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U-Th DISEQUILIBRIUM DATING OF AUTHIGENIC CALCITES IN THE MAZAMA (MZI-IIA) GEOTHERMAL WELL, OREGON

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ABSTRACT

U-Th geochronological techniques have been used to approximate the ages of precipitation of authigenic calcites in nine core samples from the Mazama geothermal well (California Energy Company MZI-IIA). Vein mineralization extracted from cores at five depth intervals is predominantly calcite with associated zeolites and quartz. U concentrations in calcite are highest (>2.0 ppm) in the shallowest sampling interval and are extremely low (<0.005 ppm) in the deepest interval near the bottom of the well bore. Some vein samples contain multiple sequences of mineralization with significantly different U contents and ($^{234}\text{U}/^{238}\text{U}$). Vein samples collected adjacent to vugs in two depth intervals have lost U since precipitation. ^{232}Th concentrations are negligible in vein mineralization and intensive laboratory leaching of zeolite residues yields no measurable Th. ^{230}Th is interpreted as the result of ingrowth by decay of ^{234}U . Calcite extracted from veins in two depth intervals is older than 350 Ka (Ka=1,000 years). One morphology of calcite within a third depth interval has an approximated age of 140.3 Ka (+22.3 -19.3 Ka). None of the sampled veins have calculated ages <120-160 Ka. Authigenic mineralization extracted from the MZI-IIA well cores has been precipitated episodically for >200 Ka.

INTRODUCTION

Two shallow geothermal test wells were drilled in the Winema National Forest, Klamath County, Oregon in September of 1986 by California Energy Company (see Figure 1). The MZI-IIA well is the deeper of these two Mazama wells and penetrates volcanic ash and thin, intercalated basaltic-andesite flows in the upper 200 feet of the well bore. Thick sequences of silicic tuffs, volcanic breccias, and dacite and rhyodacite flows are encountered at depth. The upper 575 feet of the MZI-IIA well were rotary drilled and the remainder of the well bore continuously cored to a total depth of 1354 feet (only the well depths of core segments are reported in English units).

The core samples provide opportunities to study lithologies and alteration in the silicic volcanics, map fracture densities and orientations, and to identify and collect specific sequences of fracture filling mineralization. The cores contain ~.4 to >.5 cm. thick fractures that have been completely or partially filled with mixtures of calcite, zeolite(s), and quartz.

This report presents the results of age approximations for vein minerals in the Mazama geothermal well core (California Energy Company MZI-IIA) determined by U-Th disequilibrium techniques. This technique takes its name from the parent radioactive nuclide ^{238}U which decays to its long-lived daughter ^{234}U . ^{234}U decays to another long-lived radionuclide ^{230}Th which has the shortest half-life of the three at 7.52×10^4 years. ^{234}U and ^{230}Th are referred to as long-lived daughter radionuclides in the

^{238}U decay series. A parent-daughter pair is essentially in radioactive equilibrium after five half-lives of the shorter-lived radionuclide. After approximately 350,000 years, about five half-lives of ^{230}Th , the $^{230}\text{Th}/^{234}\text{U}$ ratio will equal 1.00 and radioactive equilibrium is established. Disequilibrium between parent and long-lived daughter nuclides in the ^{238}U decay series has long been recognized and exploited for dating a variety of young (late Pleistocene - Holocene) geological and archeological samples (Kigoshi, 1967; Allègre and Condomines, 1976; Ku, 1976; Schwarcz, 1982). Ages up to 350 Ka (Ka=1,000 years) can be approximated using the $^{230}\text{Th}/^{234}\text{U}$ method only if the authigenic minerals have not lost or gained U or Th isotopes since precipitation; i.e., the mineralization has remained "closed" to all U and Th isotopes. A few grams of calcite from each sequence of mineralization to be analyzed are usually required for adequate measurement of uranium concentration.

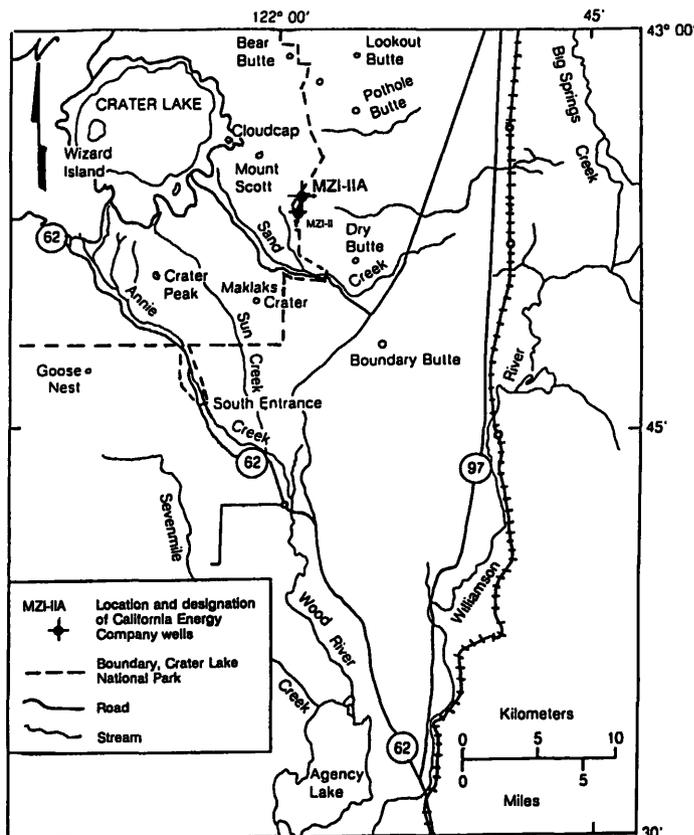


Figure 1. Map showing locations of the California Energy Company wells and selected geographic features. Figure modified after Sammel and Benson (1987).

