



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Earth and Planetary Science Letters 219 (2003) 209–219

EPSL

www.elsevier.com/locate/epsl

U–Th/He age of phenocrystic garnet from the 79 AD eruption of Mt. Vesuvius

Sarah Aciego^{a,b,*}, B.M. Kennedy^a, Donald J. DePaolo^{a,b},
John N. Christensen^a, Ian Hutcheon^c

^a Earth Sciences Division, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^b Department of Earth and Planetary Science, University of California, Berkeley, CA 94720-4767, USA

^c Analytical and Nuclear Chemistry Division, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94551-0808, USA

Received 13 March 2003; received in revised form 1 August 2003; accepted 27 August 2003

Abstract

The U–Th/He system can potentially be used for dating volcanic rocks with ages as young as a few thousand years and as old as several million years, thus providing a valuable supplement to radiocarbon and K–Ar dating. Garnet phenocrysts from the 79 AD eruption of Mt. Vesuvius were dated to evaluate the accuracy with which the necessary measurements and corrections can be made. The determined age, corrected for diffusive loss of He, alpha ejection, and initial U-series disequilibrium, is 1885 ± 188 yr which compares well with the known age of 1923 yr. U and Th concentrations were measured by isotope dilution on different aliquots than were used for He concentration measurements. Step-wise degassing yielded an Arrhenius relationship for He diffusion in garnet with an activation energy of 91.31 ± 5.76 kJ/mol and $\ln D_0/a^2 = -2.00 \pm 0.56$. The uniformity of U and Th concentrations in garnet was checked by ion microprobe analysis. The $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios were measured by MC-ICPMS. The results suggest that with proper analysis and corrections, the U–Th/He method can be used to date young volcanic minerals with useful precision and accuracy, and may therefore be valuable for dating volcanic rocks that have low K or are otherwise difficult to date accurately with Ar–Ar or radiocarbon.

© 2003 Elsevier B.V. All rights reserved.

Keywords: garnet; Vesuvius; U–Th/He dating; Quaternary; volcanic rocks; uranium disequilibrium

1. Introduction

Determining the age of geological events that have occurred within the past million years is still a challenge in many circumstances [1–3]. Radiocarbon is applicable to ages less than about 40 000 years, but only where organic carbon is present. Despite considerable progress, few techniques are broadly applicable and reliable for ages beyond the ^{14}C limit but still within the late Quaternary

* Correspondence author. Tel.: +1-510-642-9116.

E-mail addresses: aciago@eps.berkeley.edu (S. Aciego),
bmkenedy@lbl.gov (B.M. Kennedy),
depaolo@eps.berkeley.edu (D.J. DePaolo),
jnchristensen@lbl.gov (J.N. Christensen), hutcheon1@llnl.gov (I. Hutcheon).

time period. Advances in the sensitivity of Ar–Ar dating have made the technique applicable in some circumstances down to ages of a few thousand years [4,5]. Other techniques that can be used in favorable circumstances include U–Th disequilibrium [6,7], cosmogenic nuclide dating of surfaces [8], and ion microprobe measurements of zircon [9].

The U–Th/He method, first proposed by Rutherford in 1905 [10], has considerable potential for dating Quaternary events. The technique was investigated many years ago but abandoned when the initial evaluations produced ages that were anomalously young [11]. Recently, the method has been re-evaluated with modern instrumentation and appropriate models for data reduction [12–16]. Noble gas mass spectrometers and sample preparation lines designed for helium isotope analyses now have a low enough background that samples as young as 1000 years with as little as 1 ppm U could be datable. Work on the U–Th/He technique has so far focused primarily on U–Th-rich minerals, such as apatite and titanite, from which a great deal has been learned regarding helium diffusivity, closure temperatures, and ^4He loss and/or gain associated with the ca. 20 μm range of the 4–8 MeV alpha particles released during decay [13–15]. Complementary diffusion studies have been directed at investigating the He retentivity of olivine, pyroxene, and garnet to determine the extent of preservation of noble gas isotopic signatures [17–20]. The indications are that the U–Th/He system should be a viable tool for dating young volcanic rocks that contain apatite, titanite, and possibly other minerals. The low closure temperatures of apatite and zircon make them ideal for studying the low temperature thermal history of young igneous rocks. Zircon has been used to determine the eruption age of a sample that has a well-constrained thermal history [21]. However, most volcanic rocks do not contain minerals that have been previously used for U–Th/He thermochronology, and the He retentivities of volcanic minerals are not well documented.

The goal of this study is to investigate the viability of applying the U–Th/He dating method to Quaternary volcanic rocks. The approach is to

determine the age of historical lava of known age. Several issues need to be addressed in order to evaluate the method. For very young rocks with low U and Th, background interference related to the mass spectrometric methods could be significant. More generally, there may be substantial corrections that must be applied to account for trapped helium, helium diffusion, alpha ejection, and U-series disequilibrium. It is unknown whether these corrections can be done sufficiently accurately to obtain useful age information.

