

have also recently adapted the ultrasonic attachments to a miniature X-ray diamond cell (60° cone) so that in the future both static and dynamic elasticity measurements may be carried out during the same experiment. Independent volume (X-ray) and length (ultrasonic) measurements at high *P-T* would have intriguing implications for an absolute pressure scale, and remains one of the larger goals of our technique.

V42E-05 1445h

Determination of the elastic properties at high pressure without pressure scale

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Pressure and temperature are the key parameters for determining the physical properties of earth materials in the interior of the Earth. In many laboratory studies, the determination of pressure requires pressure-standards, for example, NaCl, Au, or Pt. Recent evidence from the phase boundaries of perovskite-forming reactions suggests that the equations of state for these materials may be in error by as much as 10%.

Ultrasonic-base laboratory studies to determine elasticity require measurement of P and S-wave travel times, density and length of sample at the experimental conditions. Combining in-situ X-radiation and ultrasonic measurements, now it is possible to collect all of these parameters simultaneously and directly. This enables pressure scale-free measurements of the equation of state of the sample using a parameterization such as the Birch-Murnaghan equation of state. In addition, pressure at the experimental condition is defined by the sample X-ray volume. Therefore, this technique can be used to re-determine the equations of state for cohabitating pressure standards.

We report elasticity data for ferroperricite (Mg,Fe)O with 17 mol% Fe, a potential mantle composition. The ultrasonic velocities have been measured at high pressure and the equation of state has been determined using the pressure-scale free method. Compared with MgO, the bulk modulus and its pressure derivative of (Mg,Fe)O are comparable. But the shear modulus and pressure derivative have been reduced. The pressure suggested by the sample is higher by more than 10% than that calculated from the coexisting NaCl using the Decker pressure scale.

V42E-06 1530h INVITED

New Thermochemical Adventures in Modern Mineralogy

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Much current interest in mineralogy involves complex, hydrated, and often poorly crystalline materials found in the low temperature environment found as products of both natural processes and human activity. Examples of such materials include zeolites, clays, hydroxalicates, manganese oxides, iron-aluminum oxyhydroxides, and sulfate minerals. Such materials are active as catalysts, ion exchangers, and transport agents for contaminants. Both structural and thermodynamic characterization of such materials has been difficult in the past, but advances in spectroscopy, diffraction, and oxide melt solution calorimetry make much more definitive studies possible at present. Systematic energetic trends have been recently observed for the formation and hydration of framework-structured zeolites and manganese oxides. Similar trends are being sought for the layered materials, clays, and hydroxalicates. The role of water in the stabilization of low temperature phases reflects a close balance between energetically favorable bonding and loss of entropy during hydration. Detailed compositional, structural, and thermochemical analysis of the same samples is required to properly interpret calorimetric data.

V42E-07 1600h

Recent Advances in Research on Silicate Solid Solutions

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The Earth, as well as other solid planets and meteorites, is largely made up of solid-solution minerals. An understanding of their microscopic, mesoscopic and macroscopic properties and their behavior under different *P-T* conditions is a challenge for all disciplines concerned with the solid state. A major goal of mineral physics is to investigate how microscopic and mesoscopic properties control or affect the thermodynamic and bulk physical properties of minerals.

Advances in different spectroscopic methods such as IR, Mossbauer, Raman, NMR, and X-ray and optical absorption make this possible. In addition, developments in computational methods are increasing rapidly and allow detailed microscopic properties to be investigated. For example, ²⁹Si NMR investigations are showing that many silicate solid solutions (e.g. pyroxene, garnet, feldspar) are characterized by short-range cation order. Previously, the question of short-range order had largely been ignored in thermodynamic modeling studies because its determination by diffraction methods is very difficult. Raman and IR spectra are being used to characterize structural heterogeneity and thus lattice strain over different correlation lengths. Lattice strain, resulting from size differences of mixing atoms, is largely responsible for nonideal thermodynamic behavior in the volume and enthalpy of mixing for most silicate solid solutions. Chemical effects such as crystal field stabilization energies can also play role in affecting thermodynamic properties, but they are generally second-order compared to strain. Local-site relaxation and localized strain properties in solid solutions can also be studied with element specific methods such as XAS or optical absorption spectroscopy. Third generation synchrotrons allow XAS studies even at the trace element level in minerals.

The aluminosilicate garnet and the Na-K feldspar solid solutions have received much structural and thermodynamic study using many different experimental and computational methods. Both systems are characterized by positive excess mixing with respect to volume, enthalpy and vibrational entropy. The thermodynamic properties can be explained partly by their microscopic structural properties. These two solid-solution systems will be addressed and recent experimental results, largely spectroscopic based, will be presented and discussed with regards to their solid-solution behavior.

V42E-08 1615h INVITED

Future directions in Mössbauer spectroscopy

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Since the discovery of the Mössbauer effect more than 40 years ago, a wide range of applications in a number of different disciplines has been described. One great advantage of the Mössbauer effect is its high energy resolution, which enables its use as a highly sensitive probe of the atomic environment, providing information on valence state, site occupancies, site coordination and distortion and magnetic structure, and processes such as phase transitions, relaxation, lattice dynamics and diffusion.

