

of 100 - 150 MPa. All amphiboles and some plagioclases were xenocrysts and were entrained throughout the entire 2800 cubic km of magma. Diffusion loss modeling of the xenocrysts indicates that these phases could not have resided in the magma chamber since the Middle Toba eruption, and that some were incorporated into the YTT magma perhaps only a few years prior to eruption. This study indicates that combining petrologic and isotopic information is crucial in identifying phenocrystic versus xenocrystic phases, which then allows magmatic conditions and residence times to be estimated.

Chesner, C.A., 1998, Petrogenesis of the Toba Tuffs, Sumatra, Indonesia: *Journal of Petrology*, v. 39, p. 397-438.

V22B-1049 1330h POSTER

Multiple Uses of Hydrogen Isotopes as a Tracer of Rehydration Processes in Glassy Lavas

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Silicic lava flows contain zones of enhanced vesicularity with high total H₂O contents. This relationship between volatile content and vesicularity has promoted the monitoring of active lava domes using remote sensing techniques in an effort to forecast explosive activity. A persistent complication in attempts to relate surface texture to H₂O content and explosivity was the confounding effect of meteoric H₂O. Glassy and vesicular lavas exposed at the surface of the Earth for prolonged periods readily interact with meteoric H₂O. Rehydration is a time-, temperature-, and porosity-dependent process governed by the slow diffusion of molecular H₂O into the glass. This inevitable addition of secondary H₂O obscures the spatial distribution of juvenile H₂O in lava flows. The ability to distinguish magmatic from meteoric H₂O in glassy lavas would help identify regions of overpressure on active domes and thereby improve hazard assessment.

Three types of hydrogen isotopic studies of glassy lavas have been utilized to disentangle rehydration processes from primary magmatic ones. First, bulk hydrogen isotopic data on variably textured lava flows reveal enrichments in both δD and total H₂O as vesicularity increases. Mixing between a degassed magmatic and a partially evaporated meteoric H₂O best explains the observed trend from lower δD values in the interior massive obsidian samples to higher δD in the most surficial vesicular pumice. Second, step-heated hydrogen isotopic analyses further prove that the vesicular samples contain a high percentage of meteoric H₂O. Whereas dense massive obsidian samples release a large fraction of deuterium-depleted H₂O at temperatures above 600°C, the bubble-rich pumiceous samples lose a majority of their H₂O at temperatures below 400°C. Lastly, the Cameca 6f ion microprobe at ASU was used to measure hydrogen isotope transects into the vesicle-melt interface. The gradation from depleted δD values in the glassy interstices to more enriched δD values near the interface supports the rehydration hypothesis. Moreover, the δD value of the rehydrated glass adjacent to the vesicle-melt interface closely matches the composition of the meteoric H₂O component revealed by the step-heated extractions.

V22B-1050 1330h POSTER

Open System Processes in Basaltic Magma Genesis: Evidence from High-Precision U-Th-Pb Isotopic Measurements of Phenocrysts

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The Pb isotopic compositions of phenocryst phases in young mafic lavas have been investigated using the Getty-DePaolo (GCA, 1995) method. This approach may complement melt inclusion studies and help in the evaluation of the significance of isotopic heterogeneity in basaltic systems. In addition, if magmatic phases have a uniform Pb isotopic composition upon eruption,

the method can be used for geochronology. Although U is commonly subject to disturbance in surface environments, Th and Pb are not. The method uses ²⁰⁷Pb as a (quasi) stable isotope ratio which allows the ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb to be determined to < 100 ppm.

The samples for this study include ~16 Myr-old Innaha basalt, a zero-age MORB, a ~260-kyr-old tholeiite from Mount Etna, and a ca. 5 Myr-old tholeiite from Kauai. Plagioclase feldspar is a low-U/Pb phase in each of these samples. U-Pb and Th-Pb ages in all but the Kauai basalt are anomalously old (by 1-3 orders of magnitude), due to low ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb values for the plagioclase feldspar, which range in size from 2 cm for the Innaha basalt to 1-2 mm for the Etna sample. The isotopic heterogeneity must be a reflection of either magma mixing ± assimilation processes just prior to eruption, or melt inclusions, which could reflect mixing earlier in the magma evolution. The fact that the isotopic heterogeneity in the MORB is as large as in the continental basalts indicates that assimilation may not be the main issue. The Innaha basalt and MORB also have Rb/Sr heterogeneity, but the Mt. Etna basalt does not. The Kauai basalt does not show disequilibrium and an age assignment is possible. Microprobe studies are underway to attempt to determine the importance of inclusions. The results reinforce the conclusions from *in situ* inclusion studies that cryptic isotopic heterogeneity is common, but do not yet help identify where in the magma generation and transport process it originates.

V22B-1051 1330h POSTER

Ashes Ashes All Fall Down! Reconstructing Volcanic Eruption Rates From ⁴⁰Ar/³⁹Ar Ages of Contaminated, Ashes, Mono Lake California

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Probabilistic volcanic hazard assessments can be determined by the product of a series of conditional probabilities. The first parameter of this conditional probability, the probability of a volcanic eruption, can be determined by simply counting the number of volcanic eruptions in a given amount of time, thereby deriving an eruption rate. Radiometric dating of the relevant volcanic units is paramount in this endeavor. In addition, volcanic ashes deposited into lakes record volcanic events and can also be used to determine eruption rates.

