and Eu anomalies. Rims (metamorphic) contain very low Th/U and Th, high U, and lower, flatter REE patterns; Ce and Eu anomalies are small or absent. Zircons (magmatic) from three orthogneisses lack distinct rims, contain moderate to high Th/U, Th, U, and REE concentrations, and have small to moderate Ce anomalies, and moderate to very large Eu anomalies. SHRIMP U/Pb ages previously reported from orthogneiss are 932–1011 Ma.

### V22D-0622 1330h POSTER

## SHRIMP U/Pb age of unusually large zircon in low-T jadeitite from the Osayama serpentinite melange, SW Japan

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Porphyroblastic zircons up to 3 mm occur in nearly monomineralic jadeitite vein from the Osayama serpentinite melange, SW Japan. The Zrn-bearing jadeitite consists mainly of subhedral to anhedral jadeite (Jd<100), with minor amount of grossular, Zrn and rutile as primary phase, and shows variable degrees of retrogression. Anhedral Jd crystals show oscillatory zoning with Ca-rich bands (Jd87-91) at the rims, suggesting crystallization from an aqueous fluid. Zrn occurs as discrete euhedral to subhedral crystals up to 3 mm in size or as twinned crystals or aggregates in the matrix; Zrn contains tiny inclusions of Rt and rare Jd. Tiny Zrn also occurs as inclusions in a single Jd crystal. This evidence indicates synchronous growth of Zrn and Jd. Phase equilibria and the existing fluid-inclusion data constrain P-T conditions to P > 1.2 GPa at T < 350 çC for formation of the jadeitite. Th-U chemistry and U/Pb ages were determined using the SHRIMP-RG. The Zrn crystals show remarkable internal zoning textures including fine, euhedral growth layers with sharp contrasts in CL brightness, and are characterized by both low Th/U ratios (0.2-0.8) and low Th- and U-abundances (Th = 1-81 ppm; U = 6-149 ppm). Most U/Pb ages are concordant, with a weighted mean 206Pb/238U age of 475.4 $\pm$ 9.8 Ma [MSWD = 5.2]. The investigated Zrns were directly crystallized from a hydrothermal alkaline fluid during the jadeititeformation, and Zrn does not reach the closure T of the Zrn U/Pb system. Thus, it is interpreted the U/Pb ages, c. 475 Ma, as timing of crystallization of Zrn during HP-LT jadeitite-formation in serpentinites. The alkaline fluid with high Na- and Al-concentrations that resulted from subduction-zone metamorphism may have led to Zr concentration and the precipitation of Zrn in jadeitite. Consistent SHRIMP data for the blueschist-facies event suggest reliable dating of the LT Zrn in spite of its growth far below its closureT. The Zrn U/Pb age of this study provides likewise constraint for the timing of hydrothermal fluid-rock interaction related to serpentinization at HP-LT condition, establishing evidence for Ordovician subduction environments in SW Japan.

# V22E MCC: 3004 Tuesday 1340h

## Centennial Celebration of Radioisotopic Geochronology: Dates, Rates, and New Debates I

***Presiding:*** **P W Reiners,** Yale University; **P R Renne,** Berkeley Geochronology Center

### V22E-01 1340h INVITED

## Earth accretion dynamics and time-scales

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The degree to which efficient mixing of new material, losses of volatiles to space and changes in oxidation characterize the impact-driven growth of Earth-like planets in unclear. These processes affect calculated time-scales and can be studied by parallel modeling of data from different radiogenic isotope systems. The W isotope composition of the silicate Earth yields a model time-scale for accretion that is faster than estimates based on terrestrial Pb and Xe isotope data and on Sr, W and Pb data for lunar samples. This is hard to explain unless refractory metals in impacting core material did not always mix efficiently with the silicate portions of the Earth before being added to the Earth's core. Agreement is obtained with a Moon-forming Giant Impact 50 Myrs after the start of the solar system if only a quarter of the W from Theia's core equilibrated with the silicate Earth assuming the Hf/W in silicate reservoirs remained constant. Both W and Sr isotope compositions of the Moon provide evidence that the average composition of proto-planets was in fact more like Mars, with a low Hf/W, volatile-rich, oxidized mantle. Growth from such protoplanets decreases to a few percent the calculated amount of equilibration between Theia's core and the silicate Earth during the Giant Impact.