Properties that have not been fully exploited include spatial and time resolution. The milliprobe, for example, enables a two orders of magnitude increase in spatial resolution. Further improvement may be anticipated with developments in synchrotron studies of nuclear forward scattering. Other possibilities on the horizon include development of a Mössbauer electron microscope which would focus conversion electrons using conventional electron optics, and development of focusing lenses for gamma rays on a laboratory scale. Time resolution has also not been widely exploited. Studies with conventional techniques are possible over a wide range of time scales, from *in situ* investigations of phase transitions, oxidation and other chemical reactions, to diffusion studies, to studies at the intrinsic time scale of the Mössbauer effect to investigate processes such as electron transfer. Existing facilities for forward nuclear scattering at synchrotron installations reduce this timescale even further.

Mössbauer spectroscopy can be performed under a wide range of *P,T* conditions, and the limits have not yet been reached. Developments in nuclear forward scattering could expand the pressure and temperature limits, raising the tantalizing possibility of measuring Mössbauer parameters at mantle temperatures and pressures.

V42E-09 1645h INVITED

Experimental Mineralogy and the Origin of Life

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The origin of life on earth was a geochemical event. The first living entity must have emerged from chemical reactions of air, water and rock. Of those three raw

materials, the atmosphere and oceans have been the focus of most origins research, but rocks and minerals are receiving increased attention for their potential chemical and structural roles in assembling life. Recent research elucidates five possible roles for minerals in life's origin; each of these roles is the subject of ongoing experimental research.

(1) Porous rocks and minerals, including vesiculated volcanic rocks and weathered feldspars, may play relatively passive roles as protective environments for the concentration of organic molecules.

(2) Minerals may also serve as scaffolds for the organization and assembly of these molecules into larger structures. Clays and double-layer hydroxides are especially efficient in this regard.

(3) Mineral templates may play a more direct role in molecular selection and assembly. In recent studies we observe that scalenohedral crystal faces of calcite are chirally selective for left- and right-handed amino acids. Atomic force microscopy reveals chiral growth structures and etch morphology on these faces, and points to a mechanism for selection.

(4) Transition metal oxides and sulfides serve as catalysts for organic synthesis in hydrothermal environments. We observe two contrasting mechanisms for carbon-carbon bond formation. All transition metal minerals studied promote methylation through Fischer-Tropsch type reactions. In addition, nickel and cobalt sulfides efficiently promote carbonylation reactions, including the synthesis of carboxylic acids.

(5) Sulfide minerals may dissolve in hydrothermal systems to become reactants in organic synthesis reactions. In experiments with iron sulfides at 250C and 0.2 GPa, for example, we observe the formation of organic di- and tri-sulfides, methyl thiol, and a variety of carbonylated iron complexes in hydrothermal solutions. These reactive aqueous species, some of which resemble the active centers of metabolic enzymes, point to the possibility that minerals may have played a critical role in jump-starting the earliest metabolic cycles.

Taken together, these experiments demonstrate a central, dynamic role for minerals in the origin of life.

V42F MC: 304 Thursday 1330h

Geochemical and Isotopic Tracers of Earth Processes: Geochronology and Time Scale Issues (a session in honor of Gil Hanson) (joint with H, T, GC, MR)

Presiding: S R Hemming,
Lamont-Doherty; T Rasbury, SUNY
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V42F-01 1330h

Dating Fluvial Terraces by ²³⁰Th/U on Pedogenic Carbonate, Wind River Basin, Wyoming

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Reliable and precise ages of Quaternary pedogenic carbonate can be obtained with ²³⁰Th/U dating by TIMS applied to large suites of carefully selected small samples. Datable carbonate can form within a few thousand years of surface stabilization allowing ages of Quaternary deposits and surfaces to be closely estimated. We have dated pedogenic carbonate from glacio-fluvial terraces of the Wind River Basin to better constrain the age of the penultimate glaciation in the central Rocky Mountains.

Dense pedogenic carbonate clast-rinds from gravels of middle to late Quaternary terraces in the Wind River Basin contain 5-35 ppm U and 0.01-0.3 ppm ²³²Th, with (²³⁰Th/²³²Th)=5-7500, making them extremely suitable for ²³⁰Th/U dating. Complexities in the textures of the Wind River clast-rinds emphasized the importance of sampling horizons as thin as 0.5 mm from polished slabs to avoid averaging long (10⁴-10⁵ yr) and potentially discontinuous depositional histories. Samples meeting straightforward textural criteria

with finite $^{230}\text{Th}/\text{U}$ ages preserve within-rind stratigraphic order in all cases. Cosmogenic nuclide (^{10}Be , ^{26}Al , ^{36}Cl) dating of Wind River terraces by others yields most-probable ages that are systematically younger than those inferred from clast-rind $^{230}\text{Th}/\text{U}$ ages though the differences are not resolvable outside of the analytical and systematic uncertainties of the two techniques.

