Subduction times of oceanic crust along the Jinshajiang suture zone, Tibetan plateau, SW China

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Introduction

The central part of the Tibetan Plateau is consists of the Kunlun Terrane, Bayanhar Terrane, Qiantang Terrane and Lhasa Terrane. The Jinshajiang suture zone lies between the Bayanhar Terrane and the Qiantang Terrane. For a long time, the subduction times of oceanic crust along the Jinshajiang suture zone have been disputed. We try to give a times limit for the subduction of oceanic crust by dating of the ophiolite, IAG and CCG type granite using Ar-Ar and SHRIMP U-Pb isotope geochronological methods.

Results, Discussion and Conclusions

In the Jinshajiang suture zone, it lasted only a span of 9 Ma from the start of subduction (marked by the eruption of andesitic magmas and intrusion of intermediate rock of IAG type at about 227 Ma) to the end of subduction, consumption of oceanic crusts and the collision of terranes (marked by the fast cooling of intermediate-acid rocks at about 218 Ma). This implies that either the oceanic crusts between the Qiangtang and Bayan Har terranes were small sized, or they subducted at a very fast speed along the Jinshajiang suture zone. It also explains why there were isotope chronological records in the intrusive rocks of the Kunlun terrane for such large tectonic events like collisions between the Lhasa and Qiantang terranes and between the Himalayas and Lhasa terranes, and why very few evident chronological records were left in it for the collision between the Qiangtang and Bayan Har terranes along the Jinshajiang suture zone. Because the collisions between these three terranes took place almost simultaneously or even overlapped at a time, chronological information on the collisions in the Jinshajiang suture zone became blurred or indistinct.

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Ar-Ar dating for greenschist-facies metavolcanics in the Dabie orogen: Implication for the accretionary wedge of continental subduction

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It has hotly been debated whether sporadic low-grade metamorphic rocks in the interior of UHP metamorphic zones experienced the same history of subduction to mantle depths. Greenschist-facies metavolcanic and metasedimentary rocks were discovered to occur within UHP eclogite-facies zone in the Dabie orogen of east-central China, with the dyke-like intrusion of coesite-bearing eclogite. The metavolcanic rocks are mainly interbedded with metaconglomerate, sericite phylite, sericite-feldspar-quartz schist and silty slate. The occurrence of dyke-like coesite-bearing eclogite within the metavolcaniclastics resulted in the controversial conclusion that the eclogite and host metavolcanics shared the same UHP metamorphic history. This is in conflict with the fine-grain nature of metavolcanics. Whole-rock Ar-Ar dating for these low-grade rocks may provide a resolution.

Two metavolcanic samples were selected from ash-bearing metasilicate layers at Ganghe in the Dabie terrane. Ar-Ar isotope data on sample GH-1 yield a reasonable isochron with an age of 785.0±4.7 Ma (MSWD = 0.37) and an initial 40Ar/36Ar ratio of 280.2±31.7. The main plateau is composed of 5 to 10 steps with 91.86% of total released 39Ar, corresponding to a plateau age of 783.3±0.9 Ma. The other sample (BX-1) yields an Ar-Ar isochron age of 769.5±3.1 Ma (MSWD = 0.57) with an initial 40Ar/36Ar ratio of 308.9±16.7. The main plateau is composed of 3 to 10 steps with 97.36% of total released 39Ar and corresponds to a plateau age of 771.0±0.6 Ma. Because of the low closure temperature of Ar diffusion in silicates, these mid-Neoproterozoic ages indicate that in the process of the Triassic continental subduction, the low-grade metamorphic rocks did not suffer the high-grade metamorphism under UHP eclogite-facies conditions, so that the Ar isotopic system was not disturbed since the volcanic eruption at the mid-Neoproterozoic. Therefore, the volcanic rocks were scraped off from the upper part of subducting Yangtze Block by obduction of the North China Block, and suffered only the greenschist-facies dynamic metamorphism. They essentially correspond to the accretionary wedge of continental subduction.
Ar-Ar chronology study of the Qiugemingtashi–Huangshan ductile shear zone, Xinjiang, NW China

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The Qiugemingtashi–Huangshan ductile shear zone, situated in the middle Tianshan orogenic belt, Xinjiang, NW China, is believed to be the product of the subduction and collision of the two plates in the north and south of the East Tianshan during the late Paleozoic. It is the important part of the orogenic belt and also an important metallogenic belt, containing copper, nickel and gold deposit. According to the involved ductile deformed strata and Rb-Sr and K-Ar dating results, the shear zone age is inferred to be the late Carboniferous to the early Permian by the former researcher. Obviously, this is too extensive and we need further study. We use $^{40}$Ar/$^{39}$Ar method, which is the most suitable method to date the shear deformation age, to date the Qiugemingtashi–Huangshan ductile shear zone and define the age of the early nappe shearing and the late strike-slip shear deformation.