The capability to measure low concentrations of radionuclides of the ^{238}U decay series by alpha and mass spectrometric techniques is well established, but has only recently been applied to fluids, reservoir rocks, and authigenic minerals in active and recently extinct continental hydrothermal systems (Wollenberg, 1975; Osmond and Cowart, 1976, 1982; Goff and Shevenell, 1987; Sturchio *et al.*, 1986a, 1986b, 1987; Hammond *et al.*, 1987; Zudin, *et al.*, 1987; Sturchio and Binz, 1988; Sturchio *et al.*, 1989). The abundances and isotopic ratios of radionuclides in authigenic phases can also be utilized for non-geochronological applications to address questions such as: 1) has vein mineralization remained closed to nuclides in the ^{238}U decay series; 2) which nuclides, if any, may have been mobilized subsequent to precipitation and why; and 3) what was the chemical nature of fluids from which alteration phases precipitated or recrystallized? The capability to place temporal constraints on the onset and duration of specific sequences of mineralization in hydrothermal systems has various applications in geothermal and economic geology as well as high-level radioactive waste disposal.

METHODOLOGY

Detailed lithologic descriptions of cores were used to identify depth intervals in the well bore that contain fractures filled by authigenic mineralization with enough mass for radioisotopic analyses. Numerous thin-sections and X-ray diffraction patterns were produced of the altered volcanic host rocks and veins in each core segment. Subsequent to review of results of XRD and binocular and thin-section petrography, fifteen samples of fracture-filling authigenic minerals were collected. The main objective in sampling authigenic phases was to remove the maximum mass of vein material from each sequence of mineralization. Calcite and mixed calcite-zeolite and calcite-quartz samples were extracted from nine core samples at five depth intervals (858-859', 988-989', 1029-1031', 1245-1247', and 1275'). Three sequences of vein mineralization were identified in veins in the 858-859' and 988-989' core segments. These mineral sequences could be removed from the cores and physically separated. In many instances calcite is so intimately intergrown with zeolite(s) and/or quartz as to be physically inseparable. Vein samples extracted from the seven remaining cores contain only one clearly discernable sequence of mineralization.

Vein mineralization was extracted from the volcanic host rocks with a high-speed turbine drill and dental drill bits and burs lubricated with deionized water. All fragments of volcanic rock were completely removed from vein separates. Vein samples were powdered and splits of the homogenized powders were made for XRD, carbon and oxygen isotopic analyses, and isotope dilution alpha spectrometry. Uranium concentrations in two powder splits from a 1029-1030' vein separate were determined by neutron activation analysis at the Radiation Center, Oregon State University prior to undertaking alpha spectrometry for any of the samples.

Chemical separations of U and Th radioisotopes and production of thin-source alpha mounts were performed in the Geochemistry Laboratory at the University of Southern California. A Th isotopic analysis was completed for one sample to determine whether appreciable ^{232}Th activities were to be expected in the remaining samples and required the use of chemical separation procedures for impure carbonates as proposed by Ku and Liang (1984). The ^{232}Th content in the first vein sample that was analyzed is extremely low so leaching of the remaining vein samples was performed using procedures for dissolution and radioisotopic separations for pure carbonates using a modified single ion-exchange column technique after Luo *et al.* (1987).

The 988-989 VW_{C-2} sample contains the most silicate residue after leaching the sample in concentrated HCl. The silicate residue of this sample was taken up in HClO₄ and HF and used

to produce a thin source mount for alpha spectrometry (Ku and Liang, 1984). These precautions are necessary because the presence of ^{232}Th in a vein sample indicates that all of the ^{230}Th may not be due to the decay of ^{234}U .

When the quantity of vein material was sufficient, splits of powders with similar masses were used to produce duplicate samples for U and Th isotopic analyses. Duplicate samples were treated identically during chemical procedures with the exception of U and Th isotopic spikes. Samples were spiked with ^{232}U and ^{232}Th and duplicates with ^{236}U and ^{232}Th . Duplicate analyses provide an internal control for precision. Results obtained from duplicate analyses can be reported with a greater degree of confidence, especially when duplicates are spiked with different radioisotopes and counted on different spectrometers. External control for the radioisotopic experiment was a travertine sample collected adjacent to a previously dated sample from Soda Dam, Valles Caldera, New Mexico provided by Fraser Goff of Los Alamos National Laboratories. The Soda Dam travertine was analyzed using exactly the same experimental techniques as for the Mazama samples.