Ages from $^{230}\text{Th}/\text{U}$ rind dating for terraces WR4 (163 ± 8 ka) and WR2 (55 ± 7 ka), in conjunction with constraints from WR1 and the modern floodplain, indicate incision of the Wind River is slower than previously inferred and relatively uniform from terrace to terrace over the past glacial cycle. An age of 151 ± 9 ka is interpolated for terrace WR3 that may be traced to moraines of the final advance of the Bull Lake glaciation at the type locality. The new age indicates that the Bull Lake glaciation climaxed near the end of marine isotope stage 6 rather than in early stage 5 and coincided with a global ice volume maximum. Thus, the Bull Lake glaciation is not an example of asynchrony between advances of mountain glaciers and continental ice sheets.

V42F-02 1345h

Single Phase $^{40}\text{Ar}/^{39}\text{Ar}$ Dating of Rajahmundry Trap Basalts Contemporaneous With Late Stage Deccan Trap Volcanism

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The Rajahmundry Traps of eastern peninsular India, often considered to be outliers of the Deccan Traps, occupy ~ 35 km² centered on the Krishna-Godavari Basin and extending offshore in the sub-surface. On-shore exposures average 60m in thickness, including a laterally continuous sedimentary interlayer of laterite, limestone and shale (~ 2 m thick, total) separating upper flows from lower flows. $^{40}\text{Ar}/^{39}\text{Ar}$ CO₂ laser incremental heating analysis of twelve plagioclase separates from Rajahmundry Trap basalts reveal an age of ~ 64.6 Ma for the entire sequence based on the FCs standard at 28.02 Ma. Flows chosen for dating include 8 sites spanning both the upper and lower flow sequences. Paleontological studies of sediments adjacent to the basalt at depth in Krishna-Godavari Basin, e.g. Jaiprakash *et al.* (1993), suggest that the period of time covered by the two flows and intertrappean sediments is up to ca. 6 myr. Dates obtained for this study, however, show that ages for both upper and lower flows are indistinguishable within 2σ error from one another, and span ~ 2 Ma at most, pointing to a substantial hiatus in the sedimentary record at the top of the upper basalt flows. Extremely high Ca/K ratios (up to ~ 400) in several samples limits precision due to error propagation attending the large correction necessary for reactor produced ^{36}Ar from Ca. However, plateau ages as precise as 64.8 ± 0.4 and 65.5 ± 0.8 from above and below (respectively, 2σ errors) the sedimentary interlayer have been obtained. Samples with both high and low Ca/K ratios confirm rapid eruption of the entire Rajahmundry Trap sequence.

A petrogenetic link between these basalts and the Deccan Trap basalts (the remains of which lie over 300 km from the nearest exposure of Rajahmundry Trap) has been suggested but has yet to be substantiated. These new data clearly place the eruption of the Rajahmundry Traps temporally close to the K-T boundary, coincident with late stage Deccan volcanism and within ca. 1 Ma of initiation of main stage Deccan volcanism in e.g. the Western Ghats. Paleomagnetic studies of Vandamme and Courtillot (1992) revealed a reverse to normal magnetization polarity sequence within the Rajahmundry Traps, supporting a temporal connection with waning of Deccan Trap volcanism, consistent with our results. This now unequivocal temporal connection between the Rajahmundry Traps and Deccan Traps may suggest a much larger area of melt generation beneath the Indian sub continent than previously estimated, or may be the result of extensive overland flow distances (e.g. Baksi, *et al.*, 1994). The latter possibility would require significant paleovalleys to be maintained even after serving as conduits for, and presumably being filled by several individual flows, evidence of which is lacking. Recent reconstructions modeling

the evolution of the Krishna-Godavari Basin and catchments clearly show that then, as now, this basin drains much of the Indian Peninsula, including the main Deccan Traps at their time of eruption (Halkett, *et al.*, 2001). Overland flow of Deccan Trap volcanism thus remains a plausible origin for the Rajahmundry Traps.

V42F-03 1400h

Constraints on the timing of the Permian-Triassic biotic crisis: New U/Pb zircon-ages