The Wilson Creek FM, Mono Lake, CA, contains 19 ash layers, recording volcanic eruptions from the Mono Craters Long Valley region. The top of the Wilson Creek FM is approximately 11 ky old and the base of the section is constrained to be greater than 50 ka, and may be as old as 75 ka. This yields an eruption rate of 2.9 to 4.8 events per 10,000 years. In addition, we have dated sandine from four volcanic ash layers in the Wilson Creek FM, Mono Lake, CA, by the single crystal laser fusion ⁴⁰Ar/³⁹Ar method (ashes 8,15,16 of Lajoie, 1968 U.C. Berkeley Ph.D. thesis). These data and single crystal ⁴⁰Ar/³⁹Ar results from Chen et al. (1996, *Science*) from ashes #5 and 12 all show a significant degree of contamination from older volcanic material.

Analysis of the population distribution of these data are used to extend the record of volcanic events beyond the 40 to 65 ky time interval sampled by the Mono Lake sediments to about 120 ka. The age distribution of the single crystal ⁴⁰Ar/³⁹Ar results also indicate an episodic nature for the volcanism in the Mono Craters Long Valley region. Approximately 4-5 additional volcanic events between 60 and 120 ka are implied by the extra sandine populations. In addition, the ⁴⁰Ar/³⁹Ar ages of the single crystal data also indicate a limited volcanic activity between 760 ka (Bishop tuff?) and 120 ka.

V22B-1052 1330h POSTER

Laboratory synthesized oxygen isotope zonings in plagioclase

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Stable oxygen isotope behaviors in high-temperature melt have been poorly understood due to lack of crystal-synthesis experiment with O-isotope evaluation. The distribution of trace elements along with ¹⁸O in volcanic mineral should provide important information about growth history under various conditions (e.g., supercooling, convection, and volatile-degassing). For interpretation of naturally grown volcanic minerals, it is especially necessary to understand the formation mechanism of O-isotope zoning for synthesized crystals. We performed crystal growth experiments of anorthite by FZ method that can realize the control of the growth velocity and stirring rate individually and aid to interpret the formation process. We have conducted two different experiments: (1) anorthite growth in varied growth velocity; (2) growth in varied stirring rate. Obtained crystals were profiled along the growth direction by CO₂-laser and electron microprobe analyses.

A single- to poly-crystal of anorthite crystal synthesized by experiment (1) showed a visible negative shift in δ¹⁸O value (-0.5‰/‰) with a tiny change in growth velocity from slow to fast (V = 0.310 to 0.344 mm/hr). Across this gap, major impurity of MgO (initial content: 0.1 wt%) showed a slightly positive fluctuation in fast growth zone (0.05 to 0.1 wt%). Another result of experiment (2) exhibited a large shift in δ¹⁸O (+1.5‰/‰) with change in melt-stirring rate from slow to fast (50 to 70 rpm). Across this gap, MgO was more enriched in fast-stirred zone (0.05 wt%) than in slow-stirred (0.01 wt%).

It is concluded from these above results that ideal equilibrium isotope fractionation factor between crystal and liquid anorthite α_{x-l} may not be 1.0 but > 1.0 even at melting temperature, and that growth kinetics may play an important role to modify the resultant δ¹⁸O in crystal. Probably, change in interfacial concentration of ¹⁸O by diffusional isotope transport is the most dominant cause for the formation of O-isotope zoning. Fast growth causes slight δ¹⁸O decrease in crystal by δ¹⁸O-depletion in the interfacial melt, and slow growth increases δ¹⁸O by attaining the equilibrium against bulk melt. Fast and slow stirrings provide similar situation to the case by slow and fast growth, respectively. Fast melt-stirring decrease the thickness of diffusion layer near the interface. In contrast, incorporation of impurity MgO into crystal can be promoted by dominant control of interface kinetics when the melt is stirred. Difference in growth in dynamic or static magma may be isotopically reflected in natural volcanic plagioclase having MgO-coupled or decoupled δ¹⁸O zonings.

V22C MC: Hall D Tuesday 1330h Developments in Geochronology

Presiding: N Dunbar, New Mexico Bureau of Geology and Mineral Resources

V22C-1053 1330h POSTER

Ion Microprobe U-Pb Dating of Calcium Phosphates in Martian Meteorites

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Studies of the SNC (Shergottite, Nakhlites, Chassignite) meteorites, which are thought to be impact ejecta from the planet Mars, have contributed significantly to the understanding of the igneous history of the planet. So far, an intensive work on the radiometric dating of Martian meteorites has been carried out, and it is well documented that some isotopic systems had been disturbed by the impact shock, which could be related to the ejection from Mars. Since the U-Pb isotopic system in phosphate is more resistant to secondary process, U-Th-Pb dating could be a reference for the comparison of the date of the pre-shock igneous event via other dating techniques. We have attempted to investigate the U-Th-Pb systematics of phosphates in various Martian meteorites (basaltic Shergottite, Nakhlite, Chassignite) using the Sensitive High Resolution Ion MicroProbe (SHRIMP) installed at Hiroshima University,

Japan. Our techniques take advantage of the high sensitivity at high mass resolution, and are superior to the conventional TIMS analyses in the following ways: (1) a much smaller amount of sample is required, (2) because it is a quasi-destructive technique, after U-Pb analysis, the sample can be used for other studies such as REE analysis by SIMS, observation of texture and chemical composition by EPMA. These techniques are suitable for especially precious sample such as Martian/Lunar samples.