Ar-Ar isotope chronology study reveals that the activity of Qiugemingtashi–Huangshan ductile shear zone show different time in the different area of the shear zone. In the early, the shear zone show nappe shearing and its upper limit on the age is 280Ma. In the late, it shows strike-slip shear deformation. In the Kanggur, situated in the middle-western shear zone, the $^{40}$Ar/$^{39}$Ar age of the mylonites is mainly ~260Ma while in the southern Tuwu, situated in its east, the $^{40}$Ar/$^{39}$Ar age of the mylonites is mainly 240-250Ma. Because the metal deposits of the East Tianshan are mostly located in this shear zone, the above results not only deepen the study on the tectonic history of the East Tianshan but also provide new age evidence for the further understanding the controlling of the shear deformation on the mineralization.

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Laser-ablation ICP-MS zonation-dependent $\alpha$-ejection correction of zircons in (U-Th)/He chronometry

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We use LA-ICP-MS depth profiling of standards and zoned zircon samples together with a new LabVIEW-based numerical model to examine whether U-Th zonation is responsible for overdispersion and age bias observed in some (U-Th)/He data sets. Our model uses integration over 3-D matrix with isotropic grid spacing to determine zonation-dependent bulk retentivity, $F_{ZAC}$ as the relative-\$alpha$-productivity-weighted average of local $\alpha$-retentivity values. Integration occurs over three spatial dimensions and all relevant $\alpha$-producing isotopes. Modeling of bipyramidal prisms with synthetic, geologically realistic zonation demonstrates that crystal morphology and zonation can conspire to create $>30\%$ $\alpha$-ejection-corrected age bias when homogeneity and simplified geometries are assumed $a$ priori.

In practice, our approach uses laser-ablation ICP-MS depth profiling on whole, unmodified zircons in grain-mount. Internal fragments of Sri Lankan detrital zircons are used as external concentration standards, and to monitor depth-dependent Th/Zr and U/Zr fractionation. Fractionation-corrected data for unknowns are used in the zonation-dependent bulk retentivity model to populate 3-D $\alpha$-productivity matrices assuming self-similar crystal growth.

Results from two analytical systems are compared: 1) New-Wave 193 nm excimer laser–Element2 magnetic sector ICP-MS (Yale); and 2) Merchantek 213 nm Nd:YAG laser – VG PQ ExCell quadrupole ICP-MS (BU). Reproducibility of unbiased ages from un-zoned Fish Canyon Tuff zircon standards with multiple depth profiles indicate that helium is not quantitatively lost from the remaining volume during laser ablation. This method can be used to pre-screen candidate aliquots to identify homogeneous grains, or to calculate customized $F_{ZAC}$ $\alpha$-ejection corrections for zoned grains. A demonstrably un-zoned Tardree Rhyolite zircon produces a homogeneous $\alpha$-ejection corrected age of $59.7 \pm 4.8$ (2$\sigma$) Ma in agreement with the accepted emplacement age of $58.4 \pm 0.7$ Ma, whereas the $F_{ZAC}$ $\alpha$-ejection correction for a Tardree zircon with a factor of $\sim40$ U-depleted rim, yields an $F_{ZAC}$-corrected age of $57.8 \pm 4.6$ Ma (2$\sigma$) compared with a $F_1$-corrected age of $64.5$ Ma assuming U-Th homogeneity.
Shear deformation ages of the Xianshuihe fault zone in SE Tibetan plateau

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The NWW-SEE striking Xianshuihe fault zone slices the southeastern Tibetan plateau and connects southeastward with the Amninghe-Zemuhe-Xiaojiang fault zone, they together forming a huge, active sinistral strike-slip fault zone. The total late Cenozoic left-lateral offset along the Xianshuihe fault is estimated to 100~78 km. However, the onset of these offset accumulations and cooling ages for left-lateral shear of the Xianshuihe fault has been poorly studied. Based on field geological survey, structural measurements and classical ⁴⁰Ar/³⁹Ar dating technique, we obtain cooling ages for Miocene left-lateral shear along the Xianshuihe fault zone.

⁴⁰Ar/³⁹Ar stepwise heating dating of mica, biotite and K-feldspar from both the shear zones and undeformed granites show a complex cooling history. Two cooling events can be identified. The early event occurred at 12~10 Ma and corresponds to emplacement and rapid cooling from 700°C to near 350°C of the Zheduoshan granitic massif. The late event took place at 5.5~3.5 Ma with emplacement of fine grained granites along the megmatite zone.