U and Th planchets were counted on low-background silicon surface barrier detectors in the Geochemistry Laboratory at the University of Southern California. Spectrometry data were reduced using software developed at the University of Southern California by Teh-Lung Ku and Masashi Kusakabe.

RESULTS

Detailed petrographic descriptions, results of XRD of all volcanic rocks and vein mineralization, and light stable isotopic analyses of vein samples will be discussed in a separate paper (Hull, Ku, and Waibel, in preparation). Results of U-Th isotopic analyses of vein minerals are shown in Table 1. Sample names are derived from the depth in feet of the core interval followed by V for vein mineralization or VW for vein wall (vein mineralization closest to the volcanic rock interface). Subscripted letters refer to the mineralization present in order of relative abundance (C - calcite, Z - zeolites, Q - quartz) and numerals refer to sequences of mineralization. The capital R or G following sample names indicates which radioisotopes were used to spike the sample; R for ^{232}U and ^{232}Th and G for ^{236}U and ^{232}Th . The sample was spiked with R if not specifically designated. The activities of radionuclides are reported in decays per minute per gram of sample (dpm/g) and activities and activity ratios are enclosed in parentheses. Analytical results for duplicate samples of travertine from Soda Dam are listed at the bottom of Table 1.

The ($^{230}\text{Th}/^{232}\text{Th}$) ratios are ~ 10 for all MZI-IIA vein samples and ratios are >100 for five samples (Table 1). The chemical behavior of Th isotopes is identical so high ratios of ($^{230}\text{Th}/^{232}\text{Th}$) indicate the vein minerals have not added Th from the volcanic rocks and all ^{230}Th has "grown in" from the decay of ^{234}U . Total U concentrations vary from vein-to-vein and even within sequences of mineralization in one vein (see 988-989' and 1245-47' samples in Table 1 and Figure 2). The ($^{234}\text{U}/^{238}\text{U}$) for all of the vein samples ranges from 1.03+-0.04 to 2.02+-0.18. ($^{230}\text{Th}/^{234}\text{U}$) in authigenic calcites also spans a wide range from 0.79+-0.06 to 1.31+-0.05. ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{234}\text{U}$) for each vein sample are plotted in Figure 3.

The three sequences of mineralization extracted from the 858-859' cores have U abundances of >1 ppm and plots of these samples cluster in the upper left corner of Figure 2. These 858-859' calcites as a group are closest to the equilibrium value of 1.00 for ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{234}\text{U}$) range from 1.00 to 1.15 (Table 1 and Figure 3). The 858-859 VW_{C1} vein sample ($^{230}\text{Th}/^{234}\text{U}$) and ($^{234}\text{U}/^{238}\text{U}$) also approach equilibrium values (Figure 3) so the sample has a calculated age of >350 Ka.

All but one of the remaining vein samples contain an order of magnitude less total U than those in the shallowest sampling interval. Another three sequences of mineralization could be

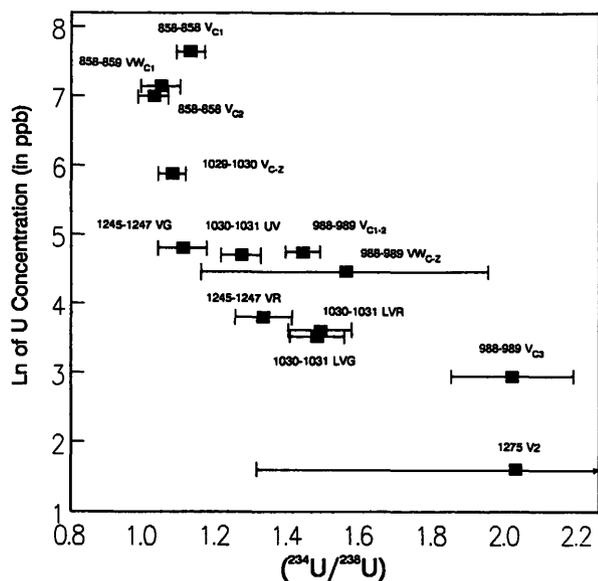


Figure 2 Natural logarithm of U concentrations (in ppb) versus $(^{234}\text{U}/^{238}\text{U})$ for MZI-IIA vein samples.

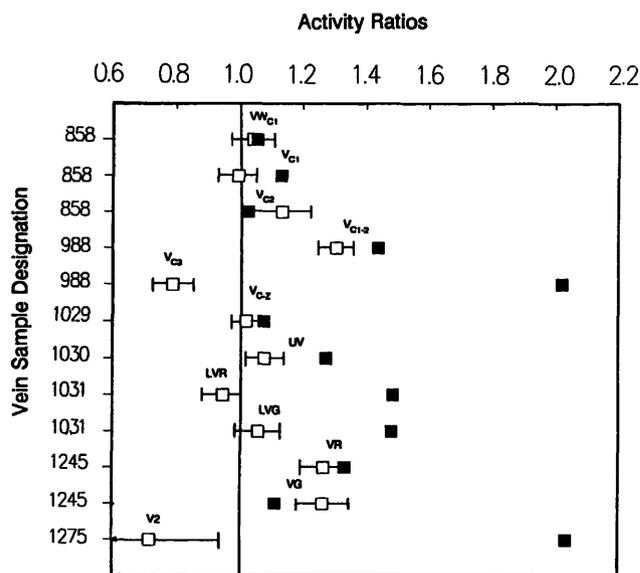


Figure 3. $(^{230}\text{Th}/^{234}\text{U})$ (\square) and $(^{234}\text{U}/^{238}\text{U})$ (\blacksquare) for MZI-IIA vein samples. Error bars shown for $(^{230}\text{Th}/^{234}\text{U})$ only. Vertical line at the radioactive equilibrium value of 1.00.