In this study, we used polished thin sections of several Martian meteorites, which were provided by the Smithsonian Institution and NASA. The observed "Total Pb/U isochron ages" in the $^{238}\text{U}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ - $^{204}\text{Pb}/^{206}\text{Pb}$ diagram of basaltic Shergotty show relatively young ages (217 ± 110 Ma for Shergotty, 359 ± 120 Ma for Zagami). On the other hand, those of Nakhilite (Nakhla & Lafayette) indicated the older ages of ~ 1.3 Ga (although these are only preliminary result). At the conference, we will present a series of results from other Martian meteorites, and will discuss about the early/recent thermal history of Mars.

V22C-1054 1330h POSTER

Extraction of In-situ Produced ^{14}C in Terrestrial Rocks

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The measurement of cosmic-ray-produced ^{10}Be and ^{26}Al in rocks exposed at the Earth's surface has enabled numerous scientific investigations aimed at quantifying landscape evolution. However, in many instances these two radionuclides alone cannot constrain the exposure history of a sample. In-situ produced ^{14}C would be a powerful complementary radionuclide that could be used to elucidate the exposure conditions of many samples. Although the measurement of ^{14}C in the organic materials in archaeological and geological studies is well established, in-situ produced ^{14}C extraction and measurement in terrestrial rocks remains difficult. We are establishing a reliable measurement system for ^{14}C extraction from quartz.

Here we present preliminary results of our experiment after several improvements in the extraction procedures. The total background of ^{14}C is typically about $2 - 3 \times 10^5$ atoms. In our original experiment, a 4:1 N_2/O_2 mixture with trace amounts of CO_2 carrier was employed. However, we have observed that considerable amount of N_2O and NO_x are formed at the higher temperature steps. These gases are not easily cryogenically separated from the CO_2 and may also inhibit the collection of CO_2 . We have installed new carrier gas mixture in the system that consists of He , O_2 , CO , and CO_2 . We have been able to eliminate above contaminant gases as well as that we can monitor the conversion efficiency from CO to CO_2 using the carrier gas. To the efficacy of our extraction manifold we are using quartz samples collected at Transantarctic Mountains in Antarctica. These are demonstrably saturated in ^{14}C activity, based on ^{10}Be and ^{26}Al concentrations. Our preliminary result indicates that we are recovering most of the expected in situ produced ^{14}C in the quartz.

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V22C-1055 1330h POSTER

Progress in zircon (U-Th)/He thermochronometry

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A number of characteristics of zircon, including high U-Th concentrations, resistance to weathering, regular crystal morphology, and common presence in a wide range of geologic samples, make it well-suited for radiometric dating by the (U-Th)/He method. Using

both laser and furnace heating of zircon crystals for He extraction and bomb dissolution for U-Th determinations, we have measured He ages of zircons from a wide range of tectonic environments and cooling rates, including detrital zircons from sedimentary and metamorphic rocks, and igneous samples from both slowly-cooled terranes and quickly-cooled tuffs. Many samples are from rocks with previously established thermal histories, as determined by other thermochronometers including feldspar $^{40}\text{Ar}/^{39}\text{Ar}$ and zircon and apatite fission track dating. Our results from samples from about a dozen different settings consistently indicate a closure temperature of about $180\text{--}210^\circ\text{C}$, similar to that of titanite (U-Th)/He, and show good agreement between thermal histories derived from (U-Th)/He dating and other systems. Reproducibility of zircon He ages is typically 4-5% (1 σ) (e.g., 27.6 ± 1.2 Ma for Fish Canyon Tuff zircon, $n = 14$), slightly worse than for apatite He ages. This may be due to more pronounced intracrystalline U-Th zonation in zircon in general, and its influence on alpha ejection corrections. Although a wide range of samples consistently indicate a $\sim 200^\circ\text{C}$ closure temperature for zircon, step-heating experiments show relatively complex He diffusion behavior, at least on laboratory time scales and between about $300\text{--}600^\circ\text{C}$. In most experiments activation energies (E_a) and closure temperatures (T_c) increase with larger integrated experimental heating time and temperature; (E_a) and (T_c) derived from later, sublinear Arrhenius portions of these experiments are 35-44 kcal/mol, and about $150\text{--}190^\circ\text{C}$, respectively. These relatively complex diffusion characteristics are similar to the expected effects of multiple diffusion domains in zircon, and may be due to radiation damage, heterogeneous U-Th (and therefore He) distribution, or microcracks in crystals. These He diffusion complexities do not appear to be reflected in observed zircon He ages and implied closure temperatures however. Ongoing work is focused primarily on 1) tectonic applications of zircon thermochronometry in settings with poorly-understood thermal histories, 2) understanding the relationships between He diffusion complexities in zircon and radiation damage (using Raman spectroscopy), crystal size, microcracks, and parent zonation, and 3) dating of young zircon-bearing volcanic rocks.