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New IDTIMS U/Pb single-zircon data from ash layers intercalated within the Permian-Triassic (P-T) deposits of the Shangsi section (Sichuan Province, Central China) in combination with recently published ages from the GSSP in Meishan (Zhejiang Province, E China) constrain the most profound biotic crisis in the Earth's history, causing the near extinction of both terrestrial and marine life, to an age of >253 Myr (Mundil *et al.*, 2001). In addition, our data indicate that either the sedimentation rate for the uppermost Permian/lowermost Triassic in the Meishan section drastically decreases or that there was a depositional hiatus. Both of these conclusions are inconsistent with the concept of extreme rapidity for the end Permian extinction as well as the hypothesis of a very short duration of the $\delta^{13}\text{C}$ excursion near the P-T boundary. The results of both our study and previous work (Bowring *et al.*, 1998) show that for the Permian-Triassic ash layers in SE China, the effects of Pb loss are combined with varying amounts and sources of inheritance, resulting in an age-scatter which prohibits the extraction of a statistically robust age in many cases. The presence within a single ash layer of multiple generations of older xenocrysts has made quantitative interpretation even more difficult. If multi-grain analyses are used, these combined phenomena are extremely difficult to resolve and can become impossible to recognize (due to age-averaging). As a result multi-crystal analyses may be inaccurate by 1% or more and implications may be misleading. Single-zircon analyses from an ash layer 6 m below the first appearance of *parvus* (the biostratigraphic definition for the P-T boundary) from the Shangsi section yield a preliminary mean $^{238}\text{U}/^{206}\text{Pb}$ age of 254.7 ± 0.7 Myr (95% conf.). Also, initial analyses from an ash layer just below the final stage of the Permian (Changshingian) yield an age of 260 ± 0.4 Ma. Both ages are consistent with the results obtained on the ash layers from Meishan. Our estimate of 253 Myr for the P-T boundary (based on U/Pb ages) is in agreement with Ar/Ar ages of 250 Myr presented in Renne *et al.* (1995) for the Siberian Trap basalts and ash falls at the P-T boundary in Meishan and Shangsi, as well as new Ar/Ar ages from Shangsi, if systematic errors are taken into consideration. In addition, we find that Ar/Ar ages are systematically younger, which agrees with ongoing research suggesting that there is a systematic bias of 1-2% between U/Pb and Ar/Ar isotopic systems (Min *et al.*, 2000). Our combined evidence is at variance with recent studies (Rampino *et al.*, 2000; Becker *et al.*, 2001) which suggest a rapid extinction caused by a bolide impact. Although we cannot exclude an impact at or near the P-T boundary, a more gradual scenario and a causal relation between the massive continental basalt volcanism in South China at the end of the Permian and Siberia at the Permian-Triassic boundary - possibly in combination with other factors - and the biotic crisis must be considered.

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Bowring *et al.*, Science 280, 1039-1045, (1998).
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Renne *et al.*, Science 269, 1413-1413, (1995).

V42F-04 1415h

Uranium-Lead Ages of Lake Margin Tufa Calcite From the Middle Miocene Barstow Formation, Southern California

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The Barstow Formation crops out in the Mud Hills near the city of Barstow in the Mojave Desert. The deposits consist mostly of sandstones and mudstones with intercalated ash and carbonate horizons. Localized deposits of well-laminated to spongy non-laminated limestone occur throughout the Barstow Formation and are referred to as tufa deposits. The Barstow Formation has excellent mammalian fossil preservation and represents the type section for the Barstovian North American Land Mammal Age. Ashes within the Barstow Formation have been dated by Ar-based techniques and constrain it to be middle Miocene. However, the ages of the carbonate layers have not previously been constrained by any radiometric technique. Collected carbonate samples from different horizons within the middle member of the Barstow Formation and focused on pristine calcite samples for U-Pb analyses. We characterized our samples on three different scales to determine which samples should provide the best U-Pb ages. Polished slabs from our hand samples were evaluated with phosphor imaging technology to identify areas of high radionuclide concentration. Using transmitted light, polarized light, and cathodoluminescence petrography we carefully selected samples that did not have a complicated alteration history. Fission-track analyses were used to help identify uranium incorporation on the thin section scale. Synchrotron-based techniques, such as x-ray fluorescence (XRF) mapping, helped us to see U and other trace element concentrations on the micron scale. Phosphor imaging proved to be the most helpful technique for sample selection. Tufa deposits are enriched in U, with up to about 170 ppm as measured by isotope dilution and over 500 ppm as measured by in situ XRF. Based on isotope dilution measurements, $^{238}\text{U}/^{204}\text{Pb}$ ratios range between 400 and 6500, making the tufa deposits excellent candidates for U-Pb dating. Our most precise age thus far is 16.36 ± 0.16 Ma, giving a 2-sigma uncertainty of just less than 1%. Our results show that lake margin tufa deposits as young as Miocene can preserve original U-Pb systematics and provide precise and concordant ages. This tool should be helpful in constraining the ages of similar sedimentary deposits that lack other datable materials.

V42F-05 1430h

New $^{40}\text{Ar}/^{39}\text{Ar}$ ages for Basalts From the West Siberian Basin and Links With the Siberian Flood Basalt Province

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The Siberian Traps represent the worlds largest subaerial flood basalt province, and may be responsible for the Permo-Triassic mass extinction at 250 Ma (e.g., Campbell et al. 1992 Science 258, 1760). The total extent of the Traps, and whether or not the volcanism is a contributor to the Permo-Triassic mass extinction, are both still matters of debate. Basaltic and gabbroic rocks occur throughout the West Siberian Basin (WSB), but are covered by a thick succession of Mesozoic and Cenozoic sediments, unlike the more accessible Traps on the Siberian craton to the east. We have obtained material from three deep industrial boreholes (Hohryakovskaya, Permyakovskaya, Van Egan-skaya), and show that basalts and gabbros from the WSB have ages indistinguishable from the Traps to the east.