We present He concentration data, U and Th concentration data, U and Th isotopic data, and U and Th distribution data for phenocrysts of garnet from the 79 AD eruption of Vesuvius [4]. The age of this eruption, which was responsible for destroying the town of Pompeii, is well established and at the time of the current work is 1923 yr. Our data are used to produce an age determination by incorporating models for diffusion and alpha ejection, and data on U-series isotopic disequilibrium. The activation energy and frequency factor for He diffusion in the garnet phenocrysts is also measured, as well as the intragrain distribution of U and Th documented. Initially, we intended to use the garnet phenocrysts to establish the age limits of the U–Th/He technique for minerals with low U and Th concentrations (~ 1 ppm) and high helium retentivity, because garnet crystals normally are U- and Th-poor. However, the Vesuvius garnets have high U and Th concentrations (~ 20 ppm). Addressing the geochronological value of minerals with low U and Th concentrations remains a problem for future work.

2. Samples and analytical techniques

Garnet grains were separated from white pumice [4] using magnetic separation, gravitational separation and handpicking techniques. The samples were sieved to 500–1000 μm in maximum dimension. The sample was divided into five aliquots totaling 4 g. Two aliquots were used for helium concentration measurements. A third aliquot was used to measure helium diffusivity. The remaining aliquots were subdivided and used for

U, Th, and Ba concentrations, U and Th isotopic data, major element analysis, and a grain mount for studying the U, Th distribution within a garnet crystal using ion microprobe techniques.

To measure both the initial or trapped helium and the radiogenic helium, three separate aliquots of garnet were used. The initial or trapped helium component was isolated by in vacuo crushing of a 0.5 g sample for 5 min using a manual mortar and pestle attached to a vacuum line. Two 1 g aliquots of garnet grains contained in aluminum capsules were heated in a furnace to determine the radiogenic helium component. The heating procedure included holding the samples for 30 min at

1500°C; the total heating and cooling time was 1 h. A second extraction was done at 1650°C to determine whether all of the helium had been released.

The heating procedure used was based on previous work [20] that suggests a closure temperature of 1100°C for (Ca-poor) garnet. Because of the high closure temperature, which we assumed would apply to our sample, complete extraction requires heating to a temperature well above the closure temperature and into the melting range. Consequently we were unable to retrieve the samples after He extraction, which necessitated using separate aliquots for the U and Th concentration

Table 1
He extraction data for aliquots Cr, 1, B, A

Sample AM1	Weight (g)	[⁴ He] (10 ⁻¹² cm ³ STP/g)	1σ ^a	Blank ^b (%)	[³ He/ ⁴ He] (R/R _a)	1σ
Split Cr						
Crush	0.6600	154.55	10.83	20	-1.63	20.81
1500°C extraction	0.4235	3520.97	246.79	4	0.76	0.39
1500°C re-extraction		-35.30	-3.45	128	-35.31	85.09
Total		3640.22	506.56			
Split 1						
1500°C extraction	1.0237	4149.98	291.08	2	1.66	0.24
1500°C re-extraction		5.80	0.90	92	154.18	135.91
Total, crush subtracted		4001.23	291.28			
Split B						
600°C extraction	1.0535	611.09	42.83	17	2.29	0.92
1500°C extraction		3204.29	224.97	2	1.47	0.63
1500°C re-extraction		36.84	2.73	65	45.28	5.36
Total, crush subtracted		3697.66	229.28			
Split A						
600°C extraction	0.9509	372.50	26.25	15	0.56	1.51
600°C extraction, crush subtracted		217.94	70.84			
800°C extraction		1009.94	46.18	6	0.82	0.61
900°C extraction		658.57	30.24	10	0.83	0.92
1000°C extraction		425.00	39.79	14	0.21	1.43
1100°C extraction		566.76	41.87	11	1.36	0.97
1200°C extraction		596.82	4.67	11	0.96	1.05
1300°C extraction		57.96	3.50	56	11.54	9.92
1500°C extraction		36.75	110.11	68	-2.38	14.84
Total		3569.74	347.19			
Average for age calculation		3727.22	190.02 ^c			

^a 1σ errors are propagated to include errors in sensitivity, cryofinger adsorption efficiency, and blank subtraction.

^b Concentration data has been blank corrected, typical blanks are $\sim 5 \times 10^{-11}$ cm³ STP/g.

^c 1σ is the standard deviation of the concentration data, Gaussian error propagation of the mean results in $1\sigma = 179.3 \times 10^{-12}$ cm³ STP/g.

determinations [20]. To investigate the diffusion characteristics of the Vesuvius garnets a separate aliquot (~ 1 g) was outgassed over 7 temperature steps ranging from 600°C to 1300°C, with a final 1500°C step for complete extraction. Extraction temperatures were established with an accuracy of $\pm 10^\circ\text{C}$ using a thermocouple in contact with the heated crucible.

After extraction, the released gases are purified on a series of getters, and a small aliquot is admitted to the mass spectrometer for analysis of all the noble gases to determine relative abundances. The remaining purified noble gas fraction is adsorbed onto a charcoal trap held at 30 K. The activated coconut charcoal used in the trap has a He adsorption efficiency of $89 \pm 7\%$ at 30 K. Following an adequate adsorption time, the trap is heated to 40 K, releasing the adsorbed He, which is expanded into the mass spectrometer for analysis. Adsorption on the charcoal trap introduces some uncertainty to the measured He amounts, but eliminates uncertainties that would come from estimating the volumes of the sample purification and mass spectrometric systems. The trap also improves the procedural sensitivity by approximately a factor of three. The isotopic and abundance analyses were made using a VG5400 mass spectrometer equipped with a Faraday cup and an electron multiplier operated in ion pulse-counting mode. The abundance measurement was calibrated using an aliquot of air and a reference sample of He as standards run before and after the set of samples. Procedural blanks for the furnace extractions were $\sim 5 \times 10^{-11}$ cm³ STP and significant only for the re-extraction analyses.