V22C-1056 1330h POSTER

Multi-Step High-Resolution Pb/U and Pb/Pb Zircon Age Spectra: Combined Annealing, Partial Dissolution, and TIMS Analysis

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Isotopic analysis of zircon by one or more partial dissolution steps, followed by total dissolution of the remaining residue, has been attempted (with varying degrees of success) for many years. A new approach combining pre-analysis annealing of radiation damage, multi-step partial dissolution analysis (PDA), and high-resolution TIMS measurements demonstrates considerable promise. Annealing of radiation damage prior to the multi-step dissolution procedure suppresses elemental and isotopic fractionations related to radiation-damage-mediated leaching effects. Multi-step partial dissolution permits the analysis of zircon Pb/U and Pb/Pb age spectra in a manner similar to Ar/Ar release spectra. Rigorous chemical procedures to quantitatively extract all Pb and U associated with each partial dissolution step typically yield 0.2 percent reproducibility for $^{206}\text{Pb}/^{238}\text{U}$ ages. Initial dissolution steps remove almost all the common Pb associated with zircons. Later dissolution steps contain little or no initial Pb, yielding very high precision $^{207}\text{Pb}/^{206}\text{Pb}$ ages - the errors are almost entirely due to uncertainty in the isotopic fractionation correction. Minimally disturbed zircons containing no inherited component of zircon yield excellent plateaus for both Pb/U and Pb/Pb ages. Slight but consistent differences in Pb/U versus Pb/Pb age plateaus are related to the combined effects of intermediate daughter product disequilibrium at the time of crystallization, and small errors in the U decay constants - both can be evaluated by analyzing zircon samples with a wide range in age. Zircons containing inheritance yield more complex spectra, depending in large part on the relative solubility of the zircon components. The high-precision age spectra are particularly sensitive to even small amounts of slightly older inheritance. These new approaches thus significantly enhance the precision and accuracy of "traditional" TIMS zircon analysis.

V22C-1057 1330h POSTER

Whispers of Time: Lowest-Temperature Regions of Argon Age Spectra

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The true power of the Ar-Ar method lies in its ability to explore age differences and gradients within a single sample, using the step-heating approach. Following Turner's pioneering studies, this technique has been applied to determine closure times recorded as plateau ages, or to deduce thermal histories by applying diffusion theory to age spectra. In step-heating experiments, the emphasis has traditionally been on obtaining ages representative of the bulk of a sample's argon release, because the gas initially released at low temperature can be affected by atmospheric contamination, excess ^{40}Ar or ^{39}Ar recoil. Despite this, however, the record of subtle events might be extractable from the first small amounts of argon evolved. These traces would normally be released in the first fraction in a conventional analysis, where any delicate details of age structure would be averaged together and lost.

To explore this possibility, we have examined the low-temperature spectra of feldspar, mica and whole-rock samples from sedimentary rock and mylonite of Mesozoic to Cenozoic age. We used low-power laser heating to obtain step-heating fractions having very small gas volumes but adequate signal/noise levels for meaningful analysis. Analyses of both rock types gave initial fractions having zero apparent age, before climbing to the igneous and detrital precursor ages that dominate the age spectra. However, the detailed low-temperature spectra do not resemble the smoothly climbing patterns expected for volume-diffusive Ar loss. Instead, the profiles display pronounced age steps which may be reproducible between samples, even using variable heating schedules. In the sedimentary samples, these discontinuities point to a time of overprinting. In the mylonites, they correspond to progressively older times of post-crystallization regional tectonic activity. These ages are derived from gas fractions which can contain as little as 0.2% of the total sample ^{39}Ar . In a conventional step-heating approach, all of the steps bearing traces of such post-crystallization events would be easily subsumed in the first fraction.

The nature of the phases that release this low-temperature argon is unknown. They could, for example, be alteration products, trace phases, or the outermost portions of bulk K-bearing phases. In any case, it thus appears that although the imprints of these late-stage events are minor, they may nevertheless be encoded in discrete low-temperature clocks. Many samples may be capable of recording not only their igneous or metamorphic crystallization ages, but much more recent geologic history as well.

V22C-1058 1330h POSTER

Dating Basalts using the $^{40}\text{Ar}/^{39}\text{Ar}$ Method- Improvements Based on Electron Microprobe Evaluation of Samples

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A study of 85 samples of basaltic lava and cinders from the Los Lunas volcano, central New Mexico, demonstrates that the accuracy and precision of $^{40}\text{Ar}/^{39}\text{Ar}$ Ar dates for young basalts can be maximized by selecting samples that contain K-feldspar as a late-crystallized phase, and contain little or no glass or alteration phases. On the basis of optical observations of thin sections, it has long been recognized that abundant groundmass glass is detrimental to K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ Ar dating of basalts. The electron microprobe offers a means of assessing and quantitatively analyzing basaltic groundmass features that are too small to be assessed optically. X-ray mapping and quantitative analyses accurately distinguish among crystal and glass phases as small as $2 \mu\text{m}$. The crystallinity of smaller areas can be qualitatively assessed by multiple analyses, where homogeneous compositions indicate glass and heterogeneous composition indicates multiple crystal phases.

Samples from Los Lunas volcano were examined by electron microprobe, with the first step in the evaluation process being collection of potassium x-ray maps of polished surfaces. Once the locations of K-bearing phases were determined, the compositions of the phases were measured using quantitative analysis. Some otherwise well-crystallized samples were found to contain small amounts of groundmass glass in interstices between crystals; in these cases, virtually all K was concentrated within the glass. In other samples the groundmass was fully crystallized. In these cases K resided in K-feldspar, either as thin ($<10 \mu\text{m}$) rims on plagioclase or as fine ($<15 \mu\text{m}$) groundmass crystals intergrown with albite. This K-feldspar would be impossible to identify optically due to the small grain size and intergrown nature of the crystals. Samples were

rated on the basis of glass content versus K-feldspar content.