⁴⁰Ar-³⁹Ar dating of plagioclase (from basalts) and phlogopite (from a gabbro) separates from 6 samples from three boreholes give ages of 249.3 to 250.5 Ma (plagioclase) and 253.4 Ma (phlogopite) (relative to GA1550 biotite at 98.79 Ma). The results are obtained by step heating and the apparent plateau ages include more than 90 percent of the total argon released. Two sigma errors are better than 1.0 Ma for 5 of the samples. Normalised to the same standard, these ages are in good agreement with ages obtained for the Siberian Traps (250 Ma: Renne and Basu 1991 Science 253, 176).

On the basis of major and trace element data, the basalts from the WSB show affinities with the Nadezhinsky suite (Norilsk area), which is known to immediately precede the main pulse of volcanism that extruded over large areas of the craton. Limited recovery from the boreholes indicates that the basalts were erupted subaerially or possibly into shallow water (e.g. presence of abundant, large amygdaloids). Lava flows are at least 20 m thick, indicating voluminous eruptions.

The results from the Ar-Ar dating and chemical analysis emphasise a clear correlation between basalts from the WSB and the Siberian Traps. This dramatically expands the extent of the Siberian large igneous province. However, the total extent remains conjectural, because the locations of the southern and western boundaries of the eruptives are not yet constrained.

V42F-06 1445h

Problems With Correlation of the Carboniferous-Permian Boundary in North America

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Based on precise ages from paleocaliches and good fusulinid fossil control we estimated the age of the Carboniferous boundary from the Central Basin Platform of the Permian Basin of West Texas and the Sacramento Mountains of New Mexico to be 301 ± 2 Ma. The best constraint for the boundary age is from a paleocaliche that occurs 7 cycles above the first appearance of *Pseudosaggersia* in a core from the Central Basin Platform. This caliche gives a concordant U-Pb age of 298 ± 1 Ma and requires that the Carboniferous-Permian boundary, on the basis of fusulinids, is older than the estimates on most published time scales. However, more recent results from the northern Appalachian Basin suggest there is a problem with the biostratigraphy. In eastern Ohio a paleocaliche that lies just below the Ames Limestone, a unit with two diagnostic conodont fauna (*Idiognathodus simulator* and *Streptognathodus pavhuskensis*) that place it in the Early Virgilian, gives a concordant age of 292 ± 6 Ma. From this we have to infer that the Carboniferous-Permian boundary cannot be older than 298 Ma and in fact the paleocaliche age suggests that it is more like the 290 Ma suggested by the Harland et al. (1990) time scale. We see no reason to doubt the work of the paleontologists who established the biostratigraphic framework and we are confident that our ages are meaningful. Soils from during the time of subaerial exposure and during the Permo-Carboniferous, the large-scale sea level changes that resulted from the advance and retreat of glaciers were quite rapid. Estimates range from 100-400 ky for the cycles and whatever the choice, the duration of the exposure during which the caliches formed is short. Thus the age of the paleocaliches is the time of sedimentation and the concordancy of the ages as well as the petrography of the caliches that were sampled establishes that they have not suffered a later diagenetic history. Our efforts to establish new ways to date the sedimentary rock record offers the possibility of looking harder at assumptions that fossils appear and disappear synchronously everywhere.

V42F-07 1520h

Experimental Study of Grain Boundary Partitioning of Argon

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Despite the ubiquitous use of noble gases as tracers of Earth processes and as chronometers, some fundamental aspects of their geochemical behavior remain poorly understood. Here, we address a particularly critical characteristic of noble gas geochemistry, about which no data exist: at equilibrium, how do noble gases partition between grain boundaries and crystals? Understanding grain boundary partitioning of noble gases is important for applications in geochronology as well as models involving the transport and siting of noble gases within the crust and mantle.

As an example, standard models of isotopic closure for Ar (or He) in slowly cooled geologic systems require an effective zero concentration boundary condition for ⁴⁰Ar in the intergranular transporting medium (ITM) surrounding the mineral of interest to accommodate diffusive loss of ⁴⁰Ar* from the mineral. An exception to this condition results in the buildup of excess Ar in the source mineral. In detail, whether or not the local ITM satisfies this condition depends on a parameter called the transmissive timescale, defined as LMK/D, where L is the distance from the source mineral to some sink for Ar, M is the solid/ITM mass ratio, K is the solid/ITM partition coefficient, and D is the diffusivity of Ar in the ITM. The local ITM itself may act as an adequate local sink in a closed system if the value of MK << 1. While estimates of M are possible, currently, few constraints are available on K, in particular for nominally dry settings where the ITM consists of non-wetted grain boundaries.

We have designed and implemented experiments to determine the equilibrium partitioning of Ar between solid interiors and grain boundaries in a closed system. Experiments consist of sealed Pt capsules of polycrystalline synthetic diopside doped with ³⁷Ar that were equilibrated at conditions of 20 kbar and 1350 - 1500 C for 3 - 24+ hours. Preliminary results indicate that, while some of the ³⁷Ar initially residing in the solid diopside has diffused to the grain boundaries, a significant amount of ³⁷Ar (broadly analogous to an "excess" Ar component) remains in the solid - thus permitting measurement of the partition coefficient, K. Time series experiments will confirm whether or not the experiments have reached an equilibrium state or if the apparent partitioning is a kinetic effect.