The helium concentration data are corrected for procedural blanks measured prior to each sample analysis. The ⁴He blanks were typically $< 15\%$ of the total helium. The tabulated 1σ errors in the ⁴He concentrations and ³He/⁴He ratios (Table 1) contain uncertainties associated with peak height measurements, blank corrections, corrections for mass spectrometer fractionation, and cryogenic trap efficiency, which have been propagated by quadratic expansion. The ⁴He released during in vacuo crushing (155×10^{-12} cm³ STP/g) represents ~ 3.7 – 4.3% of the total ⁴He released during

sample fusion and is accompanied by a small, indeterminate amount of ³He (³He/⁴He ~ -1.65 Ra, blank corrected). In calculating the He concentrations, we corrected the fusion data for trapped helium by subtracting the blank-corrected total ⁴He released during crushing from the total ⁴He released during sample fusion for each fused split.

For the uranium and thorium concentration and isotopic measurements, ~ 30 mg splits of garnet and crushed whole rock were dissolved in a nitric-HF mixture. Aliquots of the dissolved samples were spiked with ²²⁹Th and ²³³U. Unspiked aliquots were analyzed for ²³⁴U/²³⁸U and ²³⁰Th/²³²Th ratios. Isolation of U and Th was accomplished using Tru-Spec column resin following established procedures [22]. Uranium and thorium isotopic compositions of spiked and unspiked aliquots were measured on a Micromass IsoProbe, MC-ICPMS. Samples were introduced to the instrument using a CETAC Aridus desolvation system. For spiked samples, mass fractionation was corrected using bracketing measurements of a natural uranium in-house standard. The estimated uncertainty in the measured concentrations is $< 0.5\%$. ²³⁴U/²³⁸U and ²³⁰Th/²³²Th of unspiked aliquots were measured using separate static routines that placed ²³⁴U and ²³⁰Th on the Daly photomultiplier ion counting system, while ²³⁵U, ²³⁸U, and ²³²Th were measured on Faraday cups. The measured ²³⁵U/²³⁸U of the sample was used for internal mass fractionation correction. Measurements of a secular equilibrium U in-house standard provided calibration of the ion-counting system. The ion-counting system is situated behind a wide aperture retarding potential filter, providing an abundance sensitivity (mass 237 compared to mass 238) of better than 100 ppb. Measured ²³⁰Th/²³²Th was combined with Th and U concentrations to provide ²³⁰Th/²³⁸U activity ratios. Ba was measured in dissolved splits of garnet and powdered whole rock by standard ICP-AES techniques. Uranium, thorium, and barium results are given in Table 2. The U and Th concentrations were also measured by ion probe to determine the level of homogeneity within garnet grains, because alpha recoil corrections are sensitive to the distribution of the parent nuclides within the mineral [21,23].

Table 2
U, Th, and Ba concentrations, U-series activity ratios

Sample AM1	Weight U (mg)	U (ppm)	1 σ	Th (ppm)	1 σ	Th/U	1 σ	$\left[\frac{^{230}\text{Th}}{^{232}\text{Th}}\right]_{\text{act}}$	1 σ	$\left[\frac{^{234}\text{U}}{^{238}\text{U}}\right]_{\text{act}}$	1 σ	$\left[\frac{^{230}\text{Th}}{^{238}\text{U}}\right]_{\text{act}}$	1 σ (ppm)	Ba	1 σ
Garnet split E	27.50	19.02	0.04	27.71	0.06	1.46	0.003	0.89	0.001	1.00	0.001	0.43	0.007		
Garnet split F	23.00	16.24	0.03	23.45	0.05	1.44	0.003	0.89	0.001	1.00	0.001	0.42	0.007		
Garnet split K	114.07													7.890	0.394
Whole rock split WR	67.89	16.03	0.03	32.65	0.07	2.04	0.004	0.90	0.001	1.01	0.001	0.58	0.009	76.594	3.830
Garnet average for age calculation		17.63	1.39	25.58	2.13	1.45	0.002	0.89	0.001	1.00	0.001	0.42	0.005	7.89	0.39

3. Results

3.1. He, U and Th concentrations in garnet

The ^4He concentration in garnet was determined by averaging four different determinations on separate aliquots of garnet grains (Table 1). The measurement of four different aliquots gives us a means of estimating the variability and, hence, the uncertainty in the determined value. The measured values vary from 3570 to $4001 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$, and the weighted average is $3727 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$, with a standard deviation of $1\sigma = 190 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$. Quadratic expansion error propagation yields an uncertainty in the mean of $1\sigma = 179 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$. The similar size of the two errors indicates that they are reasonable estimates. The uncertainty of approximately $\pm 6\%$ is two to three times larger than other careful measurements of He concentration by isotope dilution found in the literature [14–16,21], and may be inflated due to variations in U and Th concentration, as noted below.