After excluding samples containing abundant (>10%) glass, 19 samples were dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ resistance furnace incremental heating method. The shape of spectra and the accuracy and precision of plateau and isochron ages correspond closely to the ranking assigned based on the microprobe evaluation. Glass-free, K-feldspar-rich samples have generally flat spectra, relatively high radiogenic yields ($\%^{40}\text{Ar}^*$), and ages with precision values ($\pm 2\sigma$) ranging from 1-5%. These ages agree well with stratigraphic order. Samples with increasing amounts of groundmass glass have increasingly disturbed spectra, reduced radiogenic yields, and low precision ($\pm 5-20\%$) plateau or isochron ages, which in some cases violate stratigraphic order. The consequences of even small amounts of groundmass glass are attributed to various combinations of atmospheric argon acquired during hydration, ^{40}Ar or K_2O loss, and ^{39}Ar recoil artifacts. $^{40}\text{Ar}/^{39}\text{Ar}$ results from higher ranking samples indicate that Los Lunas volcano consists of a 3.81 ± 0.10 Ma southern cone overlapped by a 1.25 ± 0.02 Ma northern cone; this relationship agrees with geologic map patterns. Within the northern cone, geologic mapping has delineated a sequence of five eruptive events. The ages of high ranking samples from the northern cone all agree within analytical error, suggesting that the entire period of eruptive activity spanned less than 30,000 years.

The precision and accuracy of data in this study was much enhanced by using microprobe observations of groundmass glass and K-feldspar to aid in the sample selection process. Sample selection based on only thin section observations would have yielded lower quality data.

V22C-1059 1330h POSTER

Single Grain (U-Th)/He Ages from Apatites in Acapulco Meteorite

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Acapulco meteorite is thought to have cooled extremely fast ($\sim 100^\circ\text{C}/\text{Ma}$) at high T ($\sim 1000^\circ\text{C}$) followed by very slow cooling ($\sim 2^\circ\text{C}/\text{Ma}$) without any significant later-stage reheating. The timing, temperature and cause of the dramatic change of cooling rate are still controversial. The most important evidence of slow cooling at low T is from extinct-Pu fission track dating for orthopyroxene, whitlockite and apatite crystals. Because the parent ^{244}Pu is extinct, this method yields only relative ages that may differ for different minerals as a result of differential track retentivity. Determining absolute ages from the fission track method is hampered by several fundamental uncertainties in estimating U and Pu concentrations, and in distinguishing fission tracks from other tracks produced by cosmic ray and spallation/recoil processes. One way to anchor the drifting (i.e. relative) fission track ages is dating the same sample with other chronometers which can give absolute ages in the same T range. For this purpose, we have applied single grain (U-Th)He dating techniques to apatite grains which have almost identical closure T as that of fission track retention.

Four apatite grains with 150 micrometer \sim 230 micrometer size were analyzed for U, Th (with ICP-MS) and ^4He (laser extraction Quadrupole MS) concentrations, and one grain ca. 200 micrometer \times 200 micrometer was step-heated to determine diffusion parameters. Imaging of the sample shows anhedral crystal shapes such that for most apatites it's almost impossible to reconstruct the original crystal morphology from the mineral separates, preventing precise estimation of alpha particle ejection loss (F_T) for each sample. The uncorrected ages, therefore minimum ages, are: 4462 ± 51 (analytical error only; 1 σ) Ma, 4326 ± 51 Ma, 4386 ± 52 Ma and 2718 ± 39 Ma. The first three ages are indistinguishable when considering possible large variation of F_T values for those samples. The oldest age of 4462 ± 51 Ma is interpreted as the minimum age for helium closure in the Acapulco apatites. The step heating analyses revealed a simple volume diffusion at temperatures below 300°C , yielding closure T of 90°C at a cooling rate of $2^\circ\text{C}/\text{Ma}$.

The 110 Ma age difference between apatite (closure T $\sim 90^\circ\text{C}$) and orthopyroxene ($\sim 280^\circ\text{C}$) fission track is combined with the new (U-Th)/He data ($> 4462 \pm 51$ Ma at 90°C). According to this simple comparison, significant retention of fission tracks in orthopyroxene began as early as approximately 4570 ± 50 Ma which is identical with PbPb isochron age of 4557 Ma. This calculation suggests rapid cooling down to 300°C

, around the closure T of plagioclase Ar diffusion, then followed by slow cooling. This interpretation suggests that the younger $^{40}\text{Ar}/^{39}\text{Ar}$ age (4507 ± 9 Ma) obtained from Acapulco plagioclase, which should reflect cooling through $\sim 300^\circ\text{C}$, is spuriously young due to systematic errors (i.e., decay constants and/or standard data) in the $^{40}\text{Ar}/^{39}\text{Ar}$ method, as suggested by comparison between high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ and U/Pb ages for terrestrial volcanic rocks.