V42F-08 1535h

Comparison Between ⁴⁰Ar/³⁹Ar and U/Pb Geochronometers at ca. 2.1 Ga

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Recent studies have revealed 1-2% age bias between conventional calibrations of the ⁴⁰Ar/³⁹Ar and U/Pb geochronologic methods applied to quickly cooled volcanic rocks whose isotopic systems should be uncomplicated by differential retention of radiogenic daughter isotopes. The U-Pb system serves as an ideal basis for comparison because of its rigorous internal reliability criteria and precisely-determined decay constants via alpha counting. Studies capable of providing useful comparison have been limited to samples younger than 1.1 Ga, which offers useful constraints primarily on ⁴⁰Ar/⁴⁰K of ⁴⁰Ar/³⁹Ar standards and the electron capture decay constant of ⁴⁰K. The magnitude of observed bias for these samples is within the range of realistically propagated errors in those quantities. The beta decay constant of ⁴⁰K is comparably poorly constrained, leading to ambiguities about early solar system cooling rates among other issues, and is more

difficult to test directly due to a paucity of appropriate (e.g., minimally altered with demonstrably simple thermal history) rocks for comparison. A strikingly fresh hornblende-biotite dacite from the Eglab region of the Rehbait massif, West Africa, offers an exceptional opportunity for head-to-head comparison of the two geochronometers at nearly twice the age limit currently available. Zircon from this unit are concordant to nearly concordant and indicate an age of ca 2076 Ma. ⁴⁰Ar/³⁹Ar analysis of individual hornblende grains, step-heated with a CO₂ laser, reveal some complexities but generally yield plateau ages of 2050-2060 Ma based on IUGS 1977 decay constants and 28.02 Ma for the Fish Canyon sanidine. Thus the bias between ⁴⁰Ar/³⁹Ar and U/Pb systems in this case is of order 1%, suggesting that relative error in the conventional beta decay constant is somewhat less than that of the electron capture constant for ⁴⁰K.

V42F-09 1550h

⁴⁰Ar/³⁹Ar Dating of Permo-Triassic Bentonites from the Shangsi Section, China

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The age and tempo of events near the Permian Triassic boundary (PTB) remain controversial. Ashfall deposits (bentonites) from the recently established GSSP at Meishan (Zhejiang Province, China) have so far been the focus of geochronological work. The Shangsi section of northern Sichuan Province was also proposed as a candidate for the GSSP of the PTB, and offers excellent opportunities for complementary geochronologic studies. The Shangsi section displays continuous carbonate-dominated marine sedimentation in the upper Permian overlain by lower Triassic clastic sediments. Overall, its sediments record a longer biostratigraphic time interval than the Meishan section. Several bentonites spanning this interval contain both unaltered feldspars and zircons suitable for dating. We report here new ⁴⁰Ar/³⁹Ar data on sanidine phenocrysts separated from three bentonites. One sample (SH-08) is from 30 m below the P-T boundary, near the base of the Changhsingian. Sample SH-27 is about 6 m below the FAD of *Hindooodus parvus* (defined as the biostratigraphic PTB at Meishan), and sample SH-09 is about 3 m above SH-27, i.e., about 3 m below the *H. parvus* FAD.

These samples were irradiated with geometry sufficient to ensure negligible fluence gradients between standards (28.02 Ma Fish Canyon sanidine) and samples. All three samples have been analyzed by total fusion of single crystals, and for SH-08 and SH-09, by incremental heating of multigrain samples with a CO₂ laser. Single grain analyses of these two samples revealed no evidence of inherited components, and both yield highly concordant plateaux for the multigrain samples. Single grains of SH-27 were large enough (up to 500 microns) to step-heat in 8-9 steps, and yield mutually consistent plateau ages for 4 individual crystals. Samples SH-09 and SH-27, from just below the PTB, yield nearly irresolvable ages of ca. 250 Ma, consistent with the previous ⁴⁰Ar/³⁹Ar reported by Renne et al. (1995). Sample SH-08 yields a plateau age of ca. 254 Ma.

These data indicate a duration of at least 4 m.y. for the Changhsingian stage, the last stage of the Paleozoic. This result is in excellent agreement with new high resolution U/Pb single zircon data from the same bentonites, reported by Mundil et al. (2001) and in a companion abstract. An important implication is that massive extinctions and paleoenvironmental crises which began at the end of the Wujiaopingian through the Changhsingian (final two stages of the Tethyan Permian), were more protracted than has recently become fashionable to invoke. A second important conclusion is that these ⁴⁰Ar/³⁹Ar data are 1-2% younger than the new Shangsi U/Pb data of Mundil et al. (2001), providing further documentation of bias between these methods which is most likely due to systematic errors in the current calibration of the ⁴⁰Ar/³⁹Ar system. Despite its presently limited absolute accuracy, our results illustrate the excellent utility of the ⁴⁰Ar/³⁹Ar method for measuring differential time.

