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

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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 1866 ± 243 yr which compares well with the known age of 1923 years. U, 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 activation energy of 100.12 ± 0.83 kJ/mol and $\ln D_0/a^2 = -1.07 \pm 0.1$. 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.

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 where organic carbon is present. Despite considerable progress, there are few techniques that are broadly applicable and reliable for ages beyond the ^{14}C limit but still within the late Quaternary 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]. Nevertheless, a broadly applicable geochronological method that can be used both within and beyond the limit of radiocarbon dating is still a major goal of geochemical research.

The U-Th/He method, first proposed by Rutherford in 1905 [10], has considerable potential for dating Quaternary events. The technique was abandoned when the initial evaluations produced ages that were anomalously young [11], but is being reevaluated 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 low enough background that samples as young as 1000 years with as little as 1 ppm U could be datable. Recent work on the U-Th/He technique has 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 to 8 MeV α -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 titanite make them ideal for studying the low temperature thermal history of young igneous rocks. Titanite 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 begin 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. There are several issues that 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 might be a limiting factor. 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 A.D. 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 years. 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, and 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 and high helium retentivity, since garnet crystals normally are U- and Th-poor. However, the Vesuvius garnets in fact have high U and Th concentrations. 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 the white pumice described by [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 5 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 used for U, Th, and Ba concentrations, U and Th isotopic data, for major element analysis, and to make 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 about 5 minutes using a manual mortar and pestle attached to a vacuum line. The radiogenic helium component was determined by heating in a furnace of two 1g aliquots of garnet grains contained in aluminum capsules. The heating procedure included holding the samples for 30 minutes at 1500°C; the total heating and cooling time was 1 hour. We repeated the extraction at 1500°C and at 1650°C to determine whether all of the helium had been released.

Our heating procedure was based on the work of [20] whose data indicate a closure temperature of 1100°C for the (Ca-poor) garnet they investigated. 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. As a consequence we were unable to retrieve the samples after He extraction, which necessitated using separate aliquots for the U and Th concentration determinations. The He diffusivity for garnet reported by [20] may not be applicable to the Ca-rich garnets in this study. Therefore, to refine the diffusion corrections, a diffusivity measurement was conducted on a separate aliquot (~1g) which 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 30K. 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 40K, releasing the adsorbed He, which is expanded into the mass spectrometer for analysis. 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. Calibration of the abundance measurement was done using an aliquot of air and a reference sample of He as standards run before and after the samples. Procedural blanks for the furnace extractions were $5 \times 10^{-9} \text{ cm}^3\text{STP}$ and significant only for the re-extraction analyses.

For the uranium and thorium concentration and isotopic measurements, ~30mg splits of garnet and crushed whole rock were dissolved in a nitric-HF mixture. Aliquots of the dissolved samples were spiked with ^{229}Th and ^{233}U . Unspiked aliquots were analyzed for $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{232}\text{Th}$ ratios. Isolation of U, Th was accomplished using Tru-Spec column resin following the procedures of [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 for through bracketing measurements of a natural uranium in-house standard. The estimated uncertainty in the measured concentrations is $< 0.5\%$ (while sample inhomogeneity is much greater). $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{232}\text{Th}$ of unspiked aliquots were measured using separate static routines that placed ^{234}U and ^{230}Th on the Daly photomultiplier ion counting system, while ^{235}U , ^{238}U and ^{232}Th were measured on Faraday cups. Measured $^{235}\text{U}/^{238}\text{U}$ of the sample was used for internal mass fractionation correction, while 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 100ppb. Measured $^{230}\text{Th}/^{232}\text{Th}$ was combined with Th and U concentrations to provide $^{230}\text{Th}/^{238}\text{U}$ 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 the garnet grains, since alpha recoil corrections are sensitive to the distribution of the parent nuclides within the mineral. The results of one traverse (of one grain) with a maximum dimension of about 1mm are shown in Figure 2. The Th and U concentrations are given in parts per million by weight (ppmw). The uncertainty in absolute concentration is about $\pm 10\%$; the U/Th ratio is accurate to $\pm 2\%$. The spacing between analysis points is about 50 microns.

