytical uncertainty. The mean $^3He/^4He$ of all Vesuvius analyses performed in our lab is 2.48 R$_A$ ± 0.30 (2 S.D.; $n = 11$).

It is not possible for us to fully determine the cause of the disagreement, but several points are relevant. Firstly, we have not measured any difference in $^3He/^4He$ ratio between gas extractions performed by crushing or by fusion. As expected for such young lavas, this eliminates the possibility

Fig. 1. $^3He/^4He$ ratio vs. eruption date for historical lavas from Mount Vesuvius. Bars show ±2 S.E.M. The shaded band shows the range of data (2.2–2.8 R$_A$) from this study and from Graham et al. [2].

that a significant component of cosmogenic ^3He is present. (When present, a cosmogenic ^3He component lies in the solid phase and in young rocks, it is released by fusion but not by crushing [4]). Secondly, we have not measured a significant difference in $^3He/^4He$ ratio between olivine and clinopyroxene crystals. Olivine shows a slightly higher $^3He/^4He$ ratio than clinopyroxene in the 1631 lava (just outside analytical uncertainty) and in the 1855 lava, it is identical to the coexisting clinopyroxene (although with a somewhat larger uncertainty due to the small amount of olivine available). Notably, each of these paired results lies between 2.2 and 2.8 R$_A$, within the range of the other analyses we have performed. This shows that analyses of bulk crystals at Vesuvius (olivine+clinopyroxene, as carried out by Tedesco et al. [1]) would not be expected to show variations due to changing mineral proportions, as might result from the mixing of deep and shallow magmas having different $^3He/^4He$ ratios.

The analytical procedures outlined by Tedesco et al. [1] indicate that He and Ne were not separated prior to helium isotope analysis. The presence of a Ne interference on the measured helium isotope ratio is well known (e.g. [5,6]) and led to the development of a cryogenic separation technique using activated charcoal [7,8]. Due to the much higher He/Ne ratio typically present in volcanic rocks and geothermal fluids relative to air, the lack of a He–Ne separation step may lead to measured $^3He/^4He$ ratios in volcanic samples that

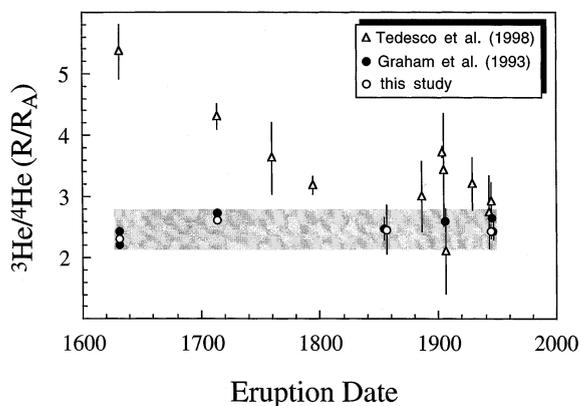are inaccurate by as much as 30% [9]. Furthermore, this effect is a very complicated function of the amount of He present, the He/Ne ratio and the tuning of the mass spectrometer ion source. While this effect probably does not fully explain the disagreement over Vesuvius samples, we note that our extraction procedure quantitatively separates He from Ne using a charcoal trap held at 38 K (adsorbing >99% of the Ne and <1% of the He), thereby minimizing any possible Ne interference on the measured ^{3}He/^{4}He ratio [10].

We have used both marine air as a standard (collected in Santa Barbara, CA, USA, and in Newport, OR, USA, respectively, for our crushing and fusion studies) as well as a geothermal gas (MM gas) collected from the Mud Volcano area of Yellowstone Park. This MM gas is used as a He isotope standard in four different laboratories (Scripps, NOAA/PMEL, Univ. of Rochester and CalTech) and is known to have a ^{3}He/^{4}He ratio of 16.45 R_A [5,10–12]. Splits of the MM standard in the size range of samples have been routinely analyzed during the course of both our crushing and fusion studies, to assure an accurate determination of the variation in mass discrimination with sample size; this variation is less than 3%.

There is currently no evidence in our data for a changing ^{3}He/^{4}He ratio in Mount Vesuvius historical lavas. If a residual magma with a highly fractionated ^{3}He/^{4}He ratio could be produced by preferential degassing of ^{3}He, it would have profound consequences for studies of the mantle origin of mid-ocean ridge, ocean island and subduction zone magmas. In numerous studies which have been carried out to date, there is no evidence for such a fractionation process. Wherever geothermal fluids and associated lavas have been analyzed for helium isotope composition, they have been shown to have similar ^{3}He/^{4}He ratios (examples include Loihi Seamount, Iceland, Reunion and Mount Etna [5,13–23]). *[CL]*

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Reply to 'Helium isotopes in historical lavas from Mount Vesuvius', a comment on 'Noble gas isotopic ratios from historical lavas and fumaroles at Mount Vesuvius' by D. Tedesco et al.