The concentrations of U and Th in the two splits that were measured differ by about 15% (Table 2). The Th/U ratio is much less variable, showing only a little more than 1% difference between the two analyses. The results of an ion probe traverse of a garnet grain (Fig. 1) with a maximum dimension of about 1 mm are shown in Fig. 2. The U and Th concentration in garnet, determined by ion probe, are 40% lower than the average of the two aliquots that were measured by isotope dilution mass spectrometry. This difference further emphasizes the variability in U and Th concentrations. Considering that the ion probe results represent only one grain, the 40% difference is not inconsistent with the observation that 50–100 grains included in the two aliquots yielded a 15% difference in concentration. More importantly, the ion probe traverse shows no indication that the U and Th concentrations are particularly high or low near the grain edges, which means that an assumption of uniform distribution within the grains for the purposes of estimating recoil and diffusive losses of helium is adequate.

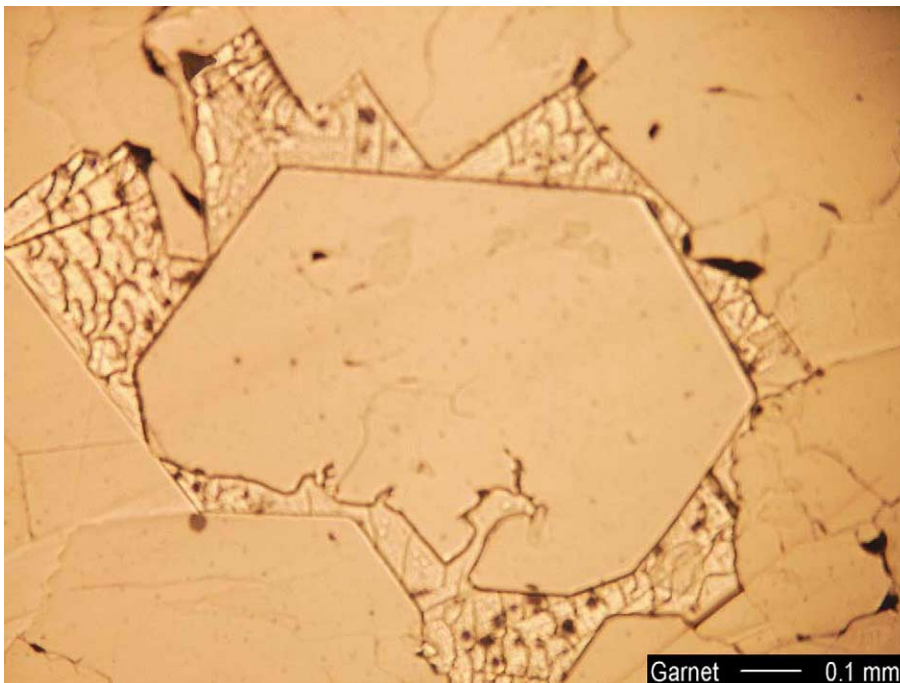


Fig. 1. Photomicrograph of single garnet grain used for U and Th ion probe analysis.

3.2. Correction for alpha ejection and implantation

The helium concentration measurements must be corrected for the fact that the helium produced by radioactive decay starts out as alpha particles that are ejected from the decaying nuclei with energies of 4–8 MeV. Stopping distances were calculated using range data for pure elemental targets [24] and a garnet composition determined by electron microprobe techniques of $\text{Ca}_{2.87}\text{Mn}_{0.08}\text{Al}_{0.97}\text{Fe}_{1.27}\text{Ti}_{0.20}\text{Si}_3\text{O}_{12}$ (see [13]). Alpha emission corrections are based on models for spherical grain geometry and a homogeneous distribution of the parent atoms [25,13]. Based on the ion probe analyses, the concentrations of the parents do not vary by more than a factor of two, significantly less than the order of magnitude variations in parent U and Th needed to affect the ejection calculation [23]. We assume that the concentrations of U and Th in the groundmass are equal to the concentrations measured for the whole rock. The total fractional excess of alphas in the garnet grains is calculated to be $F_T = 1.001 \pm 0.005$. The alpha ejection correction is therefore

insignificant, considering the other sources of uncertainties in He, U, and Th concentrations.

3.3. Correction for diffusive loss of helium

To estimate the diffusive loss of helium we first determined the diffusivity of helium in the Vesu-

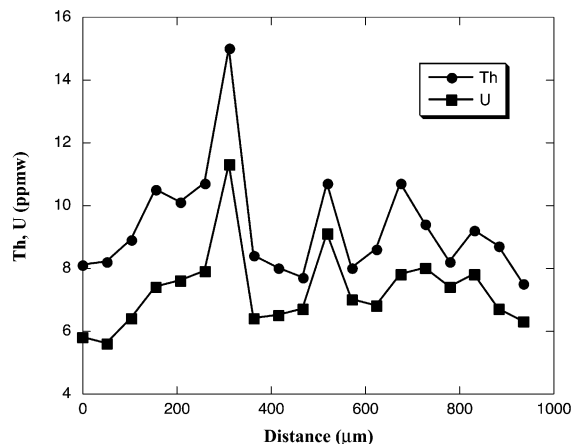


Fig. 2. U, Th distribution in garnet grain (from Fig. 1).