### V22E-02 1355h

## Dating Earth Core and Atmospheric Formation Through Hf-W and I-Pu-Xe Clocks

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It was the discovery of the radioactivities and nuclear energy at the beginning of last century that settled the long lasting debate about the ages of the Earth and the Sun, between elegant physical arguments advanced by Lord Kelvin favoring short timescale vs. Charles Darwin's trouble for not having enough time for evolution of species, hence resorted to geological observation of sedimentation rate favoring long-time scale. Claire Patterson's landmark work on Pb isotopes (1956) establishes the age of meteorites and the Earth at 4.56 Ga, albeit with somewhat wrong half-life of U and wrong sample (one ocean sediment landing on meteorite isochron). Modeling of planetary accretion rate via statistical approach pioneered by Safranov suggested planet formation lasted over 100 Ma. This long timescale was shaken by modern computer simulation. When actual orbital characteristics of the accreting bodies were considered (aided by ever-increasing computing power), the timescale for the inner planet formation is typically around 30 Ma. Discoveries of extrasolar planets place demanding constraints for the timescale of planet formation, i.e. gaseous giant planets must form before the disk dissipation (typically less than 10 Ma). No conventional long-lived isotopic systems are likely to place constraints for the planet formation with sufficient precision and resolution (30/4567), nor do we have 4.56 Ga-old terrestrial sample to work with. Modern approach to the problem is to exploit the now-extinct radioactive isotopes that were once extent at the beginning of the solar system, and look for radiogenic signatures of its daughter isotopes affected by planet wide fractionation. In this sense, we treat the Earth as one piece of whole rock; metallic core, silicate mantle and atmosphere are its mineral constituents. Both Hf-W and I-Pu-Xe clocks are uniquely affected by large-scale processes, core-mantle segregation in the Hf-W system and atmosphere-solid Earth segregation in the I-Pu-Xe system. And the ruler sizes are just right: 182Hf (9Ma); 129I (15.6 Ma); 244Pu (80 Ma). The first-discovered extinct-radionuclide (129I) by Reynolds (1960) played important role in planetary chronometry over the last four decades. The persistent timescale of 100 Ma provided by terrestrial I-Pu-Xe system all goes back to the influential paper by Wetherill (1975). We will show that the atmospheric retention age (Xe closure) is only 30 Ma, in remarkable agreement with the radiogenic 182W signature of the silicate Earth that argue for rapid core-mantle segregation of 30 Ma at most (Yin et al., 2002). Missing Xe event lasted another 90-120 Ma, possibly associated with early continental crust formation, a timescale consistent with 146Sm-142Nd clock. It is interesting to note in this regard that Xe could form silicate compound under lower crustal pressure and temperature, as shown by recent experiments at Geophysical Lab. What need to be shown are Kr, Ar, and Ne do not form silicates under the same condition, or released readily, in order to explain the fact the only Xe is missing.