This study confirms that emplacement and rapid cooling of the Zheduoshan granitic massif and left-lateral shear along the Xianshuihe fault zone were synchronous. Moreover, structural and thermochronology data reveal a late shear event occurred at 5.5~3.5 Ma, possibly synchronous with emplacement and cooling of fine grained granites along the eastern side of the Xianshuihe fault zone. One of the important conclusions we can draw is that the eastward extrusion of the Chuan-Dian Block started at 16~12 Ma and occurred episodically.

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Provenance of the Middle Jurassic strata of the Tornquist Shear Zone in southern Sweden

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Aim and used provenance techniques

The aim of this study is to investigate the provenance of the Jurassic Glass Sand Member and the underlying Fuglunda Member of the Tornquist Shear Zone in the south-western parts of the Baltic shield and to compare the provenance of the two different strata. The provenance techniques used are SIMS U-Pb and Pb-Pb dating of single detrital zircon grains (Whitehouse et al., 1999) and Ar-Ar dating of detrital muscovite grains. Chemical zoning and inclusion patterns in garnet, rutile and other heavy minerals, and trace element data, are also considered as these may give important information on the metamorphic source terrain.

Discussions of preliminary results

Preliminary SIMS U-Pb and Pb-Pb dating of detrital zircon grains shows trends of provenance of a western source, such as the Sveconorwegian Orogen. The preliminary results also show a difference in provenance between the two studied members of the informal Mariedal Formation (Ahlberg et al., 2003). Rutile is present in all samples while garnet is only found in the Glass Sand Member.

References

U-Pb zircon and Sm-Nd data for rocks of the Murmansk domain (Kola Peninsula, NE Baltic Shield)

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The Murmansk domain is located in the eastern part of the Kola Peninsula (NE Baltic Shield) and consists mainly of plagiogranitoids and plagiomicrocline granites. Plagiogranites contain a plenty of xenoliths of amphibolites, amphibole-biotite gneisses, diorites, and two-pyroxene schist which are considered to be xenoliths of the basic rocks in primary - crust granitites or relics of more ancient magmatic basement, altered by granitization or a product of structural - metamorphic reorganization of the uniform stratified complex of primary - crust granitoids. To understand a geological history of this structure we need careful geological study with the modern geochronological data for the subsequent opportunity of correlation of the Murmansk domain with similar Archaean structures of the Kola Peninsula, the Canadian Shield and Greenland. New geochronological results (U-Pb zircon and T(DM) Sm-Nd) are obtained for some rock complexes spatially placed in the eastern part of the Murmansk domain. U-Pb zircon age for biotite gneisses is 2724 +/-7 Ma; T (DM) Sm-Nd is 3068 Ma. The age of zircon from xenolith of amphibolites is determined as 2739 +/-7 Ma, T (DM) Sm-Nd is 2638 Ma. Plagiogranites from different parts of the investigated territory gave U-Pb ages 2771 +/-10 Ma and 2748 +/-7 Ma, T (DM) Sm-Nd - 2936 Ma and T (DM) Sm-Nd - 2868 Ma, respectively. For diorites U-Pb zircon age is obtained - 2717 +/-7 Ma, T (DM) Sm-Nd - 2862 Ma. The given data testify to the Late Archaean time of formation of the investigated rocks of the Murmansk domain with ages, limited by an interval of 2.7-2.8 Ga. The work is supported by scientific school N 2305.2003.5.

Combined (U-Th)/He and U-Pb thermochronometry of rift-flank exhumation in east-central Africa

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A thermochronologic study combining U-Pb and (U-Th)/He analysis of apatite and zircon was conducted up the eastern slope of the Rwenzori Massif in Uganda to characterize the timing and rate of rift-flank exhumation related to continental rifting in east-central Africa. Rising more than 4 km above the adjacent Albertine Rift Basin floor, the Rwenzori represent an extreme example of basement rift-flank uplift, a phenomenon common throughout the East African Rift System and characteristic of continental rift systems in general. New thermochronologic work coupled with field and remote sensing observations makes the case for recent and non-steady state uplift of the massif. U-Pb apatite results indicate that, prior to Neogene rifting, the rocks of the Rwenzori experienced a protracted history of slow cooling without major tectono-thermal perturbation since at least the Paleoproterozoic (>1550Ma). Comparably old (U-Th)/He zircon and apatite (>400Ma, >70Ma respectively) ages reflect a transient lag period before sufficient exhumation has occurred to remove the inherited pre-rift thermal structure. This non-steady state condition of rapid uplift outpacing erosion has resulted in preservation of relict landsurfaces, truncated spurs, hanging valleys, vast stranded bogs and uplifted river terraces at high elevation. Given the typical continental geothermal gradient prior to rifting implied by U-Pb thermochronology, no more than 2km of erosion could have accompanied uplift on the order of 5km in the Rwenzori region. This requires a minimum average uplift rate of 1.6km/Myr based on biostratigraphic evidence suggesting the range rose from beneath local baselevel within the last 2.5Ma. Regardless of the active rock uplift rate of the Rwenzori, net exhumation can not yet have exceeded the depth of the (U-Th)/He closure isotherm in apatite (~2km). These results highlight the danger of modeling young orogenic systems using the simplifying assumption of topographic steady state.
Lu-Hf geochronology of eclogites from Pfulwe, Zermatt-Saas ophiolite, western Alps, Switzerland