V22C-1060 1330h POSTER

^{39}Ar Recoil Distance and Implantation Efficiency

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Surface loss of ^{39}Ar from vacuum encapsulated coarse-grained muscovite and biotite supports previous estimates for a mean recoil depletion distance of 100 nm and empirically describes the degree to which recoiled atoms implant into neighboring crystals. Most experiments involved cutting single mica pieces into controlled shapes (6.3 mm dia. circle, 9x15 mm rectangle) of varying thicknesses (30 to 220 microns) that were then wrapped in Al foil, vacuum encapsulated and irradiated for 100 hours. For one experiment a rectangular muscovite was cut into twelve sub-equal size pieces, stacked together and wrapped in Al foil prior to vacuum encapsulation and irradiation. Following irradiation, the capsules were loaded into the argon extraction system and punctured with a CO_2 laser. After argon analysis, the samples were recovered and the Al foil was removed. The Al foil and the individual mica crystals were fused separately within a standard double vacuum resistance furnace in order to determine the total ^{39}Ar concentration in the micas and assess the amount of implanted ^{39}Ar into the Al foil.

In all cases, readily detectable ^{39}Ar was measured in both the encapsulation tube and the Al foil. Of the total ^{39}Ar recoiled from the micas, between 30 and 68% was implanted into the Al foil. Summing the encapsulation gas with the Al foil gas to represent the total ^{39}Ar recoil loss and with knowledge of the sample thickness and total ^{39}Ar concentration allows calculation of the mean recoil depletion depth. The four single crystal experiments yield a mean recoil depletion depth of ca. 104 nm that is in excellent agreement with several other estimates for this parameter. Based on the experiment that involved multiple pieces of muscovite sandwiched together, it is determined that only 18% of the total recoiled ^{39}Ar implanted into adjacent crystals. The Al foil from this experiment contained 30% of the recoiled ^{39}Ar , which indicates that it is overall easier to implant ^{39}Ar atoms into foil compared to mica.

These simple experiments have implications regarding vacuum encapsulation studies of fine-grained samples and high precision geochronology. For instance, if the ^{39}Ar implanted into the material (foil, quartz ampoule) used to house the mineral separate is ignored a significant underestimation of the true recoil loss will result. Because ^{39}Ar does not readily implant into neighboring grains, the loss of ^{39}Ar from the bulk system will increase the apparent age of a given sample. The age increase will be proportional to the surface area to mass ratio of the sample. Surface loss of recoiled ^{39}Ar from biotite accounts for part of the age discordance (0.1 to 0.3 Ma) commonly observed between cogenetic biotite and sanidine.

V22C-1061 1330h POSTER

Chemical variations in the Cerro de Mercado (Durango, Mexico) fluorapatite: Assessing the effect of heterogeneity on a geochronologic standard.

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Despite the lack of an official pronouncement, the fluorapatite of Cerro de Mercado, Durango, Mexico has become the *de facto* standard for (U-Th)/He geochronology. In addition to being relatively inclusion-free and easily obtained, these crystals are commonly in excess of 5mm in diameter, permitting the removal of the outer skin of the crystal, theoretically eliminating the alpha-ejection correction. However, bulk analyses of the Durango fluorapatite indicate a substantial variation in U and Th concentrations from aliquot to aliquot (167-238 ppm Th; 9.7-12.3 ppm U, [1]). If similar variations were to occur on the sub-grain scale, small fragments of single crystals could contain helium excesses or deficiencies due to alpha-ejection exchange between zones with varying parent element content.

We have performed a series of experiments to quantify the intra-grain variation in U and Th, in order to model the effect of this variation on ages determined on Durango fluorapatite. X-ray maps show concentric zonation in U and Th, with similar, but more apparently pronounced zonation in Si and Cl. Preliminary laser-ablation ICPMS data indicate, not surprisingly, that intra-grain variations in U and Th concentrations obtained by analysis of ~ 35 μm spots are larger than that which had been previously obtained by bulk analytical techniques (with overall concentrations greater than for bulk analyses). Thus far, analyses yield U concentrations varying from 11 to 16 ppm, and Th concentrations ranging from 220 to 340 ppm.

Modeling underway suggests that parent element variations on the order of 50%, such as those observed, and the resulting differential alpha-exchange could lead to several percent error in age, for ~ 100 μm fragments. The effect scales inversely with fragment size, with 300 μm fragments (roughly the size of a large, single grain analysis) having only $\sim 1\%$ error. This may offer an explanation for the previously observed inability to reproduce ages for the Durango fluorapatite within the theoretical uncertainty [2].

[1] Young, E.J. et al., 1969. Mineralogy and geochemistry of fluorapatite from Cerro de Mercado, Durango, Mexico. USGS Professional Paper 650-D, pp D84-D93.

[2] House, M.A. et al., 2000. Helium chronometry of apatite and titanite using Nd-YAG laser heating. Earth and Planetary Science Letters, v. 183, pp 365-368.

V22C-1062 1330h POSTER

The Importance of Lithology in the Interpretation of Apatite U-Th/He Ages

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The low closure temperature of the apatite U-Th/He system makes it useful for understanding the long-term post-tectonic history of decaying orogens. However, apatite U-Th/He ages, which reflect the specifics of the minerals cooling history, must be interpreted within the context of both regional tectonic setting and local geologic factors. The retention of radiogenic helium within an apatite is the result of several geologic factors that affect the apatite host rocks cooling history. In areas lacking substantial heat advection or production (tectonic activity or volcanism), rocks that have been exhumed to the surface have thermal histories that are linked to the local geothermal gradient. Generally a geothermal gradient of 25 C/km is assumed for a tectonically passive continental crust; but, the geothermal gradient is a construct of two major factors: (1) basal heat flow, and (2) the thermal conductivity of the rocks below the surface. Radiogenic heat production in the crust is an additional, but secondary, factor. While basal heat flow may not vary significantly across a region, the thermal conductivity of rocks in the upper crust may differ by more than 100%.