### V22E-03 1410h

## The Coupled Hf-Nd Isotopic Perspective on Crust-Mantle Evolution

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The Sm-Nd and Lu-Hf isotope systems have been valuable tools in trying to understand the differentiation and evolution of bulk silicate Earth (BSE). Together these systems allow us to constrain important processes such as the evolution of the crust and mantle as well as provide a basis for quantifying bulk Earth isotopic mass balance. Linking these systems is especially important for examination of the early Earth as they complement each other and provide independent records in rocks with long and complex tectonothermal histories. Ultimately, the utility of these systems in this regard will depend on how well we know both the decay constants for $^{147}$Sm and $^{176}$Lu as well as the Lu-Hf and Sm-Nd isotopic composition of BSE. Both sets of parameters, however, have been the subject of recent debate and this uncertainty has prevented these systems from achieving their full potential. Recent work on the $^{176}$Lu decay constant by cross-calibration of U-Pb and Lu-Hf isotope systems on mineral isochrons in terrestrial rocks [1,2] have determined values (1.865 x $10^{-11}y^{-1}$) considerably lower than the value currently in use (1.93 x $10^{-11}y^{-1}$) and lower still than the value determined from examination of various meteorite groups [3,4]. The value of 1.865 x $10^{-11}y^{-1}$, if true, would result in initial $\epsilon_{Hf}$ values for the Early Archean Greenland gneisses [5] to be on average chondritic instead of having a depleted mantle signature ($\epsilon_{Hf}$=$^{+}$2-$^{+}$4). While this is certainly plausible, it conflicts with the dominantly depleted signature in the Nd isotopic record for these rocks. More significantly the lower value for $\lambda^{176}$Lu would result in the Jack Hills detrital zircons [6] having initial $\epsilon_{Hf}$ of $^{-}$2 to $^{-}$4 at 4.0 Ga which would have profound implications for the existence of continental crust at or near 4.4 Ga. One notable aspect of the existing Hf-Nd isotopic record from Earth's reservoirs is the apparent mismatch of $\sim$3 $\epsilon_{Hf}$ units between the current BSE value (based on an average of ordinary and carbonaceous chondrites) and the center of the Hf-Nd terrestrial array, which would seem to require a hidden reservoir in order to achieve isotopic mass balance [7]. Recent work [8] has demonstrated a large range in Lu-Hf isotopic composition in chondrites and a systematic difference between carbonaceous and ordinary chondrites. Therefore, unlike the Sm-Nd system, there is considerable latitude in how the Lu-Hf chondritic parameters are chosen. The average of carbonaceous chondrites are $\sim$7 $\epsilon_{Hf}$ units higher than ordinary chondrites and $\sim$3 $\epsilon_{Hf}$ units higher than the current chondritic value. If BSE is closer to that of carbonaceous chondrites, the BSE point would lie in the middle of the terrestrial array and solve the Hf-Nd isotopic mass balance problem. A higher $^{176}$Hf/$^{177}$Hf value, however, would have little effect on Archean initial Hf values because of the correspondingly higher chondritic $^{176}$Lu/$^{177}$Hf. The lack of coherence between the Hf and Nd records for the early Archean demonstrates that there are still some critical unresolved issues that need to be addressed. [1] Scherer et al., 2001., Science, 293: 683-686. [2] Söderlund et al., in review, EPSL. [3] Bizzarro et al, 2003, Nature, 421: 931-933. [4] Blichert-Toft et al., 2002, EPSL, 204: 167-181. [5] Vervoort and Blichert-Toft, 1999, GCA, 63:533-556. [6] Amelin et al., 2000, GCA, 64: 4205-4225. [7] Blichert-Toft and Albarède, 1997, EPSL, 148: 243-258. [8] Patchett et al., in review, EPSL.

### V22E-04 1425h INVITED

## The Geochronology of Terrestrial Meteorite and Cometary Impacts

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Geochronology has become a crucial part of the debate over the influx of extraterrestrial material and its long term importance to terrestrial life. Many of the known terrestrial craters have ages attached to them, but all too often the ages are imprecise and unfortunately some are inaccurate. Despite these problems the database of measured ages has been used to support hypotheses of clustering and periodicity in the impact record, and compare ages with those for mass extinctions in the fossil record. Over 170 craters have been identified on the Earth's surface, but the ages of less than half are known to better than 10 million years. The crucial question of peak eruption ages for large igneous provinces (LIPs) formed during the Palaeozoic, such as Deccan and the Siberian Traps, has been resolved using radiometric dating techniques such as Ar-Ar and U-Pb dating. The precision of measured ages for LIPs is better than 1% in most cases, but the precision and accuracy of ages determined for impact events is very variable. The ages of the largest 5 known terrestrial impact craters (>100 km diameter) have been established using radiometric dating techniques such as Ar-Ar and U-Pb and are known to precisions of better than 1%. However, the ages of many smaller craters,