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Major-element zoning patterns in garnets from eclogite-facies metabasalts of the Zermatt-Saas ophiolite complex, western Alps, record large segments of the prograde P-T-t path to HP/UHP conditions. Ca, Fe, Mg, and Mn contents in garnet from core to rim are indicative of prograde growth zoning. Core to rim trace element analyses and 3-D imaging of garnet by laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) and x-ray tomography indicates strong HREE (Er, Yb, Lu) zoning, where the highest concentrations occur in the garnet core. Lu zoning is typically characterized by a very sharp, narrow spike in concentration (50 to 170 ppm) in the garnet core flanked by concentration values of 10 to 20 ppm that decrease toward the rim. Zr, and by proxy Hf, concentrations are typically constant across garnet traverses.

Lu and Hf garnet zoning patterns have important implications for Lu-Hf geochronology because they indicate that the Lu/Hf ratios are highest in the garnet core, though we note that the very highest values are in a very small volume of the garnet (1-2%). Therefore, if bulk garnet separates are used for geochronology, the measured Lu-Hf ages are strongly skewed toward the early prograde growth because the majority of the Lu is within the first 30% (by volume) of grown garnet.

Five ages from samples collected along the trail to the Pfulwe pass and from the famous Pfulwe pillow locality (near Zermatt, Switzerland) range from 46.5 to 54.5 Ma, as determined by MC-ICP-MS. These Lu-Hf ages, which overlap within error, reflect early garnet growth during subduction and prograde metamorphism, not the peak P-T conditions. Sm-Nd ages obtained on the same samples are very imprecise or undeterminable due to the presence of LREE inclusions in garnet. The relative insensitivity of Lu/Hf ratios to common LREE rich inclusions in eclogitic garnet highlights one advantage of Lu-Hf geochronology over Sm-Nd.

Grenville-age metamorphism on the western margin of Laurentia, northern Idaho: Evidence from Lu-Hf garnet geochronology

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Lu-Hf geochronology of garnet-bearing amphibolite facies rocks in northern Idaho reveal a complex multistage metamorphic history. We determined Lu-Hf ages on amphibolite and pelitic schists from the Clearwater complex of northern Idaho and on a pelitic schist more proximal to the Cretaceous Idaho batholith. The core and rim of the garnet amphibolite have Lu-Hf ages of 1149±4 and 118±4 Ma, respectively. Very high Lu/Hf ratios in the garnet core (εHf up to 17.83) result in extraordinary present day 176Hf/177Hf ratios as high as 0.688932 (εHf = +13,656). Grenville ages of 1056±57 and 1006±5 Ma are recorded in the pelitic schists samples. In contrast, the pelitic schist near the Idaho batholith yields a well-defined age of 89.6±2.6 Ma.

The ~1.1 Ga metamorphic ages combined with polyphase penetrative structures observed in metamorphic tectonities and metasedimentary rocks north of the Idaho batholith strongly suggest that Grenville-age tectonism in the northwestern U.S. Cordillera was widespread and reflects a period of Proterozoic crustal thickening prior to or during the assembly of Rodinia. Thus Early and Middle Proterozoic basins of western Laurentia may record deposition and contraction in an intracontinental setting or may have developed during a history of both passive margin and convergent margin tectonism. The younger Lu-Hf ages are consistent with widely observed evidence for Cretaceous metamorphism in the region.