Table 3
Results of step-heating runs for diffusion profile

T (°C)	Duration (s)	^4He (pmol/g)	F^{Hea} (%)	$\ln D/a^2^b$
600	2700	217.94	6.11	−15.93
800	2700	1009.94	28.29	−12.26
900	2700	658.57	18.45	−11.25
1000	2700	425.00	11.91	−10.72
1100	2700	566.76	15.88	−10.05
1200	2700	596.82	16.72	−9.05
1300	2700	57.96	1.62	−8.78
Final extraction	2700	36.75	1.03	
Total		3569.74		

^a Fractional loss in percent, $0 \leq F^{\text{He}} \leq 100$.

^b Calculated using measured values of F^{He} and equations in [25].

vius garnets. The helium diffusivity determination is based on the step-wise degassing of Split A (Tables 1 and 3) and the equations for diffusion from a homogeneous sphere [25]. The data follow an Arrhenius relationship (Fig. 3). We subtracted the total ^4He released during sample crushing from the 600°C step to calculate the total ^4He released due to heating, and then used the 800–1300°C steps to determine the diffusivities. Up to the 1300°C step, the diffusivity remains linear. A least squares regression line, based on the error-weighted data points for the 800–1300°C extractions, yields a value for E_a , the activation energy, of 91.31 ± 5.76 kJ/mol and a frequency factor, $\ln D_0/a^2$, of -2.00 ± 0.56 .

The garnet helium concentration is corrected for diffusive loss [18] assuming a maximum mean annual temperature of 35°C and a calculated $D/a^2 = 1.40 \times 10^{-9} \pm 0.086 \times 10^{-9}$ for garnets with typical diameters of 1 mm. This value corresponds to less than 1% helium loss over the age of the sample, and is therefore marginally significant. The error in the diffusivity of $\sim 6\%$ adds additional uncertainty to the fractional loss of helium due to diffusion, F_{diff} , such that $F_{\text{diff}} = 0.004 \pm 0.0003$. A solution to the production–diffusion equation that includes the effect of alpha ejection from the mineral has also been determined [26], but we can ignore this effect because the magnitudes of diffusive loss and alpha ejection are insignificant for the Vesuvius garnets.

3.4. Corrections for U-series disequilibrium

The rate of production of helium from alpha decays in the U and Th decay series depends on the concentrations of each of the intermediate daughters as well as on the concentrations of ^{238}U and ^{232}Th . If the age of the sample is much greater than the mean life of the longest-lived intermediate daughter, then the concentrations of the intermediates can be assumed to ad-

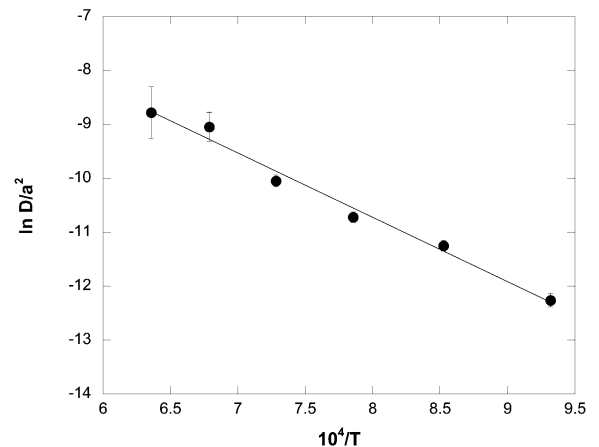


Fig. 3. Arrhenius diagram for diffusion coefficients across a range of temperatures. The error bars show the propagated errors in D/a^2 . The slope of the regression line (not the error weighted best fit line) is proportional to E_a (the activation energy) = 91.31 ± 5.76 kJ/mol and the Y -intercept is proportional to $\ln D_0$ (the frequency factor) = -2.00 ± 0.56 .

here to the secular equilibrium values. Compared with the age of the Vesuvius sample (1923 yr), most of the intermediate daughters are short-lived and hence attained secular equilibrium with their immediate parent nuclides rapidly after the eruption. The exceptions are ^{234}U (248 kyr), ^{230}Th (75 kyr), and ^{226}Ra (1622 yr). We have measured the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios of garnet (Table 2), so for these terms the corrections can be made accurately. For the $^{226}\text{Ra}/^{230}\text{Th}$ activity ratio, we have made measurements of the Ba/Th ratios of both garnet and whole rock as a guide, but use available information on crystal residence times [27] to argue that the initial $^{226}\text{Ra}/^{230}\text{Th}$ of the garnet phenocrysts was the secular equilibrium value.