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even some over 50 km in diameter, are less well constrained. It is the record of these smaller impacts which is littered with low precision ages, inaccurate ages and impacts whose age is constrained only by the age of the target rock and the youngest overlying sediments.
Why is the record of smaller impacts so poorly constrained? The main reason is the scarcity of samples and post impact alteration. The largest impacts form significant quantities of melt and which remain liquid for sufficiently long to coalesce and form conventional igneous bodies. It is these bodies which have been dated using radiometric dating techniques, often U-Pb dating of zircon crystallized from the melt. Smaller impacts form little or no melt and where present, they are heterogeneous mixtures of melt and host rock clasts of all sizes. The task of dating such samples is often made more difficult by alteration as a result of post impact hydrothermal activity. In addition, unlike LIPs, samples of impact melt are often rare even within the crater. Ar-Ar dating has become the technique of choice for these samples since both furnace heating and laser heating extraction techniques lend themselves to analysis of small heterogeneous samples. Ar-Ar analysis has been used to separate and identify components such as host rock clasts and the effects of later alteration, to reveal precise ages for the impacts. The Ar-Ar technique can also be used to determine argon loss in the host rock as a result of heating during the impact, and measure the remnants of host rock Ar dissolved in melt which can also indicate the rapidity of melt formation and freezing.
In fact the geochronology of impacts is fast improving area and although more work is required before we can determine whether impacts fall randomly, with a periodicity, or in clusters, there are some strong indications of future directions. Some apparent clusters of impacts appear to warrant further study, whereas others may disappear as new geochronological data is acquired. In particular the long known 450-500 Ma asteroid breakup event seems to have a terrestrial corollary in a mid-Ordovician cluster of impacts.

## V22E-05 1440h

### High-Precision U-Pb Zircon Dates as Benchmarks in Absolute Time

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High-precision IDTIMS U-Pb zircon dates provide the most precise and accurate isotopic benchmarks in absolute time, due to the concordancy check of the paired U-Pb decay schemes, the precisely measured $^{235}$U and $^{238}$U decay constants, very high initial parent/daughter ratios, and the robust nature of zircon to loss or gain of U and Pb over geologic time. However, caveats to the use of such zircon dates include the accurate assessment and minimization of random and systematic errors in the analytical methods, and decay constant uncertainties. Unfortunately, there exists little consensus within the U-Pb geochronological community regarding an international zircon standard for the external assessment of interlaboratory reproducibility, while residual questions remain regarding the potential for systematic error in the single available high-precision counting experiment of the U decay constants[1]. Stringent criteria are imposed on candidates for zircon geochronology standards including the absence of inheritance and Pb-loss at both the single grain scale and the resolution of microbeam techniques. We present an example of the potential and limitations of a possible zircon standard, AS3, from the Duluth Complex, North American Midcontinent Rift[2]. New data for 27 single zircons are indistinguishable from prior results, with $^{207}$Pb/$^{206}$Pb and upper intercept dates identical within error to a U-Pb concordia date of 1099.1±0.2 Ma (±1.2 Ma with systematic errors) based on 12 concordant and equivalent analyses. However, we must reiterate that a zircon population exhibiting consistent concordancy remains elusive, as AS3 and all Paleozoic and older standard candidates so far examined contain grains exhibiting Pb-loss, although rigorous selection and preparation of zircons through diamagnetic separation and aggressive abrasion can mitigate this phenomenon. The continued screening of candidate standards by both IDTIMS and SHRIMP techniques should be an organized, international endeavor involving all high-precision geochronology laboratories. Under the single assumption that the equivalent data represent the approach to closed system behavior, the correspondence of the AS3 zircons with the presently defined concordia curve suggests the accuracy of the ratio of the presently accepted decay constants[1] to within their 0.1% ($2\sigma$) counting errors. While a proposed revision of the $^{235}$U decay constant[3] is apparently unnecessary, additional high-precision, high n, statistically equivalent zircon population samplings are necessary to further evaluate decay constants and their uncertainties at the per mil level. When measured on appropriate lithologies, high-precision U-Pb dates also become powerful tools for the intercalibration of other radioisotope decay rates more difficult to measure through counting or accumulation (e.g. $^{40}$K, $^{176}$Lu, $^{187}$Re). We will present several new high-precision data sets for quickly cooled Oligocene to Archean extrusive and intrusive rocks, and assess their usefulness as benchmarks for the intercalibration of radiometric time; a growing number of high-precision U-Pb zircon and $^{40}$Ar/$^{39}$Ar feldspar, biotite or hornblende pairs spanning more than 3 Ga in absolute time indicate a consistently younger bias in $^{40}$Ar/$^{39}$Ar dates of between 0.7 and 1%. [1]Jaffey et al. (1974) Phys Rev C 4:1889-1906; [2]Paces and Miller (1993) J Geophys Res 98:13997-14013; [3]Mattinson (2000) EOS 81:S444