The presence of domains within a single garnet that record ages differing by over a billion years clearly supports a complex tectonic history for these rocks. This juxtaposition of ages demonstrates the potential of the Lu-Hf isotope system in garnets to see through younger metamorphic overprints and resolve an earlier metamorphic history. Taken together with regional structural analysis, this work illustrates the utility of the Lu-Hf system in dating complex, polymetamorphic histories associated with regional deformation.
Tectonic basement of South China
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Our researches on pre-Mesozoic rocks of South China suggest that a Precambrian continental block had ever occurred in the Wuyishan-Wugongshan-Nanling-Yunkaidashan region according to middle-high grade metamorphic rock assemblages, structural deformational styles and newer data of isotopic ages. This oldland, with the oldest isotopic age of 2100 Ma, named the Cathaysian Oldland, is characterized by large scale of schist, gneiss and migmatic rocks dated at 1800Ma to 1200 Ma, which consist of a continental crustal basement. About 1100–900Ma, the Cathaysian Oldland collided with the Yangzi continental plate to form the Shaoxing-Jiangshan-Dongxiang-Pingxiang Suturing Zone. Not long time, about 800 Ma, the Cathaysian Oldland was dispersed into three blocks with different striking and distinct outline, that is, the NEE striking southeastern Zhejiang-northwestern Fujian block, the sub-N-S-striking central Jiangxi-southern Jiangxi block and the NE striking Yunkaidashan block, respectively. The Sinian-Early Paleozoic sedimentary materials with a large thickness were filled among these three blocks, which, together with three blocks,. consist the tectonic basement of Late Mesozoic (mainly Cretaceous) volcanic-intrusive complexes. Study proposes that this Old-land had subjected to three phase tectonic-thermal events at least, that is, Luliang event (1800–1600Ma), Jinning event (1100–900Ma) and Caledonian event (420–400Ma). The tectonothermal event during Silurian-Middle Devonian time is a strong compressure-thickening work to form the South China Caledonian folding-rogenic belt marked by numerous granitic bodies, folded greenschist facies metamorphic and mylonitic rocks. This ancient tectonic framework constrains large scale of Mesozoic tectonic-magmatism, difference of magmatic compositions and distribution.

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Apatite fission track and (U-Th)/He thermochronometers contraints on the development of two high elevation passive margins
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Apatite fission track (AFT) and (U-Th)/He thermochronometers are used to constrain continental rifting and escarpment development of the high elevation Eritrean and south-eastern Australian passive margins.

AFT and (U-Th)/He data have been determined from four coast perpendicular traverses. Along both margins the He and AFT ages at the present coast broadly correspond to the time of sea-floor spreading and they increase approaching the foot of the escarpments. On the plateau, He and fission track ages are much older than breakup time and the track length distributions indicate that denudation has been slow and constant since at least mid-Mesozoic times.

The combination of AFT ages, track length distributions and He ages indicates that both margins were rapidly eroded by in-situ excavation of a pre-existing plateau rather than parallel escarpment retreat. A comparison of the measured He ages from the coastal plain with He ages predicted by a forward model indicates that the main phase of denudation in the Eritrean margin started at around 15 Ma, closer to the initiation of seafloor spreading in the Red Sea than previously thought. In the south-eastern Australian case, the forward modelling suggests that denudation was enhanced at 120 Ma, some 35 Myr before sea-floor spreading, in agreement with the hypothesis that magma-poor margins evolve more slowly than magmatic ones.

The comparison of the Eritrean and eastern Australian margins indicate that they evolved in much the same way, despite differences in climate, lithology and modes of rifting. This study suggests that the primary control on syn-rift denudation is exerted by the topography.
Petrogenesis of Mesozoic strongly peraluminous granites in South China: Implication for tectonic domains transform

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Geological background

The number of strongly peraluminous granites (SPGs) is more than 1/3 of total number of all granite bodies in South China. All SPGs from South China bear strongly peraluminous minerals such as muscovite, Al-rich biotite, tourmaline, garnet. 13 representative granite bodies are studied though petrography, geochemistry, Sr-Nd isotope and zircon U-Pb isotopic dating.

Results and discussions

The results show that these granites formed in two stages: late Indosinian (228.0~207.6 Ma, ~T3) and early Yanshanian (173.0~155.4 Ma, ~J2~3). These SPGs have low CaO/Na2O ratio and εNd(t) (-11.9~−8.9) values, high Al2O3 value and Rb/Ba, Rb/Sr ratios, and high TE1,3 (1.13~1.34) of REE tetrad effect and Nd(t)DM values of 1.9 Ga~1.7 Ga. The geochemistry of high aluminous minerals show that these SPGs were crystallized from primary peraluminous magmas. We suggest that these Mesozoic SPGs were generated though partial melting of early Proterozoic pelitic metamorphic rocks.

Conclusions

Indosinian SPGs were formed under post-collision extensional tectonic setting which was constrained by Tethyan Tectonic Domain. Whereas the early Yanshanian SPGs were formed under back-arc extensional tectonic setting which was controlled by Pacific Tectonic Domain. Therefore, the transform of Tethyan to Pacific Tectonic Domains happened during early Jurassic in South China.

Reference


SHRIMP zircon U-Pb dating for impure marbles in the Jiaobei terrane of east-central China: Implication for its tectonic affinity

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The application of carbonate Pb-Pb and U-Pb dating has contributed a lot to timing of limestone deposition or marble metamorphism. However, difficulties were encountered in obtaining reasonable isochrons because the U-Pb isotopic system of carbonate rocks is prone to disturb by diagenesis or retrograde alteration. As a result, the carbonate U-Pb or Pb-Pb ages sometimes do not provide a definite dating with the geological meaning. SIMS zircon U-Pb dating coupled with CL imaging is proven to be a successful way to date the impure marble for its ages of both protolith deposition and metamorphism. This is illustrated for impure marbles from the western part of Shandong Peninsula (i.e. the Jiaobei terrane) in east-central China.