TABLE 1

RESULTS OF ISOTOPE DILUTION ALPHA SPECTROMETRY FOR MZI-IIA VEIN MINERALIZATION

SAMPLE NAME*	CaCO ₃ (wt.%)	U (ppm)	$(^{234}\text{U}/^{238}\text{U})$	$(^{230}\text{Th}/^{234}\text{U})$	$(^{230}\text{Th}/^{232}\text{Th})$	Age** (Ka)	Comments
858-858 VW _{C1}	99.4	1.281+-0.067	1.05+-0.06	1.04+-0.07	99.1+-16.4	> 350	Extremely low abundance of ²³² Th.
858-858 V _{C1}	98.8	2.080+-0.110	1.13+-0.04	1.00+-0.06	49.9+-6.5	> 350	Recounted for 25K min. at USC on a low background detector. Excellent statistics.
858-858 V _{C2}	98.4	1.095+-0.057	1.03+-0.04	1.17+-0.09	176.+-68.	> 350	Underspiked in ²³² U.
988-989 VW _{C-Z}	19.3	0.087+-0.014	1.56+-0.43	-	-	-	Statistics insufficient - recounting at USC on a low background detector.
988-989 V _{C1-2}	96.8	0.114+-0.003	1.44+-0.05	1.31+-0.05	50.2+-4	-	U loss from the sample.
988-989 V _{C3}	85.6	0.019+-0.001	2.02+-0.18	0.79+-0.06	9.77+-2.02	140.3 ^{+22.3} -18.3	Recounting on low background detector.
1029-1030 V _{C-Z}	78.8	0.356+-0.010	1.08+-0.04	1.02+-0.04	> 1000	> 350	Excellent counting statistics.
1030-1031 UV	67.9	0.110+-0.004	1.27+-0.06	1.08+-0.06	> 900	> 350	Extremely low ²³² Th in this interval.
1030-1031 LVR	81.3	0.037+-0.002	1.49+-0.09	0.95+-0.06	> 700	225.2 ^{+80.2} -36.9	Recounting for better statistics.
1030-1031 LVG	81.1	0.034+-0.001	1.48+-0.08	1.06+-0.07	27.0+-1.1	> 350	Some overlap of ²³⁰ Th spike peak. This is a duplicate of 1030-1031 LV.
1245-1247 VR	28.1	0.045+-0.002	1.33+-0.08	1.27+-0.07	11.7+-1.8	-	U loss from the sample.
1245-1247 VG	31.3	0.122+-0.006	1.11+-0.07	1.27+-0.08	9.72+-1.23	-	U loss from the sample.
1275 VR	90.0	<.003	-	-	-	-	Below detection limit. Very long recount.
1275 VG	91.3	<.003	-	-	-	-	Below detection limit. Very long recount.
1275 V2	93.6	0.005+-0.002	2.03+-0.77	0.72+-0.22	1.89+-0.71	119.2 ^{+80.8} -48.8	Statistics insufficient. Recounting at USC on a low background detector.
F88-4 R	95.6	1.368+-0.056	2.33+-0.05	0.060+-0.004	5.46+-0.54	6.7 ⁺⁴ -4	External standard for calibration of experiment. Soda Dam travertine from Fraser Goff.
F88-4 G	98.8	1.464+-0.047	2.31+-0.04	0.062+-0.003	5.85+-0.41	6.9 ⁺³ -3	Duplicate of Soda Dam travertine.

* Sample names are derived from depth (ft.) of core interval, V-vein mineralization, VW-vein wall. Subscripted letters refer to authigenic phases in vein; C-calcite, Z-zeolites, Q-quartz. R - spiked with ²³⁵U and ²³²Th. G - spiked with ²³⁴U and ²³⁰Th.

** Ka = 1000 years

separated from the vein in the next depth interval at 988-989'. Total U concentrations are similar in the 988-989 VW_{CZ} and V_{C1-2} samples, but U is lower by a factor of ~5 in 988-989 V_{C3}. The low U concentration in 989-989 V_{C3} is associated with high (²³⁴U/²³⁸U) as noted for the vein samples as a group (Figure 2). The 988-989 V_{C3} sample contains the lowest (²³⁰Th/²³⁴U) and therefore has the youngest calculated age of ~120-160 Ka (Table 1).