V42F-10 1605h

Coupled U-Pb isotopic studies and synchrotron x-ray microbeam analysis of geologic systems

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Analytical advances in thermal ionization mass spectrometry now allow for precise measurement of U and Pb abundance and Pb isotopic composition in minerals where U and Pb may only amount to a few picograms by weight. High precision analysis at such low levels means that a much wider variety of mineral species can be considered as potentially useful U-Pb chronometers. However, evaluating the potential use of these minerals for high-precision dating requires understanding the environmental and crystal chemistry of the U and Pb being analyzed in these minerals. Advances in the production of microfocused synchrotron x-ray beams allow more unambiguous evaluation of uranium partitioning and speciation in these geochemical systems. The microbeam capabilities of these instruments, such as the X26A beamline at the NSLS, allow for near simultaneous evaluation of major and trace elements using synchrotron XRF, elemental speciation and coordination using x-ray absorption spectroscopy (XANES and EXAFS), and mineralogy using micro-XRD at resolutions of 10 microns or less. Additionally, the synchrotron hard x-ray microprobe allows for non-destructive analysis of the same hand specimens or thin sections from which samples are separated for isotopic analysis with a detection sensitivity often of 1 ppm or better. Some examples illustrate how these combined studies can help characterize the U and Pb geochemistry of the host environments in which these minerals formed. Andradite garnets from the Grand Canyon Supergroup (1178+/-26 Ma) are shown to be compositionally homogeneous in U abundance (10-25 ppm), with U as a 4+ species. Fossilized Jurassic fish coprolites from the Shuttle Meadow Fm. (ca. 200 Ma) show that although they are dominated by apatite the highest U abundance is consistent with adsorption onto organic C at the time of sedimentation. Examples of U analyzed from a number of terrestrial carbonates shows that U can be incorporated as both 4+ and 6+ species and may also be strongly influenced by the amount of organic material present, fluid chemistry, and source materials.

V42F-11 1620h

Determining the age and Original Seawater ⁸⁷Sr/⁸⁶Sr From Altered Aragonite Marine Cements of the Laborcita Formation, New Mexico

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Water-rock interaction modeling suggests that altered aragonite marine cements with abundances of Sr greater than a thousand ppm should yield both accurate U-Pb ages and the original seawater ⁸⁷Sr/⁸⁶Sr ratio. The exact Sr concentration depends on the composition of the diagenetic fluids. Aragonitic botryoidal cements are common within the algal mounds of the Laborcita Formation of the Sacramento Mountains, New Mexico. While other aragonitic components underwent early dissolution, the botryoids have been converted to calcite but have preserved their original fibrous aragonite textures. Multiple aliquots of the altered aragonite cements with fibrous texture from several samples representing the stratigraphic range of the mounds yield a minimum ⁸⁷Sr/⁸⁶Sr of 0.708393±8 that is more radiogenic than is expected (0.70793) for the Early Wolfcampian age (earliest Permian) of the Laborcita Formation. There is no apparent trend with the position of the samples in the mounds. Samples lacking fibrous texture have much higher ⁸⁷Sr/⁸⁶Sr ratios. The

Sr isotopic compositions and the concentrations show a trend consistent with an end member value for the diagenetic fluids of 0.70993. The botryoidal cements also yield a concordant U-Pb age of 304±2. While the Laborcita Formation is considered to be Wolfcampian, the ⁸⁷Sr/⁸⁶Sr ratio and the age suggest that it may be equivalent to the Missourian (late Pennsylvanian) from the mid continent based on Denison and Keopnicks (1994) Sr isotope seawater curve. Marine cements are common in the Late Paleozoic and samples that can be precisely dated and retain their original Sr isotopic compositions offer great possibilities for sorting out biostratigraphic problems as well as for refining the Sr isotope seawater curve.

URL: <http://pbisotope.ess.sunysb.edu>

V42F-12 1635h

(U-Th)/He Geochronology of Zircon Using Nd-YAG Laser Heating

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Developments of (U-Th)/He dating have demonstrated its potential and applicability as a low-temperature thermochronometer (e.g., Zeitler et al., 1987; Farley et al., 1996; Farley, 2000, 2001; Stockli et al., 2000). Recent success of dating apatite and titanite using laser extraction (House et al., 2000) enabled faster He analysis as well as single crystal dating due to far lower, more reproducible He blanks compared to conventional furnace heating. Here we report results of a systematic attempt at (U-Th)/He dating of known-age zircons using Nd-YAG laser extraction.

We analyzed single zircon grains separated from four rapidly cooled rocks of known ages, i.e., Fish Canyon Tuff (FCT; 27.8 ± 0.7 Ma), Buluk Tuff (BT; 16.3 ± 0.2 Ma), Tardree Rhyolite (TR; 58.4 ± 0.7 Ma) and Utaosa Rhyolite (UR; 2.52 ± 0.02 Ma). Zircon-containing Pt micro-crucibles were outgassed at 1300 degree C for thirty minutes. The evolved helium was spiked with 3He, cryogenically concentrated and purified, and analyzed by quadrupole mass spectrometry. After He extraction, the same zircon was melted using Pt fluxing crucibles with about 7 mg of ultrapure Li metaborate at 1400 degree C for 2 hours. The sample was spiked with 235U and 230Th and dissolved with 250 micro l HNO₃ by heating for 10 hours at 90 degree C. The resulting solution was then analyzed on a double focusing inductively coupled plasma mass spectrometer.