SHRIMP zircon U-Pb dating and CL imaging for two samples of impure marble from the Fenzishan Group in the Jiaobei terrane yield consistent ages of 786±67 Ma and 240±44 Ma for igneous and metamorphic zircons, respectively. Both detrital and metamorphic zircons are identified in the samples of interest. Oxygen isotope fractionation between calcite and garnet from one sample gave a temperature of 680ºC, pointing to upper amphibolite-facies metamorphic conditions. Positive δ13C values as high as +5.6‰ are measured for both pure and impure marbles, consistent not only with the worldwide Neoproterozoic limestones in connection with the global glaciation, but also with the marbles associated with UHP metamorphic eclogites in the Dabie orogen. These results indicate that protolith of the marbles is a kind of limestone that was synchronously deposited with volcaniclastic rocks in the mid-Neoproterozoic rift basin of continental margin. Like the UHP metamorphic rocks in the Dabie-Sulu orogenic belt, both mid-Neoproterozoic magmatism and Triassic metamorphism occurred in the hotly debated region. Therefore, the Jiaobei terrane belongs to the South China Block, corresponding to the seaward flank of rift shoulders during the mid-Neoproterozoic rift magmatism along the continental edge of the South China Block.
Tectonothermal evolution of Olkhonskaya collision system: Constraints from $^{40}$Ar/$^{39}$Ar data on granite veins sealed inside ultramafic bodies

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A mobility of K/Ar system depends on deformations and presence of fluids. When a rock is protected from access of deformations and fluids micas can retain radiogenic argon during superimposed metamorphic events. Such protection can often be observed inside rigid bodies of magmatic origin. We present results of $^{40}$Ar/$^{39}$Ar dating of granitic veins which are sealed inside ultramafic-mafic massifs of the Olkhonskaya collision system. Metamorphic framing of massifs was also investigated.

Phlogopite of granite vein sealed inside dunite body (Shidinskaya zone of Olkhonsky region) yielded $^{40}$Ar/$^{39}$Ar age of 497.1±1.2 Ma. It is concordant with U/Pb zircon data on age of metamorphism of granulite facies [Bibikova et al., 1990; Letnikov et al., 1990; Gladkochub, 2004; Khromykh et al., 2004]. At the same time biotites from metamorphic framing of dunite bodies yielded age of 432 Ma. Thus metamorphic event characterized by intense strike slip deformations and amphibolitic PT-conditions is shown to be noticeably (about 70 Ma) distant from granulitic metamorphic stage. It is remarkable that K/Ar of phlogopite of granite vein sealed inside dunite body preserved information about the age of early granulitic stage. Using numerical modeling of phlogopite K/Ar system behavior essential constraints on duration of late metamorphic event have been obtained. If we assume that volume diffusion mechanism promoted argon loss, digital modeling results show that duration of event should be noticeably shorter than 1 Ma. This limitation should be taken into account in regional tectonic reconstructions.

Acknowledgements

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$^{40}$Ar/$^{39}$Ar cooling ages from a vertical transect through the Patagonian batholith 46°S, Chile

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Mesozoic-Cenozoic granitoids of the North Patagonian Batholith in southern Chile have been key to understanding magmatism associated with subduction processes and tectonic uplift of the Southern Andes. Although Rb-Sr and Sm-Nd and fission track (FT) results have revealed the origin and timing of emplacement of several intrusions, and the denudation history of the Andes, thermochronology of the ~500–200°C history of this mountain range has not been explored. To better resolve the cooling history, particularly prior to the closure of zircon and apatite fission-track chronometers, we performed $^{40}$Ar/$^{39}$Ar incremental heating analyses, using a defocused CO$_2$ laser beam, on amphibole, biotite, plagioclase and K-feldspar from granodioritic/tonalitic plutons exposed on the south flank of Cerro Blanco, north of Lago General Carrera at 46° S. Six rocks were collected every 200 m along a vertical transect of 1.2 km through the intrusions between 200 and 1300 masl.

Concordant spectra from 1-3 crystal aliquots (1-2 mg) yield plateau ages as follows: (1) orthoclase correlates with elevation; ages at 410 and 1345 masl are 76 and 82 Ma, respectively, (2) biotite varies from 149 to 152 Ma and amphibole from 144 to 160 Ma; there is no correlation with the elevation. Discordant saddle-shaped spectra are common for plagioclase, and to a lesser degree, amphibole.