Total U concentrations in the 1029-1031' vein samples are extremely variable (Table 1). U concentrations in splits of the 1029-1030 V_{CZ} sample are 0.358±.010 ppm from alpha spectrometry results and 0.33±.04 ppm by neutron activation analysis. The (²³⁰Th/²³⁴U) of 1.02±.04 for the 1029-1030' sample is indicative of equilibrium and has a calculated age of >350 Ka (Table 1). (²³⁴U/²³⁸U) also approaches 1.00 for this sample. (²³⁴U/²³⁸U) are higher in the 1030-1031' samples compared to those at 1029' and 1030', but (²³⁰Th/²³⁴U) closely approach the equilibrium value of 1.00. Results for sample duplicates for 1031 LV are well within the limits of precision for U concentrations and isotopic ratios. (²³⁰Th/²³⁴U) for these duplicates are very slightly above and below 1.00 (Table 1 and Figure 3).

Samples 1245-1247 VR and VG are not duplicates but were collected within one centimeter of each other and received different spike nuclides. Samples 1245-1247 VR and VG have different (²³⁴U/²³⁸U) but identical (²³⁰Th/²³⁴U) (Table 1 and Figure 3). Samples from the quartz-calcite filled fracture at 1275' have extremely low abundances of total U (<0.003? ppm). An additional vein separate from this core, 1275 V2, contains very little U (0.005±.002 ppm).

DISCUSSION

Hydrothermal systems are not renowned for remaining chemically closed. Total U concentrations and radioisotopic ratios in geothermal fluids are known to differ from system-to-system (Osmond and Cowart, 1976, 1982) and within systems (Hammond *et al.*, 1987; Sturchio and Binz, 1988). Open-system behavior in the ²³⁸U decay chain has been demonstrated to have been the case in volcanic host rocks or vein mineralization in two continental hydrothermal systems (Sturchio *et al.*, 1986a, 1986b). However for U-Th dating techniques to be applicable, authigenic phases must remain chemically and isotopically closed. It cannot simply be assumed that authigenic mineralization has not recrystallized or exchanged chemical components with groundwater and/or hydrothermal solutions. Even if minerals in one vein or within one core segment can be demonstrated to have remained isotopically closed, it cannot be guaranteed that other veins, or even sequences of veining in the same fracture, have not been isotopically reset.

One or more of the following processes or sampling biases may affect the isotopic ratios: 1) contamination of the authigenic mineralization by ²³⁰Th from the volcanic host rocks; 2) inadvertent sampling of more than one sequence of mineralization having different U concentrations and radioisotopic ratios; 3) selective leaching of ²³⁰Th from the zeolite residue; 4) open-system behavior caused by exchange of radioisotopes in the vein minerals with fluid(s).

The first process above was excluded by removing all volcanic rock and often zeolites lining the vein wall by polishing with dental burs. The high (²³⁰Th/²³²Th) for all of the vein samples confirms that ²³²Th contamination has not occurred (Table 1) so addition of ²³⁰Th directly from the volcanic rocks is highly improbable. The inadvertent sampling of more than one episode of mineralization in the sample could alter isotopic ratios and shift (²³⁰Th/²³⁴U) values. This type of sampling error was avoided by carefully studying thin-sections of each vein to identify sequences of mineralization.

The Th alpha mount prepared from the silicate residue of 988-989 VW_{CZ} sample has natural Th radioisotope activities of

only 0.0018 dpm/g; an order of magnitude less than the sum of (²³⁰Th) and (²³²Th) in the leachate of this sample. Any Th that was present in the powdered zeolite is believed to have been completely leached by the hot, 12M HCl (personal communication, Teh-Lung Ku, 1989). The third process, selective leaching of the silicate residue, is therefore considered unlikely since the 988-989 VW_{CZ} residue, which is almost all zeolite(s) and ~80% of the sample mass, contains very little of any isotope of Th. Whether the zeolites and calcite are preferentially leached or have added radioisotopes subsequent to precipitation raises the question of open-system behavior and its possible effects on (²³⁰Th/²³⁴U) and (²³⁴U/²³⁸U).

Thorium occurs only as Th⁴⁺ with high ionic potential in aqueous solution; it immediately hydrolyses in groundwaters (Hostetler and Garrels, 1962). These insoluble Th hydroxide complexes are quickly absorbed onto particulate surfaces and results in extremely low Th solubility in natural waters. Even when Th daughters are produced by the decay of U, the Th rapidly hydrolyses and adsorbs onto the nearest solid surface (Gascoyne, 1982). Th is generally considered as immobile. Uranium also occurs as U⁴⁺, but oxidizes to U⁶⁺ in slightly acidic groundwaters and forms uranyl (UO₂²⁺) complexes. The uranyl dicarbonate complex is usually the most stable U species in solution in pH ranges of ~4 to 10 and uranyl tricarbonates at higher pH depending on the partial pressure of CO₂ (Hostetler and Garrels, 1962). This is fortuitous for investigating radioisotopic ratios of U decay series nuclides in calcites; however, U can readily remobilize and reset isotopic ratios upon recrystallization in an oxidizing environment. Preferential leaching of ²³⁴U from calcite cleavage surfaces into solution is another example of open-system behavior that may affect isotopic ratios.

Open-system behavior with respect to U radioisotopes is indicated by (²³⁰Th/²³⁴U) ratios >>1.00 in at least two sequences of authigenic mineralization in the MZI-IIA well cores. Eight, perhaps nine, vein samples are believed to have remained isotopically closed and ages can be approximated by U-Th disequilibrium techniques. The radioisotopic characteristics of authigenic phases from each sequence of vein mineralization are discussed below.