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Following the remarks by D.W. Graham and J.E. Lupton [1] about our paper on the He isotopes in historical lavas from Mount Vesuvius [2], one of us, P.S., has re-run at Scripps Institution of Oceanography, La Jolla, one of the Vesuvius samples previously analyzed.

The results of the experiment confirm the values obtained by Lupton and Graham in their first measurement [3] as well as that reported in this issue, in disagreement with those published by Tedesco et al. [2].

We report here the new data obtained with the methodology obtained at Scripps Oceanography.

The helium isotope ratio analysis has been made on a sample of lava belonging to the 1631 eruptive cycle of Mount Vesuvius. Approximately 0.75 g of pure clinopyroxene were hand picked from the crushed lava; adhering groundmass and alteration products were eliminated during microscopic inspection. The purified separates were cleaned ultrasonically in distilled water and acetone and dried at 100°C before crushing. Three crushing steps were performed under vacuum in the same conditions and for different times using a crusher on line. The gas extracted was then transferred in the inlet system of the mass spectrometer and the Ne was removed cryogenically in a charcoal trap at 34 K. The $^3He/^4He$ ratios and concentrations were measured statically on the double-collecting split-tube mass spectrometer GAD using the methodology described by Rison and Craig [4]. The measured isotope ratios were normalized to aliquots of a high $^3He/^4He$ (R/$R_A = 16.45$) standard gas (MM). ^3He was measured by ion counting with a Johnson electron multiplier and ^4He by collection in a Faraday cup.

Blanks averaged 0.17 nccSTP of ^4He.

Table 1 shows the results of the experiment carried out in La Jolla.

Table 2 shows the results obtained crushing under vacuum as well as the data obtained from different laboratories on the same sample.

Taking into account Graham and Lupton's comment, we have tried to find out the reasons for the discrepancy between the remeasured values and the data we have previously reported. As pointed out by Graham and Lupton, an important analytical difference exists and it should be definitely taken into account. It is a fact that we were not able to separate He from Ne prior to the analysis, and therefore a real possibility exists that

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Table 1

Results of the experiment carried out in La Jolla

Sample V5 (1631) Cpx (0.75 g)	Time (min)	^{3}He/^{4}He (R/R$_A$)	σ (±)	[He] (10^{-9} cm^3 STP/g)	[^{4}He] bulk (%)
	2	2.245	0.07	12.410	1.23
	5	2.306	0.34	3.240	3.53
	10	2.195	0.33	0.893	11.45
Total	17	2.245[a]	0.004[b]	16.540	–

[a]Weighted inversely to the analytical error.

[b]Calculated as uncertainty of the three measured ratios.

some amount of Ne may have influenced the helium isotopic ratio in the analysis.

Obviously, the interference of Ne on He analysis strongly depends on the relative abundance of both components, which means that the samples with low to very low He content will be affected more than the ^{4}He-rich samples. It is also a fact that samples with lower He content are the oldest of the Mt. Vesuvius eruptive cycle and therefore these have suffered more from the Ne interference. This would also explain the presence of a trend in the time sequence, reflecting the varying amount of contamination.

On the other hand, there is also the possibility of some memory effect of the mass spectrometer due to previous analyses of samples with helium isotopic ratios much higher than those belonging to Mt. Vesuvius. Obviously, memory effects, while negligible on ^{4}He-rich samples, are increasingly important on ^{4}He-low samples, specifically on the first samples of the series analyzed (i.e. the oldest lava samples).

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Table 2

Results obtained crushing under vacuum as well as the data obtained from different laboratories on the same sample

Sample	Phase	Laboratory	Method	^{3}He/^{4}He (R/R$_A$)	σ (±)	[He] (10^{-9} cm^3 STP/g)	Ref.
V4 (1631)	cpx	UCSB	crushing	2.23	0.08	9.23	[3]
V4 (1631)	cpx	NOAA/PMEL	melting	2.30	0.07	32.40	[1]
V4 (1631)	cpx	O.U.	melting	5.36	0.22	1.66	[2]
V4 (1631)	cpx	SIO-UCSD	crushing (3 steps)	2.245[a]	0.004[b]	16.54	

[a]Weighted inversely to the analytical error.

[b]Calculated as uncertainty of the three measured ratios.