3. Results and Discussion

The helium data (Table 1) are blank corrected using the procedural blanks measured prior to each sample analysis. Except for the high temperature (1500 °C) re-extractions the ^4He blanks were typically <15% of the total helium. The tabulated 1σ errors in the ^4He concentrations and $^3\text{He}/^4\text{He}$ ratios contain uncertainties associated with peak height measurements, blank corrections, and corrections for mass spectrometer fractionation, which have been propagated by quadratic expansion. We estimate that there is an additional $\pm 10\%$ error in the ^4He concentration reflecting uncertainties associated with the procedural He sensitivity for converting peak height to concentration and daily variations in the helium adsorption efficiency of the charcoal trap.

The ^4He released during *in vacuo* crushing ($155 \times 10^{-12} \text{ cm}^3 \text{ STP/gm}$) represents ~ 3.7 - 4.3% of the total ^4He released during sample fusion and is accompanied by an indeterminate amount of ^3He ($^3\text{He}/^4\text{He} \sim -1.65 \text{ Ra}$, blank corrected). In calculating the U-Th/He ages 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.

Diffusivity calculations (Table 3) are based on the step-wise degassing of Split A (Table 1) and the equations given in [23] for diffusion from a homogeneous sphere. The relationship between diffusion and temperature define an Arrhenius relationship (Figure 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 100.12 ± 0.83 kJ/mol and a frequency factor, $\ln D_0/a^2$, of -1.07 ± 0.1 .

In general, 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 to 8 MeV. The range (or stopping distance) of these particles is between 15 and 30 μm depending on energy, particle mass, and sample density. For the correction, we calculate the fraction of radiogenic He atoms that will come to rest inside and outside of a grain. 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 the model of [25] as modified by [13] assuming a spherical grain geometry and a homogeneous distribution of the parent atoms. Based on the ion probe analyses, the concentrations of the parents does not vary by more than a factor of two, significantly less than the order of magnitude variations in parent U and Th discussed by [26]. We assume that the concentration of U and Th in the groundmass are not significantly different from the concentration measured for the whole rock. Because the concentration of U in the groundmass is approximately the same as the concentration within the garnet grains, the injection and ejection of alphas produced from U decay are balanced and the correction is zero. However, the concentration of Th in the garnet is

approximately one third that of the groundmass, so that there is a net gain of alphas to the garnets. The total fractional excess of alphas in the garnet grains is estimated to be $F_T = 1.001 \pm 0.005$. The alpha ejection correction is therefore insignificant considering the other sources of uncertainty.

Diffusion also has a small effect on the He concentration of the garnet grains. We correct for this loss using the diffusion model given by [18]:

$$\frac{t'}{t} = \frac{1}{1 + \frac{3D}{a^2} - \frac{4D}{\sqrt{\pi}a^2}} \quad (1)$$

where t' = apparent age, t = true age, and D/a^2 = normalized frequency factor. Given a maximum mean annual temperature of 35°C, we calculate that $D/a^2 = 9.79 \times 10^{-11}$ for garnets with typical diameters of 1 mm. The equation is solved iteratively to give $t'/t = 0.9985$. A solution to the production-diffusion equation that includes the effect of alpha ejection from the mineral has been determined [27], which modifies the concentration profile and decreases diffusive losses. We are able to ignore this effect because the magnitudes of diffusive loss and alpha ejection are negligible for the Vesuvius garnets.

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 on the concentrations of ^{238}U and ^{232}Th . Only if the age of the sample is much greater than the mean life of the longest-lived intermediate daughter can the concentrations of the intermediates be assumed to adhere to the secular equilibrium values. In comparison to the age of the Vesuvius sample (1923 years), 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 (237 kyr), ^{230}Th (75 kyr), and ^{226}Ra (1600 yr). We have measured the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios of garnet (Table 2). 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 [28] to argue that the initial $^{226}\text{Ra}/^{230}\text{Th}$ of the garnet phenocrysts was the secular equilibrium value.