## V22E-06 1455h

### CA (Chemical Abrasion) - TIMS: High-Resolution U-Pb Zircon Geochronology Combining High-Temperature Annealing of Radiation Damage and Multi-Step Partial Dissolution Analysis

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Recent advances in methods for U-Pb geochronology of zircon demonstrate excellent potential for high-accuracy (sub 0.1% uncertainty) dating of magmatic events, and also shed new light on complexities in isotopic systematics related to intermediate daughter product disequilibrium and decay constant uncertainties. Multi-step analysis of zircon by "PDA" (partial dissolution analysis) has long shown promise. Unfortunately, leaching effects related to alpha-recoil and other forms of radiation damage seriously compromise results for many samples. However, radiation damage can be removed prior to PDA by annealing in the range of 800 to 1100°C, dry, at 1 Atm, for 48 hours. Subsequent multi-step analysis is largely free from any leaching effects, and represents a progressive stripping (Chemical Abrasion) of zircons, typically from high U-Th rim material to low U-Th core material. For zircons lacking inheritance, initial steps showing Pb-loss are followed by a plateau of 206Pb*/238U ages, commonly yielding plateau ages with uncertainties in the range of 0.05 to 0.1% (2-sigma). Obviously results are more complex when inherited components (especially of multiple ages) are present. However, since early steps remove virtually all Pb-loss effects for most samples, inheritance is easier to recognize and interpret. Multi-step high-precision 207Pb*/206Pb* ages for samples yielding excellent 206Pb*/238U plateau ages shed new light on isotopic complexities related to intermediate daughter product disequilibrium effects. For example, results from zircons from plagiogranites in Jurassic ophiolites indicate that minor but significant 231Pa excess is quite common. Thus high-precision 207Pb*/206Pb* ages are not necessarily high in accuracy, and should be interpreted with some care. In such cases, approximate agreement of the 206Pb*/238U and 207Pb*/206Pb* ages provides a first order indication of "concordance" or "discordance" at best. A high-resolution 206Pb*/238U multi-step plateau age is a superior measure of the true magmatic age.