To evaluate the effect of variable thermal conductivities on the cooling history of an apatites host rock, we modeled thermal histories for samples slowly exhumed from crust having two very different steady-state geothermal gradients, using the thermal properties of shales, sandstones, and limestones from the Appalachians. The two geothermal gradients were constructed by stacking these lithologies in different orders. Thermal histories were developed for each model, by eroding the surface unit and re-equilibrating the geotherm. Two different erosion rates were applied, one at 50 meters/m.y. and another of 10 meters/m.y., rates that bracket the upper and lower limits respectively of generally accepted values of Appalachian denudation. These rates are sufficiently slow so that heat is not being advected by rapid erosion. The thermal histories for these two cases were entered into a helium ingrowth-diffusion model for 130-micron apatites to predict the U-Th/He ages. The results for the ingrowth-diffusion model show that U-Th/He ages for the more rapid denudation rate thermal histories (50 m/m.y.) varied by $< 10\%$. The U-He ages for the protracted denudation rate thermal histories (10 m/m.y.) varied by 20%. Considering that denudation is never completely uniform, the addition of lithologic variability makes assumptions about the long-term rate of exhumation very difficult to constrain. However, it does help resolve why there can be dramatic along-strike variations in age from proximal samples in apatite U-Th/He and fission track ages from the central Appalachians and northern Blue Ridge. In tectonically active regions, the effect of variable thermal conductivity may be small on the final

U-Th/He age, but in areas of slow cooling, the effect might be significant.

V22D MC: 304 Tuesday 1330h

Heavy Element Stable Isotope Fractionations II (joint with B, OS, P)

Presiding: M Rehkamper, ETH Zurich; A D Anbar, University of Rochester

V22D-01 1330h INVITED

Iron Isotope Variations in Natural Aqueous Systems: Further Clues to Fractionation Mechanisms

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A number of recent pioneering studies into the potential of iron isotopes to be fractionated by natural processes have revealed a complex web of possible isotope fractionation mechanisms. For example, processes involving microbially-mediated reduction of mineral-bound Fe(III) to Fe(II) have been shown to result in fractionation of the ⁵⁶Fe/⁵⁴Fe ratio of from 0 to 2.5‰/‰, with the lighter isotopes being concentrated in the Fe(II)-bearing aqueous or solid product. This fractionation clearly results from disequilibrium reactions, although it is as yet unclear whether the cause is strong complexation of iron at the mineral surface that limits back reaction or a true vital effect. Moreover, field and laboratory studies of abiotic iron oxidation under disequilibrium conditions reveal a fractionation of as much as 2‰/‰ with the heavier iron isotopes being concentrated in the Fe(III)-bearing product, requiring equilibrium fractionation among the coexisting aqueous Fe(II) species prior to oxidation. Furthermore, theoretical considerations predict that under equilibrium conditions large iron isotope fractionations are possible due to contrasts in ligand strength and atomic bonding environment, and that aqueous Fe(III) complexes will concentrate the heavier iron isotopes relative to Fe(II) complexes involving the same ligands. These observations provide important insights into possible isotope fractionation mechanisms, yet beg a more thorough examination of iron isotope fractionation in diverse, relatively simple natural systems. Here we present new iron isotope data that document fractionations accompanying processes such as precipitation of siderite from CO₂-charged springs, of schwertmannite from acid-mine drainage and of ferrihydrite from spring waters by a presumably microbial mechanism. Considered in light of previous studies the new data underscore the importance of aqueous speciation in determining iron isotope fractionations observed in natural and experimental systems.

V22D-02 1345h

Iron Isotope Fractionation in Microbial and Non-Biological Precipitates, and the Human Body