The correction for ^{230}Th – ^{238}U radioactive equilibrium is done using the equation of Farley et al. [21], which we write in the form:

$${}^4\text{He} = P_{\text{se}}(\text{U}, \text{Th})(1 + F_{\text{dis}}) \quad (1)$$

where:

$$P_{\text{se}}(\text{U}, \text{Th}) = 7(^{235}\text{U})e^{\lambda_{235}t} + 6(^{232}\text{Th})e^{\lambda_{232}t} + 2(^{238}\text{U})e^{\lambda_{238}t}$$

is the production rate of ${}^4\text{He}$ expected for a system at U-series radioactive equilibrium, and:

$$F_{\text{dis}} = \frac{1}{P_{\text{se}}(\text{U}, \text{Th})} \left\{ 6D_{230} \left(\frac{\lambda_{238}}{\lambda_{230}} \right) (^{238}\text{U})e^{\lambda_{238}t} (1 - e^{-\lambda_{230}t}) + 6(^{238}\text{U})e^{\lambda_{238}t} \left[\left(\frac{1}{\lambda_{238}} \right) (1 - e^{-\lambda_{238}t}) + \left(\frac{1}{\lambda_{230}} \right) (e^{-\lambda_{230}t} - 1) \right] \right\}$$

is the correction factor for departures from equilibrium. The terms ${}^4\text{He}$, ^{235}U , ^{232}Th , and ^{238}U refer to concentrations, the λ 's are decay constants, and $D_{230} = ^{230}\text{Th}/^{238}\text{U}$. Based on our analyses of U and Th concentrations in garnet and whole rock, we calculate that the value of the correction factor F_{dis} is 0.498 ± 0.004 .

We use Ba/Th data as a guide to the behavior of $^{226}\text{Ra}/^{230}\text{Th}$, because Ra and Ba have similar chemical behavior in silicate systems [28,29]. The data (Table 2) indicate that garnet initially crystallized from the Vesuvius magma with a large deficiency of ^{226}Ra relative to ^{230}Th , because the Ba/Th ratio of garnet is about eight times smaller

than that of the whole rock. However, it is common for lavas of the Roman magmatic province to have excess ^{226}Ra on eruption [27], so the ^{226}Ra deficit in the garnet relative to the secular equilibrium value probably would have been smaller than suggested by the Ba/Th data. Black et al. [27] also give evidence that typical crystal residence times are greater than 10^4 years, which is several half-lives of ^{226}Ra . Hence, it is a reasonable assumption that ^{226}Ra and ^{230}Th were close to secular equilibrium in garnet at the time of eruption, and therefore no correction beyond that represented by Eq. 1 is necessary.

3.5. Age and uncertainty calculations

The calculated age of the garnet sample is determined from the equation:

$$\text{age} = \frac{{}^4\text{He}(1 - F_{\text{diff}})F_{\text{T}}}{P_{\text{se}}(\text{U}, \text{Th})(1 + F_{\text{dis}})}$$

The measurements of He, U, and Th concentrations determine the factors ${}^4\text{He}$ and $P_{\text{se}}(\text{U}, \text{Th})$. As noted above, the correction factors are $F_{\text{diff}} = 0.004 \pm 0.0003$, $F_{\text{T}} = 1.001 \pm 0.005$ and $F_{\text{dis}} = 0.498 \pm 0.004$. The calculated age and uncertainty from this equation is 1885 ± 188 yr and is quite close to the actual age of 1923 yr. Table 4 shows the effects on the calculated age and uncertainty of the three correction factors. The major correction to the age is due to $^{230}\text{Th}/^{238}\text{U}$ disequilibrium, which increases the calculated age by about 50% relative to the raw age.

The uncertainty in the age determination is of considerable interest in that it helps define the ultimate broader applicability of the technique. The main sources of error are the uncertainties

Table 4
Calculated He ages

Sample AM1	Age (yr)	1 σ
Raw	1291	129
Corrected for ejection	1290	129
Corrected for diffusion	1291	129
Disequilibrium raw	1880	188
Disequilibrium corrected for ejection	1878	188
Disequilibrium corrected for diffusion	1885	188

in the helium concentration, which is about $\pm 6\%$ of the total at the 1σ level, and the uncertainty in the U and Th total concentration, which is about $\pm 8\%$ at the 1σ level, as estimated from the two determinations. If we assume that the two parameters are uncorrelated, then the total uncertainty in the age determination is about $\pm 10\%$. The effect of an error in the assumed ^{226}Ra – ^{230}Th equilibrium is such that if the $^{226}\text{Ra}/^{230}\text{Th}$ ratio were lower (or higher) than the equilibrium value by 20% it would increase (or decrease) the calculated age by about 50 yr. There is a substantial likelihood that the He concentration variations are correlated with the U and Th concentration variations, which would tend to reduce the age uncertainty to a value less than 10% of the age. Adding in all of the potential sources of error, we estimate the overall age and uncertainty based on our analyses as 1885 ± 188 yr, but recognize that the uncertainty might be smaller if the heterogeneity in U and Th concentrations could be eliminated by measurement of He, U and Th concentrations on the same aliquots of garnet.