## V22E-07 1510h

### Annealing plus chemical abrasion: A remarkably effective tool for eliminating the effects of lead loss from volcanic zircons

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Understanding short-term events and processes in Earth's history is highly dependent on the precision and accuracy of underlying radio-isotopic ages, provided in many cases by high-precision U/Pb ages of zircons in volcanic ash falls. Although low procedural blanks combined with modern mass spectrometry allow permil-precision ages to be determined on individual zircon crystals, such analytical precision does not necessarily translate into accuracy in a geological sense. Extracting robust ages from complex zircon populations is often compromised by apparent-age scatter arising both from anomalously young ages (a result of Pb loss) and by anomalously old ages (from xenocrystic contamination and/or inheritance). Such complications arise in particular for relatively young rocks (say <300 Ma, where accuracy of the more-robust $^{207}$Pb/$^{206}$Pb ages is unacceptable and even the precision is worse than for $^{206}$Pb/$^{238}$U), wherein reliable U/Pb dating requires the production of a coherent cluster of internally concordant $^{206}$Pb/$^{238}$U ages. Air abrasion (the main "traditional" technique for minimizing Pb loss) as well as leaching the zircons in aggressive reagents (HF or NaOH) have been shown to be only moderately successful in general, as demonstrated by single crystal analyses with excess U/Pb age-scatter. Multi-crystal samples aimed at improving the precision of individual analyses impose the demonstrable likelihood of averaging Pb-loss effects, and thus are prone to yield slightly younger and inaccurate age (Mundil et al., 2001). An approach pioneered and refined by Mattinson (2001), however, dramatically improves the quality of complex zircon populations by entirely eliminating (at least in all of our tests so far) the effects of post-depositional Pb loss, even for zircon populations that are profoundly affected. In the Mattinson procedure, zircons are first annealed at a temperature of 800°C, resulting in crystals devoid of radiation damage. Following annealing, the zircons are aggressively leached by HF vapor at 220°C in pressurized Teflon capsules, resulting in "chemically abraded" crystals (Mattinson, 2001). A comparison among untreated crystals, physically abraded crystals, and annealed + chemically abraded crystals from the same ash-fall unit show that only the last technique yields statistically coherent U/Pb ages, whereas the first two approaches yield U/Pb ages with significant scatter arising from variable degrees of Pb loss. We present data-sets for zircons from ash-falls (late Paleozoic and early Mesozoic) that demonstrate the dramatic improvement in statistical quality resulting from annealing plus chemical abrasion. The annealing + chemical abrasion method apparently permits, for the first time, the determination of precise, robust, and geologically meaningful U/Pb ages from complex zircon populations affected by significant post-depositional Pb loss. Mattinson, J.M., 2001, Eos Trans. AGU, 82(47), Fall Meet. Suppl., Abstract V22C-1056. Mundil, R. et al. 2001, EPSL, 187, 131-145.

## V22E-08 1525h INVITED

### ID-TIMS Geochronology of ca 1 Ma leucogranites from the core of Nanga Parbat

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Although isotope-dilution, themal-ioniaztion mass spectrometry (ID-TIMS) is the most precise method available for U-Th-Pb geochronology of accessory minerals, the technique is traditionally not applied to samples youger than ca. 10 Ma due to low concentrations of radiogenic Pb. However, recent analytical advances allow the routine measurement of less than 5-10 picograms of radiogenic Pb, and the reduction of laboratory blanks to extremely low levels. As a consequence, it is now possible to use ID-TIMS for U-Pb geochronology of very young accessory mineral suites to develop new insights regarding the time scales and patterns of inheritance, melt production, and segregation in collisional orogens. The Nanga Parbat syntaxis of the northwestern Himalaya has had a long and complex thermal history, but it is famous for the evidence it provides for extremely young (<5 Ma) metamorphism and anatexis. Some of the youngest anatexites in the core of the syntaxis are cordierite-bearing granites which intruded as dikes and sills along extensional shear zones. High-precision ID-TIMS U-Pb geochronology of these granites using single crystals and several grains of monazite, zircon, xenotime, and uraninite indicate a melt crystallization age of <1 Ma. However, mineral dates within a single sample show a dispersion of several hundred thousand years that is greater than analytical imprecision and likely to represent the timescales of melt production and segregation. These are the youngest U-Pb ages known from any Himalayan leucogranite and, combined with P-T data, show that 15-17 km has been eroded off the summit area of Nanga Parbat in less than 1 million years.