The 858-859' VW_{C1} and 858-859 V_{C1} samples are interpreted as having remained isotopically closed since precipitation and to be older than 350 Ka. The sample collected in the central portion of the vein, 858-859 V_{C2}, may be older than 350 Ka although the (²³⁰Th/²³⁴U) is somewhat high (Table 1). The 858-859' samples were underspiked in ²³²U and require long counting periods to determine precise radioisotopic ratios. The 858-859 V_{C1} sample is presently being recounted to ascertain if the elevated (²³⁰Th/²³⁴U) is simply due to insufficient counting time.

Total U concentrations are apparently not related to calcite contents in sequences of mixed carbonate vein samples or to the proximity to open cavities at the 988-989' depth interval (Table 1 and Plate 1). Open-system behavior with respect to U isotopes is indicated by the 988-989 V_{C1-2} sample that was adjacent to the central vug in the vein (Plate 1). The isotopic ratios of this sample were probably altered by loss of U or the selective leaching of ²³⁴U from the calcite that was directly adjacent to solutions flowing through the vug. The (²³⁴U/²³⁸U) for the two other 988-989' vein samples are quite high at ~1.6 to 2.0 and these vein samples are believed to have been precipitated from fluids having different redox characteristics and U concentrations. Thus lower (²³⁴U/²³⁸U) in the 988-989 V_{C1-2} sample provides no direct evidence that ²³⁴U loss from the calcite has decreased (²³⁴U/²³⁸U) and increased (²³⁰Th/²³⁴U).

If U is instantaneously removed from authigenic minerals that are in radioactive equilibrium for U series isotopes (relative to the ²³⁰Th half-life of 75.2 Ka), an extreme disequilibrium of (²³⁰Th/²³⁴U) results. The (²³⁰Th/²³⁴U) ratio of 1.31 for 988-989 V_{C1-2} may be indicative of such an extreme disequilibrium. The non-selective leaching of U from the vein mineralization would

yield ($^{230}\text{Th}/^{234}\text{U}$) >1 and ($^{234}\text{U}/^{238}\text{U}$) should remain constant. However, the preferential removal of ^{234}U will decrease ($^{234}\text{U}/^{238}\text{U}$) to <1 if the mineral was isotopically equilibrated with respect to ($^{234}\text{U}/^{238}\text{U}$). This is not observed for any of the samples (Figures 2 and 3).

The 988-989 V_{C3} sample was collected from the sequence of mineralization that lines the outer portion of the calcite vein (Plate 1) and has the youngest calculated U-Th age of 140.3 Ka +22.3 or -19.3 Ka. Total U concentration for this sample is quite low at only 0.019 ppm and ($^{234}\text{U}/^{238}\text{U}$) is the highest of the samples. The elevated ($^{234}\text{U}/^{238}\text{U}$) in the solution from which this mineralization precipitated could result from alpha-recoil of ^{234}U into a reducing fluid (Kigoshi, 1971; Osmond and Cowart, 1982). Low water/rock ratios and fluid flow rates could also contribute to an increase of (^{234}U) in the groundwater by alpha-recoil. The low U concentrations and high ($^{234}\text{U}/^{238}\text{U}$) in the 988-989 V_{C3} sample indicate that a reducing fluid was circulating through and precipitating authigenic minerals in fractures at this depth interval ~200 Ka after the precipitation of the calcites sampled in the remainder of the well cores. Even though sample 988-989 V_{C3} has the youngest calculated age, 988-989 $V_{C1,2}$ is inboard of V_{C3} in the vein (Plate 1) and therefore must be similar in age or younger than ~120-160 Ka.

The four vein samples in the 1029-1031' cores are interpreted as having been isotopically closed since precipitation and equilibrated with respect to ($^{230}\text{Th}/^{234}\text{U}$) so must be older than 350 Ka. Total U contents are different even though the veins that were sampled are within ~0.5 meter of one another. Each fracture was completely filled by mixed calcite-zeolite(s) during a single episode of mineralization. Complete sealing of the fractures by mineralization decreases the possibility of chemical or isotopic exchange of vein minerals with other sequences of authigenic mineralization or with fluids flowing through open vugs. The duplicate results for the 1031 LVR and LVG samples bracket the equilibrium value of 1.00 and provides additional evidence that these four samples are equilibrated in ($^{230}\text{Th}/^{234}\text{U}$). The 1030-1031 LVR sample is considered to be equilibrated within the limits of precision and therefore >350 Ka rather than 225.2 Ka +50.2 and - 35.9 Ka (Table 1).

The 1245-1247' VR and VG samples have ($^{230}\text{Th}/^{234}\text{U}$) >> 1.00 indicative of open-system behavior. The vein collected at 1245-1247' contains a generation of quartz that lines a central vug ~1 centimeter in width and U concentrations change over very short distances on the order of millimeters to centimeters. Both samples were collected from calcite-quartz mineralization directly adjacent to the central vug in the mineralized fracture. Leaching of U and/or preferential loss of ^{234}U from the calcite by alpha recoil is believed to be the predominant process in increasing ($^{230}\text{Th}/^{234}\text{U}$) in both samples to 1.27+-08. Both 1245-1247 VR and VG ($^{234}\text{U}/^{238}\text{U}$) ratios are shifted slightly towards lower values for the corresponding U concentrations (Figure 2) which would occur if ^{234}U was preferentially leached from the calcite. The ($^{230}\text{Th}/^{234}\text{U}$) ratios are identical which may be coincidental, but identical ratios could result if ^{234}U were similarly leached from the samples after $^{230}\text{Th}/^{234}\text{U}$ equilibrium had been attained.