We interpret these plateau ages as the result of cooling following the intrusion. Age variations among individual biotite and hornblende crystals in each sample are ascribed to disturbances imposed by the growth of minor secondary mineral phases and sub-solidus modifications during cooling. Using a simple linear T-t path and widely adopted closure temperatures for these minerals, the calculated cooling rate prior to 82 Ma was ~2-3°/myr, but this increased to ~4-5°/myr between 76 and 82 Ma. Combining with Rb-Sr ages (~160 Ma) indicates an early history of rapid cooling, followed by remarkably slow cooling for ~80 myr. Orthoclase ages overlap regional zircon FT closure between 73 and 96 Ma and predate apatite FT closure by up to ~70 myr, suggesting an average cooling rate of ~1°/myr from the Late Cretaceous to Miocene. Structural and tectonic evidence, however, led Thomson et al. (2001, Tectonics) to propose a non-monotonic cooling path that can only be fully evaluated via further vertically-controlled thermochronology in the #150° C range.
Radiometric dating for the timescale of UHP metamorphism in the Dabie orogen of China

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The peak age and duration of UHP metamorphism are very important issues with respect to geodynamic interpretation of continental collision. Triassic ages for UHP metamorphism in the Dabie-Sulu orogen have generally been accepted, but the exact timing of UHP event is still in controversy between Late Triassic and Early-Middle Triassic. While eclogite mineral O isotope studies suggest a short duration of 5 to 10 Ma for the peak UHP event, peridotite mineral Sr-O isotope studies indicate that a bulk recycling on the order of 12 to 26 Ma for continental subduction, UHP metamorphism at mantle depths and exhumation. A resolution to these necessitates comprehensive investigations concerning not only a combined study of zircon growth history and U-Pb dating but also a correct understanding of O, Pb, Sr and Nd diffusivity in radiometrically dated minerals during prograde and retrograde metamorphic processes. This study of zircon U-Pb, mineral Sm-Nd and Rb-Sr dating for low-T/UHP eclogite at Huangzhen has provided insight into these aspects.

The SHRIMP zircon U-Pb dating yielded two groups of age at 242±3 Ma and 222±4 Ma, respectively. In combination with petrologic study, these ages are interpreted to date zircon growth and overgrowth in the two episodes of dehydration, respectively, in response to decomposition of water-bearing minerals such as glaucophane, epidote and paragonite during deep subduction and lawsonite breakdown during initial exhumation. The mineral Sm-Nd and Rb-Sr isochron dates gave the concordant ages of Middle Triassic at 236.1±4.2 Ma and 230±7 Ma, respectively. O isotope equilibria were achieved and preserved between the isochron minerals, providing a test of Nd and Sr isotopic equilibria in them. Although the closure temperatures of O diffusion may not simply correspond to those of Sr or Nd diffusion in eclogite minerals formed at different P-T conditions, Sr and Nd isotopic equilibria are evident from the consistent ages. Thus the timescale of bulk continental subduction and exhumation in the HP-UHP-HP regimes may range from ca. 245-240 Ma to 225-220 Ma, on the order of 10 to 15 Ma, for the peak UHP event. The termination age of peak UHP metamorphism is probably different in different slices of deep-subducted slab in the Dabie-Sulu orogen.

The geochemistry and implications of clastic sedimentary rocks of the Baiyun-Zhashui subunit from the South Qinling orogenic belt

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The trace element, REE and Sm–Nd analyses of Middle and Late Devonian metasedimentary rocks from the Baiyun-Zhashui subunit along the Jinqian River section (South Qinling, China) in conjunction with previously published data are used to trace the crustal evolution. The εNd(t) values of the Middle Devonian are within the range of the metasediments from Qinling complex. In contrast, Late Devonian samples are above the ranges of the Qinling complex, being higher in Cr/Th ratios and lower in Th/Sc ratios. It allows us to speculate that samples from Late Devonian Formations were derived from the arc materials from the Erlangping Formation, north of the Qinling terrain. It is indicated that there is a significant provenance change between the Late Devonian and Middle Devonian clastic sediments in the Baiyun-Zhashui subunit. A further modeling using immobile elements Th, Co and REE were also made to calculate proportions of the DTT gneiss, mafic volcanic, granite as 3 possible source components, it shown that the Devonian metasediments from the Baiyun-Zhashui subunit are mainly the first-cycle erosion products of the 60% metasediments of the Qinling complex in the North Qinling, plus 30% of Early Paleozoic granites and 10% volcanics.

We propose that the South Qinling as the passive margin of the Yangtze Craton had been in a close proximity and accreted to the North China at least in the Middle Devonian times.

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Mesozoic-Cenozoic exhumation history of North Tianshan, Northwest China: Constrains from fission track analysis

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Fission track methods are used to examine the exhumation history of North Tianshan, Northwest China.