The correction for $^{230}\text{Th} - ^{238}\text{U}$ radioactive equilibrium is done using the equation of Farley et al. [21] :

$$\begin{aligned}
^4\text{He} = & 7^{235}\text{U}e^{-\lambda_{235}t} + 6^{232}\text{Th}e^{-\lambda_{232}t} + 2^{238}\text{U}e^{-\lambda_{238}t} \\
& + 6D_{230} \frac{\lambda_{238}}{\lambda_{230} - \lambda_{238}} e^{-\lambda_{238}t} (1 - e^{-(\lambda_{230} - \lambda_{238})t}) \\
& + 6^{238}\text{U}e^{-\lambda_{238}t} \left[\frac{1}{\lambda_{238} - \lambda_{230}} (1 - e^{-(\lambda_{238} - \lambda_{230})t}) \right] + \left[\frac{1}{\lambda_{230} - \lambda_{238}} (e^{-(\lambda_{230} - \lambda_{238})t} - 1) \right]
\end{aligned} \tag{2}$$

where ^4He , ^{235}U , ^{232}Th , and ^{238}U refer to concentrations, the λ 's are decay constants, and $D_{230} = ^{230}\text{Th}/^{238}\text{U}$. For $^{226}\text{Ra}/^{230}\text{Th}$, we infer from the low Ba/Th of garnet that it initially crystallized from magma with a deficiency of ^{226}Ra relative to ^{230}Th , since the Ba/Th ratio of garnet is only 13% of the Ba/Th ratio of the whole rock. However, it is common for magmas of the Roman magmatic province to have excess ^{226}Ra on eruption [28]. Black et al [28] 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 equilibrium in garnet at the time of eruption.

Table 4 shows the effects on the calculated age of the three correction factors. The only significant correction to the age is due to $^{230}\text{Th}/^{238}\text{U}$ disequilibrium, given that the assumption of ^{226}Ra - ^{230}Th equilibrium is appropriate. The correction increases the apparent age by a large amount, about 50%, and brings the calculated age of 1866 ± 243 years, to within 3% of the true age. 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 years.

The overall uncertainty on the age is reasonably large although conservative. A large proportion of the uncertainty comes from the heterogeneity in the garnet U and Th concentrations, which may be a peculiarity of this sample, but is compounded by our inability to determine He concentration on the same aliquot as U and Th concentrations. The inhomogeneity of U and Th concentration is further emphasized by the ion probe results, which are 40% lower than the average of the two aliquots that were measured by isotope dilution mass spectrometry. Considering that this traverse represents only one grain, the result is consistent with the observation that the several hundred grains included in the two aliquots yielded a 10% difference in concentration.

The age and uncertainty yielded by our U-Th/He results on garnet are compared in Figure 4 to the results of [4], who used the Ar-Ar method on separates of sanidine phenocrysts. The calculated ages, 1866 versus 1925 are quite close, and accurate by comparison 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.

4. Conclusions

We have dated samples from the 79 AD eruption of Mt Vesuvius witnessed by Pliny the Younger using the U-Th/He method on garnet phenocrysts. The resultant age of 1866 ± 243 years, which includes a large correction for U-Th isotopic disequilibrium, indicates that the U-Th/He method is applicable to dating Holocene volcanic samples with accuracy and precision of about $\pm 13\%$. The largest source of error in the age calculations comes from measuring U, Th and He on separate aliquots; future work will address this concern for samples requiring a high extraction temperature. The results presented here are encouraging in that they validate the correction due to U series isotopic 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 the unexpectedly high U and Th concentrations), and exceptionally good helium retentivity. Other available volcanic phenocryst minerals do not typically have these characteristics. On the other hand, the age of the Vesuvius samples is extremely small, compared to the 1.8 million year age range covered by the Quaternary epoch. Older samples should contain much larger amounts of radiogenic helium for the same amount of U and Th, and radioactive disequilibrium corrections will be less important.