The age and uncertainty yielded by our U–Th/He results on garnet are compared in Fig. 4 with Ar–Ar determinations on sanidine phenocrysts [4]. Both the U–Th/He and Ar–Ar ages (1885 versus 1925) are close to the known age of the eruption. The uncertainties are also comparable, insofar as Renne et al. [4] were able to decrease the overall uncertainty of their age by pooling a number of individual analyses. The size of the uncertainties ($\pm 6\%$ to $\pm 10\%$ of the age) are larger

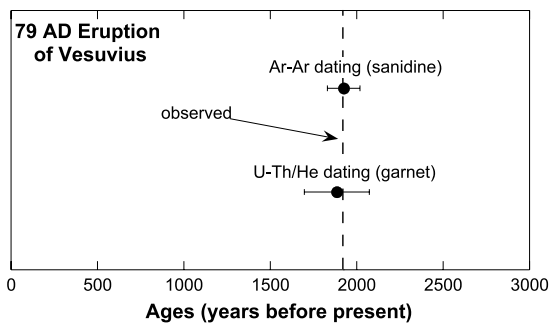


Fig. 4. Comparison of ages calculated using Ar–Ar dating and U–Th/He dating, with age determined by observations of Pliny the Younger.

than can be achieved with radiocarbon under favorable circumstances, but are more than adequate for many geological applications.

Extrapolating our results to other types of rocks and minerals raises a number of issues that still must be addressed. The data analysis will be somewhat simplified for rocks that are older than about 20000 years, because the Ra disequilibrium correction is negligible, and corrections are needed only for U and Th intermediate daughters. For rocks with relatively large amounts of radiogenic helium, the helium concentration can be measured by isotope dilution to a better accuracy [21], but the uncertainties associated with ejection/implantation and diffusive loss are likely to be larger. With isotope dilution, one must assume that the sample contains no indigenous (trapped) helium; that assumption is likely to be inadequate for some volcanic samples in which the trapped component can be as high as 10^{-7} cm³ STP/g [30]. In our case, the trapped component accounts for a few percent of the total helium, which is small but still significant. In general, trapped helium must be accounted for in young samples with low U and Th concentrations. To accurately determine the fraction of radiogenic ⁴He, it will be necessary to measure the ³He/⁴He ratio in both the crushing and step-heating released helium; therefore isotope dilution techniques will not be viable for these samples.

4. Conclusions

Garnet phenocryst samples from the 79 AD eruption of Mt. Vesuvius witnessed by Pliny the Younger were dated using the U–Th/He method. The resultant age of 1885 ± 188 yr, which includes a large correction for U–Th isotopic disequilibrium, is within 2% of the correct age and hence indicates that the U–Th/He method is applicable to dating Holocene volcanic samples accurately and with 1σ precision of ca. 10%. A significant source of error in our age calculation comes from measuring U, Th and He on separate aliquots; future work will address this issue. The results presented here are encouraging in that they validate the correction due to U-series iso-

topic disequilibrium, but they do not address the efficacy of the diffusion and alpha ejection/implantation corrections because those corrections are negligible for the samples studied. The Vesuvius garnets are also advantageous in that they combine a high He production rate (from unexpectedly high U and Th concentrations in garnet), and exceptionally good helium retentivity. Other available volcanic phenocryst minerals do not typically have both of these favorable characteristics. On the other hand, the Vesuvius samples are young. Samples with older ages (100 ka to 2 Ma) contain much larger amounts of radiogenic helium for the same amount of U and Th, and radioactive disequilibrium corrections are less important.

Acknowledgements

This research was supported by the Director, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division of the U.S. Department of Energy under Contract No. De-AC03-76SF00098. We thank Paul Renne of the Berkeley Geochronology Center for providing the sample. The ion microprobe analyses were performed under the auspices of the U.S. Dept. of Energy by the University of California, Lawrence Livermore National Laboratory under contract number W-7405-ENG-48. Peter Zeitler and Stan Williams are partly responsible for our involvement in this work. *[KF]*