Counting statistics are not sufficient for the 1275' samples so conclusions as to the state of radioactive equilibrium of this vein mineralization cannot be proposed. The 1275 V2 sample is currently being recounted for an extended period to improve counting statistics. Low U concentrations and high U isotopic ratios are similar for vein mineralization in the 988-989 V_{C3} and 1275 V2 samples.

A ($^{234}\text{U}/^{238}\text{U}$) age can be approximated in a manner similar to that for calculating U-Th ages. The initial ratio of ($^{234}\text{U}/^{238}\text{U}$) can be back-calculated from the present day ratio of ($^{230}\text{Th}/^{234}\text{U}$) if this initial ratio of U isotopes is assumed to have been that of the fluid from which the phase precipitated. Another major assumption in this technique is that the vein mineralization must remain closed to U and Th isotopes over the entire period. The

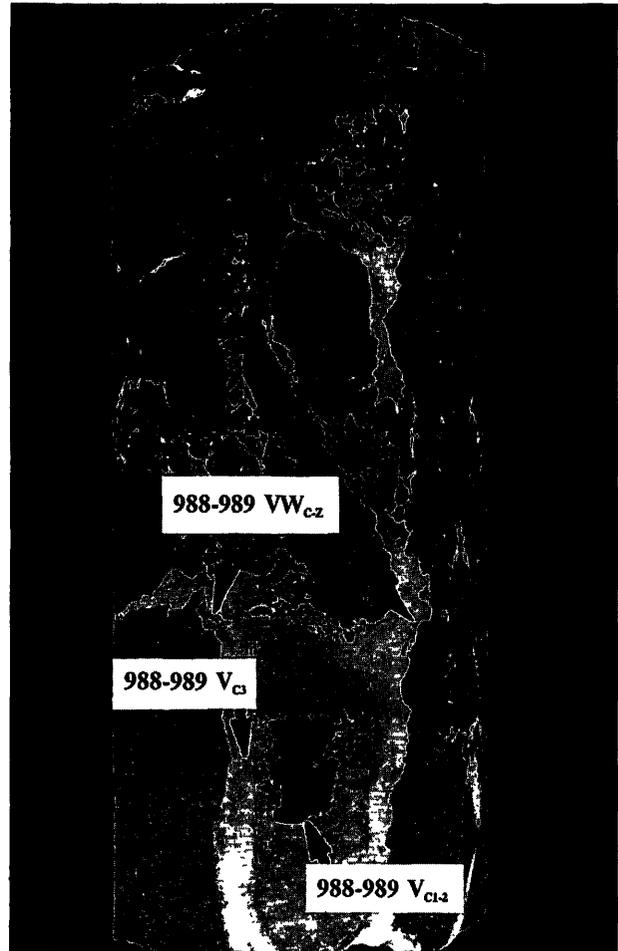


Plate 1. Photograph of the 988-989' core segment from the MZI-IIA well showing the portions of the vein from which the mineral samples were extracted.

half-life of ^{234}U is the shorter of the two at 2.48×10^5 years so ages up to ~1.2 Ma (Ma= 1 million years) can be approximated. However, many assumptions are involved in applying this technique and results should be critically evaluated when approximating ages by ($^{234}\text{U}/^{238}\text{U}$) disequilibrium methods. The age of the 858-859 V_{C1} vein wall calcite may be more on the order of ~430 Ka if the assumptions mentioned above are valid. The age calculated from U-U isotopic ratios for 858-859 V_{C1} are ~355 Ka using 1.132 as reported in Table 1 for ($^{234}\text{U}/^{238}\text{U}$) and a value of 1.00 for ($^{230}\text{Th}/^{234}\text{U}$). The ($^{230}\text{Th}/^{234}\text{U}$) of 858-859 V_{C2} is >1.00 so any ($^{234}\text{U}/^{238}\text{U}$) age approximated for this sample is meaningless.

Total U concentrations are inversely related to ($^{234}\text{U}/^{238}\text{U}$) activities as can be seen in Figure 2. Osmond and Cowart (1976, 1982) reported a general inverse relationship between ($^{234}\text{U}/^{238}\text{U}$) and U concentrations in groundwaters that is analogous to that shown in Figure 2 for vein mineralization in the MZI-IIA cores. They proposed that increased reducing conditions are encountered as a groundwater becomes more removed from the recharge zone. U is precipitated in a reducing environment but alpha-recoil of ^{234}Th (24.1 day half-life) from solid phases results in an increase of ($^{234}\text{U}/^{238}\text{U}$) in solution (Kigoshi, 1971; Osmond and Cowart, 1976, 1982).