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

Sample AM1	wt. (gm)	[⁴ He] 10 ⁻¹² ccSTP/gm	+/-	% Blank	(³ He/ ⁴ He) R/R _a	+/-
split Cr						
Crush	0.6600	154.55	0.51	20%	-1.65	21.08
1500°C extraction	0.4235	3520.97	12.60	4%	0.77	0.40
1500°C re-extraction		-35.30	2.40	128%	-35.78	86.22
Total		3640.22	15.01			
split 1						
1500°C extraction	1.0237	4149.98	18.36	2%	1.68	0.24
1500°C re-extraction		5.80	0.80	92%	156.23	138.03
Total, crush subtracted		4001.23	19.17			
split B						
600°C extraction	1.0535	611.09	2.22	17%	2.32	0.93
1500°C extraction		3204.29	17.32	2%	1.49	0.64
1500°C re-extraction		36.84	0.91	65%	45.89	5.43
Total, crush subtracted		3697.66	20.46			
split A						
600°C extraction	0.9509	372.50	3.03	15%	0.57	1.53
600°C extraction, crush subtracted		217.94	3.07			
800°C extraction		1009.94	4.55	6%	0.84	0.62
900°C extraction		658.57	2.67	10%	0.84	0.94
1000°C extraction		425.00	5.41	14%	0.21	1.45
1100°C extraction		566.76	3.03	11%	1.38	0.98
1200°C extraction		596.82	2.71	11%	0.98	1.06
1300°C extraction		57.96	2.32	56%	11.70	10.05
1500°C extraction		36.75	2.37	68%	-2.41	15.03
Total		3569.74	29.17			
Average for Age Calculation		3697.40	215.82			

* all concentration data have been blank corrected; negative concentrations indicate the measured value < blank

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

Sample Am I	U (ppm)	+/-	Th (ppm)	+/-	Th/U	+/-	$^{230}\text{Th}/^{232}\text{Th}_{\text{act}}$	+/-	$^{234}\text{U}/^{238}\text{U}_{\text{act}}$	+/-	$^{230}\text{Th}/^{238}\text{U}_{\text{act}}$	+/-	Ba (ppm)	+/-
garnet split E	19.02	0.04	27.71	0.06	1.46	0.003	0.89	0.01	1.00	0.001	0.43	0.007		
garnet split F	16.24	0.03	23.45	0.05	1.44	0.003	0.89	0.01	1.00	0.001	0.42	0.007		
garnet split K													7.89	0.39
whole rock split WR	16.03	0.03	32.65	0.07	2.04	0.004	0.90	0.01	1.01	0.001	0.58	0.009	76.59	3.83
garnet average for age calculation	17.63	0.03	25.58	0.04	1.45	0.002	0.89	0.01	1.00	0.001	0.42	0.005	7.89	0.39

Table 3. Results of step-heating runs for diffusion profile.

T (°C)	Duration (sec)	⁴ He (pmol/g)	F ^{He} (%)	ln D/a ²
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		

Table 4. Calculated He Ages.

Sample AM1	Age (yr)	+/-
raw	1291	155
corrected for ejection	1290	155
corrected for diffusion	1291	168
disequilibrium raw	1868	224
disequilibrium corrected for ejection	1866	224
disequilibrium corrected for diffusion	1866	243

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

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

Figure 3.

Arrhenius diagram for diffusion coefficients across a range of temperatures. The propagated errors in D/a^2 are shown by the error bars. The slope of the regression line (not the best-fit line) is proportional to E_a (the activation energy) = 100.12 ± 0.83 kJ/mol and the Y-intercept is proportional to $\ln D_o$ (the frequency factor) = -1.07 ± 0.1 .

Figure 4.

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