Measured (U-Th)/He ages of FCT, BT and UR are overall in agreement with their reference ages, with their mean corrected ages of 28.6 ± 1.4 (1 standard error), 16.1 ± 2.2 and 2.48 ± 0.05 Ma, respectively. These data suggest that (U-Th)/He dating using Nd-YAG laser extraction is basically applicable for zircon single grains. However, the He ages of TR are consistently too old, with a mean age of 78.8 ± 7.0 Ma. We inspected spontaneous fission track densities of TR zircons previously analyzed for zeta calibration (Tagami, 1987) and found that about 80 percent of these zircons are strongly zoned, with high track density (i.e., high U content) at core and low density at rim. This causes an overestimation of the alpha ejection correction and explains the overestimation of He ages for TR zircons.

V51A MC: Hall D Friday 0830h

New Directions in Experimental Mineralogy and Petrology III (joint with T, MR, HG)

Presiding: S Webb,

Georg-August-Universitt; J Kung,
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V51A-0967 0830h POSTER

Fe-Mg interdiffusion in (Mg,Fe)SiO₃ perovskite

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(Mg,Fe)SiO₃ perovskite is the dominant mineral in the lower mantle. Understanding the chemical and physical properties of this phase is therefore essential for understanding processes such as metal-silicate separation during core formation and mantle convection. An important parameter in describing the kinetics of such processes is the diffusion coefficient as function of P, T and fO₂. Although there is a relatively large database for diffusion coefficients in metals, oxides and silicates at 1 bar, high pressure results are still scarce due to experimental difficulties. Developments in multianvil techniques during the last 20 years allow the synthesis of high pressure phases such as (Mg,Fe)SiO₃ perovskite. Only in the last few years have diffusion experiments become possible as the result of improved pressure-temperature control, the development of large volume presses and new analytical techniques. However, there has been only one study of diffusion in perovskite (Si self diffusion, Yamazaki et al., 2000, PEPI, 119, 299-309).

In this study of Fe-Mg interdiffusion, polycrystalline samples of (Mg,Fe)SiO₃ perovskite were synthesized and then used for diffusion experiments at conditions of 23-25 GPa, 1750 °C to 2100 °C with run durations of 4 to 24 hours. In a first set of experiments we used MgO single-crystal capsules together with added Fe foil which buffer the fO₂ at relatively reducing conditions. Fe-Mg diffusion profiles are extremely short even after 24 h and cannot be measured by the electron microprobe. We therefore used EDX-TEM with which concentration profiles down to approximately 10 nm in length can be measured with relatively good counting statistics. Diffusion profiles measured on our samples are 100-600 nm long. In one sample we clearly observe that diffusion can be influenced by subgrain boundaries. Such regions of the sample have to be carefully avoided when analyzing diffusion profiles. At 1750 °C and 24 GPa a Fe-Mg interdiffusion coefficient of 3.66 × 10⁻²⁰ m²/sec is derived from our measurements. Fe-Mg interdiffusion in perovskite is therefore several orders of magnitude slower than in other phases at comparable temperatures. Currently, experiments are being performed on samples contained in Re-capsules to produce a more oxidizing environment.

These type of experiments show that it is possible to investigate transport properties of lower mantle minerals. Future progress in experimental equipment will allow higher pressures to be achieved with large sample volumes and long run durations.

V51A-0968 0830h POSTER

Finite Element Modeling of Volume Changes Produced by Heating and Pressurization of Fluid Inclusions

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Fluid inclusions are used in a variety of geologic studies including studies of metamorphic terrains, hydrothermal systems, and ore formation. By studying phase changes within inclusions, information about the temperature and pressure of entrapment can be derived. One of the basic assumptions made in these studies is that the volume of the inclusion has not changed significantly since its formation or during measurement. In general this is a good assumption, but in the case of inclusions trapped at high pressure, deformation of the inclusion may become important. For this study we focus in particular, on the elastic volume changes of the inclusion-host system that occur as the inclusions are heated during homogenization experiments. We use two-dimensional, axially symmetric finite element models to study the development of stresses in the host mineral around fluid inclusions and the resulting changes in inclusion volume. Numerical modeling allows us to estimate volume changes for shapes that cannot be described analytically. We find that elastic volume changes are a function of inclusion shape, and the distance between the inclusion and the edge of the sample. The degree to which edge proximity effects volume change is also a function of inclusion shape. We present results for a variety of inclusion shapes, host minerals and external and internal loads. These models should be particularly useful for fluid inclusion studies conducted at high pressure in externally heated diamond anvil cells (e.g. Schmidt et al., 1998, Am. Min.).

V51A-0969 0830h POSTER

The effects of fluorine on the compressibility of chondrodite structure

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