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We have investigated biotic and abiotic stable iron isotope fractionation pathways in experiments, the low-T natural environment, and the human body. Fe samples were analysed using a Nu Plasma Multicollector ICP-MS. All measured samples plot on the theoretically predicted exponential fractionation line in the Delta57Fe versus Delta56Fe space, demonstrating absence of ArN or ArO interferences. An experimental calibration of Fe isotope fractionation during abiotic formation of iron (III) oxyhydroxide and iron(II) minerals from aqueous solution resulted in significant differences: (a) During fast precipitation of FeOOH during alkalization of a Fe(III)Cl₃ solution at room temperature the solid is only slightly enriched by about 0.1permil in 57Fe compared to the solution. (b) Slow precipitation of akaganeite (beta-FeOOH) from aqueous Fe(III)Cl₃ solution leads to a depletion of 57Fe by about -2.2permil in the solid phase without a significant influence of temperature. (c) Precipitation of FeOOH during oxidation of aqueous Fe(II) solutions by oxygen yields an enrichment of up to 4.8permil in 57Fe in the solid phase. (d) Iron(II) carbonate precipitation between 20 and 60C leads to an almost negligible depletion in 57Fe compared to aqueous ferrous ions. Interpretation: Large enrichment of the heavy isotope is observed where Fe is oxidised, whereas small to intermediate depletions of heavy Fe isotopes occur upon formation of Fe-minerals without change in redox state. Additionally, kinetic effects, the speciation of the aqueous solution, or the effect of crystal structures may have to be considered. Biotic isotope fractionation by microorganisms was investigated at two field sites. In a Fe mine (Gonzen, Switzerland), Fe-precipitating microbes (*Gallionella ferrugina* and *Leptotrichia ochracea*) were formed Fe(III)-oxyhydroxides that are ca. 0.6permil heavier in Delta57Fe than the Fe-rich parent solutions. At Cady Mts, California, filamentous fabrics of goethite, thought to represent fossil remnants of microbial mats, have been found as encrustations in chalcocopyrite. Delta57Fe is 3 permil heavier than the associated calcite (representing the Fe-rich fluids). Therefore, the fractionations found in microbial precipitates are not larger than those produced in the abiotic experiments. In contrast, major Fe isotope fractionations are produced by the human body: The major iron compartments in the human body, blood, liver, muscle tissues, and also hair, are all depleted by as much as 6 permil in the 57Fe isotope relative to 54Fe when compared to the average dietary intake. Since feces are similar to the average intake, we conclude that a significant Fe isotope fractionation occurs at the absorptive stage in the intestine. In conclusion, with respect to the hypothesis that Fe isotope effects might serve as "biosignatures" it appears that microbial and abiotic reactions cause similar isotope effects which essentially depend on redox reactions and the speciation in the aqueous solution. On the other hand, higher organisms bear distinct Fe isotope signatures.

V22D-03 1400h

Copper Isotope Fractionation in Porphyry Copper Deposits: A Controlled Experiment

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Previous studies have shown that copper is fractionated in the environment. However, the mechanisms for isotope fractionation and the role of organic and inorganic processes in the fractionation are not well understood. Here we used the well controlled experiments used by Phelps Dodge Corporation aimed at leaching copper from their ore deposits to constrain the mechanism of copper isotope fractionation in natural systems.

The isotope data were collected on a Micromass Isoprobe. High temperature copper sulfides from ore deposits in Chile and Arizona yield delta 65Cu near 0 permil. The reproducibility of the data is better than 0.1 permil.

Controlled experiments consisting of large columns of rocks were fed solutions containing bacteria such as *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*. Solutions from the columns were sampled for sixty days and analyzed for copper concentrations, oxidation potential, ferrous/ferric ratios and pH. The results indicate that the bacterially aided dissolution of copper

fractionated copper. Preliminary experiments of copper dissolution not using bacteria show no isotope fractionation

The original rock in the experiment has a delta 65Cu of 2.1. The first solutions that were collected from the columns had a delta 65Cu of 5.0 per mil. The liquid changed its isotopic composition from 50 to 10 during the sixty days of sampling. The greatest shift in the isotope ratios occurred the first 30 days when the copper recovered was less than 40% and the ferrous/ferric ratios were somewhat constant. At approximately 35 days after the start of the experiments, the copper recovery increases the ferrous/ferric ratio decreased and the copper isotope ratio of the fluids remained fairly constant.

The data suggest that the bacteria are required to effectively fractionate copper isotopes in natural systems and that the mechanisms of bacterial aided copper dissolution may include a direct dissolution of the sulfides by the bacteria. Experiments underway with enzymes without the bacteria may confirm this hypothesis. The data obtained in these experiments will provide some constraints in the use of copper isotopes as proxy for life in the rock record.

V22D-04 1415h

Heavy Stable Isotopes As Indicators of Redox-Sensitive Contaminant Dynamics: Progress With Selenium

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Selenium contamination occurs in many areas of the western USA as Se is flushed from soils into irrigation wastewater. It is also elevated where fly ash from coal-fired power plants is disposed of, and in a few other settings. Predicting the long-term impacts of anthropogenic Se inputs on various systems involves understanding the redox reactions that control Se mobility and bioavailability. Detailed Se speciation studies have provided insights into such processes, but are limited in several ways. Se isotope measurements provide complementary information about redox reactions, and thus can improve understanding of these critical processes. Other heavy stable isotope systems have similar potential. Several challenges have arisen in the development of Se isotopes, and all of these apply to other heavy stable isotope systems. Because of the geochemical complexity of Se, several studies were needed to provide an initial survey of laboratory data on Se isotope systematics. Other heavy elements have similarly complex arrays of species and reactions, and detailed laboratory studies are needed to reveal the associated fractionations. Microbially mediated and kinetically complex reactions may have variable fractionations. Our microbial reduction experiments in the laboratory showed a wide range of fractionation induced by reduction of Se(VI) to Se(IV), from <1.0 to 5.0 per mil on 8076. On the other hand, sediment slurries from three different wetland settings yielded a narrow range of fractionation (2.6 to 3.1 per mil) for this reaction. This is encouraging, but further work will be needed to extend this to a wider range of conditions. Once the isotopic systematics are understood, transport dynamics in the field come into play. The effective fractionation that occurs in surface water-sediment systems may be less than the instantaneous fractionation induced by a reaction, because the sediment can be a "partially closed" system, connected to the water column via diffusion. Detailed studies of microcosms will be needed to address this issue.

V22D-05 1430h

Selenium Isotopes as Biosignatures in Seafloor Hydrothermal Systems

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Chemically similar to sulphur, Se occurs as +6, +4, 0 and -2 valences in a variety of organic compounds and geological settings. This makes the study of Se