References

- [1] J.S. Noller, J.M. Sowers, W.R. Lettis, Quaternary Geochronology, Methods and Applications, Am. Geophys. Union, Washington, DC, 2000, 582 pp.
- [2] S.R. Getty, D.J. DePaolo, Quaternary geochronology using the U-Th-Pb method, *Geochim. Cosmochim. Acta* 59 (1995) 3267–3272.
- [3] W.D. Sharp, B.D. Turrin, P.R. Renne, M.A. Lanphere, The Ar-40/Ar-39 and K/Ar dating of lavas from the Hilo 1-km core hole, Hawaii scientific drilling project, *J. Geophys. Res. Solid Earth* 101 (1996) 11607–11616.
- [4] P.R. Renne, W.D. Sharp, A.L. Deino, G. Orsi, L. Civetta, Ar-40/Ar-39 dating into the historical realm: Calibration against Pliny the Younger, *Science* 277 (1997) 1279–1280.
- [5] P.R. Renne, K-Ar and ⁴⁰Ar/³⁹Ar dating, in: J.S. Noller, J.M. Sowers, W.R. Lettis (Eds.), Quaternary Geochronology, Methods and Applications, Am. Geophys. Union, Washington, DC, 2000.
- [6] M. Condomines, Dating recent volcanic rocks through Th-230-U-238 disequilibrium in accessory minerals: Example of the Puy de Dome (French Massif Central), *Geology* 25 (1997) 375–378.
- [7] A. Heumann, G.R. Davies, U-Th disequilibrium and Rb-Sr age constraints on the magmatic evolution of peralkaline rhyolites from Kenya, *J. Petrol.* 43 (2002) 557–577.
- [8] M.G. Zreda, F.M. Phillips, Cosmogenic nuclide buildup in surficial materials, in: J.S. Noller, J.M. Sowers, W.R. Lettis (Eds.), Quaternary Geochronology, Methods and Applications, Am. Geophys. Union, Washington, DC, 2000.
- [9] J.R. de Laeter, Mass spectrometry geochronology, *Mass Spectrom. Rev.* 17 (1998) 97–125.
- [10] E. Rutherford, Present problems in radioactivity, *Pop. Sci.* May 1–34 (1905).
- [11] P.M. Hurley, The helium age method and the distribution and migration of helium in rocks, in: H. Faul (Ed.), Nuclear Geology, Wiley, New York, 1954.
- [12] P.K. Zeitler, A.L. Herczeg, I. McDougall, M. Honda, U-Th-He dating of apatite - a potential thermochronometer, *Geochim. Cosmochim. Acta* 51 (1987) 2865–2868.
- [13] K.A. Farley, R.A. Wolf, L.T. Silver, The effects of long alpha-stopping distances on (U-Th)/He ages, *Geochim. Cosmochim. Acta* 60 (1996) 4223–4229.
- [14] R.A. Wolf, K.A. Farley, L.T. Silver, Helium diffusion and low-temperature thermochronometry of apatite, *Geochim. Cosmochim. Acta* 60 (1996) 4231–4240.
- [15] P.W. Reiners, K.A. Farley, Helium diffusion and (U-Th)/He thermochronometry of titanite, *Geochim. Cosmochim. Acta* 63 (1999) 3845–3859.
- [16] K.A. Farley, Helium diffusion from apatite General behavior as illustrated by Durango fluorapatite, *J. Geophys. Res. Solid Earth* 105 (2000) 2903–2914.
- [17] H.J. Lippolt, E. Weigel, He-4 diffusion in Ar-40-retentive minerals, *Geochim. Cosmochim. Acta* 52 (1988) 1449–1458.
- [18] T.W. Trull, M.D. Kurz, W.J. Jenkins, Diffusion of cosmogenic He-3 in olivine and quartz - implications for surface exposure dating, *Earth Planet. Sci. Lett.* 103 (1991) 241–256.
- [19] T.W. Trull, M.D. Kurz, Experimental measurements of He-3 and He-4 mobility in olivine and clinopyroxene at magmatic temperatures, *Geochim. Cosmochim. Acta* 57 (1993) 1313–1324.
- [20] T.J. Dunai, K. Roselieb, Sorption and diffusion of helium in garnet: Implications for volatile tracing and dating, *Earth Planet. Sci. Lett.* 139 (1996) 411–421.
- [21] K.A. Farley, B.P. Kohn, B. Pillans, The effects of secular disequilibrium on (U-Th)/He systematics and dating of Quaternary volcanic zircon and apatite, *Earth Planet. Sci. Lett.* 201 (2002) 117–125.
- [22] X.Z. Luo, M. Rehkamper, D.C. Lee, A.N. Halliday, High

- precision Th-230/Th-232 and U-234/U-238 measurements using energy-filtered ICP magnetic sector multiple collector mass spectrometry, *Int. J. Mass Spectrom. Ion Process.* 171 (1997) 105–117.
- [23] A. Meesters, T.J. Dunai, Solving the production-diffusion equation for finite diffusion domains of various shapes. Part 11. Application to cases with alpha-ejection and non-homogeneous distribution of the source, *Chem. Geol.* 186 (2002) 347–363.
- [24] J.F. Ziegler, *Helium: Stopping Powers and Ranges in All Elemental Matter*, Pergamon Press, New York, 1977, 367 pp.
- [25] H. Fechtig, S. Kalbitzer, The diffusion of argon in potassium-bearing solids, in: O.A. Schaeffer, J. Zahringer (Eds.), *Potassium Argon Dating*, Springer, Berlin, 1966, pp. 68–107.
- [26] A. Meesters, T.J. Dunai, Solving the production-diffusion equation for finite diffusion domains of various shapes. Part 1. Implications for low-temperature (U-Th)/He thermochronology, *Chem. Geol.* 186 (2002) 333–344.
- [27] S. Black, R. Macdonald, B. DeVivo, C.R.J. Kilburn, G. Rolandi, U-series disequilibria in young (AD 1944) Vesuvius rocks: Preliminary implications for magma residence times and volatile addition, *J. Volcanol. Geotherm. Res.* 82 (1998) 97–111.
- [28] R.W. Williams, J.B. Gill, Ra-Th disequilibria systematics Timescale of carbonatite magma formation at Oldoinyo Lengai volcano, Tanzania, *Geochim. Cosmochim. Acta* 50 (1986) 1249–1259.
- [29] M.D. Feineman, D.J. DePaolo, Steady-state $^{226}\text{Ra}/^{230}\text{Th}$ disequilibrium in mantle minerals: Implications for melt transport rates in island arcs, *Earth Planet. Sci. Lett.* 215 (2003) 339–355.
- [30] D.W. Graham, Noble gas isotope geochemistry of mid-ocean ridge and ocean island basalts: characterization of mantle source reservoirs, in: D. Porcelli, C.J. Ballentine, R. Wieler (Eds.), *Noble Gases in Geochemistry and Cosmochemistry*, *Reviews in Mineralogy and Geochemistry* 47, The Mineralogical Society of America, Washington, DC, 2002.