A similar type of hydrological setting is probable for the solutions that have flowed through the volcanic rocks at Mazama. Vein samples from the shallowest sampled MZI-IIA cores contain the highest U concentrations and lowest ($^{234}\text{U}/^{238}\text{U}$). More oxygenated solutions near the surface or in recharge zones are capable of transporting higher concentrations of uranyl carbonate complexes. The U in the 858-859' samples may have been precipitated when more reducing conditions were encountered or the U was fixed by minerals with high distribution coefficients for U. The former process is considered more likely at this depth interval. Reducing conditions are implied for solutions that precipitated the vein mineralization that was collected from depths >858-859' in the well bore.

The fractured volcanic rocks that contain vein mineralization in the MZI-IIA well bore must be older than the authigenic mineralization of course. The MZI-IIA well is located on the southeastern flank of Mount Scott which is one of the oldest stratovolcanoes in the Mazama region (Bacon and Lansphere, 1983) (Figure 1). K-Ar ages of ~395-420 Ka for the Phantom Cone and Mount Scott volcanic rocks have been reported (Bacon and Lansphere, 1983; Lansphere, unpublished data, 1985). Voluminous rhyodacite lava flows that have K-Ar ages of 600-700 Ka underlie younger Mazama lavas to the south, southeast, and northeast of Mount Mazama (Bacon and Druitt, 1988). These flows are overlapped by andesitic and dacitic lavas erupted 230-355 Ka BP (before present) (Bacon, 1983). Mafic andesitic shields were built at Mount Mazama near Cloudcap ~220-290 Ka BP and near Liao Rock ~110-130 Ka BP (Bacon and Lansphere, 1983).

SUMMARY AND CONCLUSIONS

Fifteen samples of mixed calcite-zeolite(s) and calcite-quartz veins were collected from five depth intervals in the cored interval of the MZI-IIA geothermal well. Vein separates have been analyzed for ($^{230}\text{Th}/^{238}\text{U}$) and ($^{234}\text{U}/^{238}\text{U}$) for the purpose of approximating the ages of the authigenic mineralization by U-Th disequilibrium techniques. The vein mineralization has not been contaminated by ^{232}Th and at least eight of the samples have remained closed to the migration of radionuclides since precipitation and can be dated by this geochronological method. Ages calculated for the samples range from 140.3 Ka (+22.3 -19.3 Ka) to >350 Ka.

The youngest calcite-zeolite(s) mixture of those dated (988-989 V_{C1-2}) was precipitated from a fluid in a reducing environment as evidenced by very low U concentration and high ($^{234}\text{U}/^{238}\text{U}$). The 988-989 V_{C1-2} sample is necessarily younger than ~120-160 Ka or is similar in age since this mineralization occurs inboard of V_{C3} in the vein. The other seven datable vein samples have calculated U-Th disequilibrium ages of >350 Ka. Therefore, sequences of veining in the well bore have been episodic and the redox characteristics of fluids that precipitated the sequences of mineralization have changed.

At least three types of fluids have deposited or reacted with authigenic phases in the MZI-IIA well cores during the >350 Ka and <-1.2 Ma time interval. It is not implied that one fluid of similar composition and redox characteristics affected the entire sequence of volcanic rocks at the same time. The oldest group of authigenic minerals represented by these vein samples was precipitated from an oxygenated fluid with relatively high concentrations of U. Minerals deposited >350 Ka BP from this type of fluid have been sampled at the 858-859' and 1029-1030' depth intervals. The fluid from which the calcite and zeolite(s) of 988-989 V_{C3} were precipitated ~120-160 Ka BP probably had reducing redox characteristics similar to the fluid that precipitated authigenic minerals in 988-989 $V_{W_{CZ}}$ in approximately the same interval of time.

Mixed calcite-quartz samples with very low U contents in the 1275' core segment were also precipitated from a fluid under reducing conditions. The redox conditions of the fluid(s) that

precipitated 988-989 V_{C1-2} cannot be determined because sample and the samples at 1245-1247' have undergone some leaching of ^{234}U , probably at some time in the last 120-160 Ka. The fluid(s) that flowed through the vugs at 988-989' and 1245-1247' subsequent to the deposition of calcite must have been relatively more oxygenated to be able to effectively leach U from the vein mineralization closest to the vug.

Most of the authigenic mineralization may have been precipitated penecontemporaneously with construction of the Mount Scott stratovolcano on the eastern flank of Mount Mazama. The agreement of ages calculated from U-Th disequilibrium techniques for the vein mineralization with K-Ar ages of silicic volcanic rocks in the Mount Mazama region is notable. None of the authigenic mineralization sampled in the MZI-IIA well bore is related to the climactic eruption of Mount Mazama reported by Bacon (1983) as having occurred ~6,900 years ago.

The ability to identify and date specific sequences of vein mineralization in hydrothermal systems by U-Th disequilibrium dating techniques may prove to be a powerful tool in developing models for the initiation, evolution, and extinction of specific systems. This and other recent studies demonstrate that some authigenic phases remain closed to all parent and daughter nuclides in the ^{238}U decay chain and that U-Th disequilibrium dating methods are applicable in a variety of hydrothermal environments. A great deal of information can be gleaned from the study of radionuclide abundances in authigenic phases in addition to strictly geochronological applications.

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