Fifteen apatite samples and five zircon samples from volcanic rocks in Bogda mountains and granites in Harlik mountains were analysed. The apatite ages range from 109.3±6.1Ma to 11.9±4.1Ma and the zircon ages are within the range 81.7±7.8~56.8±5.1Ma. Results of calculation by paired-minerals indicate that the apparent exhumation rates range from 0.157km/Ma to 0.222km/Ma during the Late Cretaceous to Middle Cenozoic in above area. The thermal history modeled result shows four periods of exhumation in Bogda-Harlik mountains occurred in Early Cretaceous (119~105Ma), late Late Cretaceous (67~65Ma), Early-Middle Cenozoic (47~31Ma) and Late Cenozoic (12~7Ma) since Cretaceous.

Three apatite samples of Yandong pluton in Jueluotage mountains were analysed. The apatite fission track ages are within the range 94.7~87.4Ma which reveal that the uplift was initiated at least in Late Cretaceous. There is good relationship between the current altitude and the sample age, namely ages begin to increase with increasing elevation. The average uplift rate of 0.039km/Ma is calculated by extrapolation. Considering the uplift rate, the exhumation in Jueluotage mountains can be extremely slow since the Mesozoic.

Nine apatite samples are taken from Lianmuqin section in the central part of Turpan-Hami Basin and from both south and north piedmonts. Ages of seven Jurassic samples are distinctly younger than the depositional age, whereas ages of two Cretaceous samples are similar to or older than the depositional age. This indicates that annealing of the Jurassic samples is total or partial, whereas annealing of the Cretaceous samples is minimal. The thermal history modeled result shows that the samples experienced rapid tectonic uplift and cooling/exhumation during Late Cretaceous (120~100Ma) and were buried and heated up again during the Cenozoic, finally exhumed to the surface from 10 to 8Ma.

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Pressure solution and mica in quartzose sandstone: Observations and experiments

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Observations and experiments show that quartz pressure solution is greatly accelerated in the presence of micaceous clays. Quartz grains typically flatten against detrital muscovite but enhanced dissolution is not a general effect with all clays (cf., kaolinite, chlorite). In a North Sea oil reservoir, quartz dissolution causes micaceous organic lamina to deform into irregular stylolites in which the wavelength and amplitude is several times the magnitude of the mean grain diameter. No stylolites develop in lamina free sandstones. Modeling of the formation of these stylolites shows that they develop by a more complicated process than simple random differences in solubility of grains. Thus, stylolites must provide feedback to the dissolving grains. Furthermore, the tips of some stylolites have dissolution fronts or spaces that advance ahead of the stylolite, precluding a simple pressure solution mechanism for their development. Rocks from 10^2 to 10^3 m.y. show well developed pressure solution compared with younger rocks. However, incipient pressure solution occurs in marine sedimentary rocks as young as 6 m.y. at burial conditions as low as 40-50°C and lithostatic pressures of <22 M Pa (<1 km burial depth).

Using a Surface Forces Apparatus (SFA) we have measured the repulsive ‘hydration’ forces and water and ionic diffusion rates in nm-thin water films confined between mica surfaces in various electrolyte solutions. We observe (1) strong short-range repulsive hydration forces, determined by the bound solution ions to the clay surfaces, with Na^+ and Ca^{2+} having antagonistic effects, and (2) rapid ion transport rates. We have also performed SFA experiments with ‘asymmetric’ systems of mica sheets pressed against quartz crystal and silica surfaces. Unlike the symmetric systems, with the asymmetric systems we observe ‘pressure solution,’ i.e., quartz (but not mica) dissolution. Given the angstrom resolution of the optical interference technique used in the SFA, we can monitor typical geologic dissolution rates in hours and in situ, rather than over months or years.

The evolution of grain contacts undergoing pressure solution – Unique insights from a confocal viewpoint

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We used a confocal microscope to follow the evolution of a contact between a fluid saturated cone-shaped halite indenter undergoing pressure solution and a flat silicate plate. The top of the indenter initially undergoes axi-symmetric inward dissolution along its perimeter at rates that are highest at the contact plane and decrease at more elevated surfaces. During this initial phase, which generally lasts tens of hours, the surfaces of the indenter remain relatively smooth. As the contact approaches a critical size, plastic flow ensues, the contact becomes larger and its geometry becomes more complex. We observe a mesa-like structure at the contact, standing tens of microns above relatively smooth planes, that is incised by steep interconnecting channels. The location of this structure and its internal geometry constantly change, a feature we attribute to the competition between plastic flow that drives material from above downward and outwards, and strain-energy driven dissolution, which consumes the contact region along its perimeter.

3D projections of the top of the indenter immediately after brine was added to the system (left) and 120 hours later. During this period the indenter accrued 60um of vertical displacement. Field of view ~500um
**Does stress affect the dissolution of calcite?**

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In order to understand how fluids interact with loaded rocks it is important to know how much stress affects the chemical potential and dissolution-precipitation rates of common rock-forming minerals. We investigated the effect of stress (elastic strain) on the development of dissolution patterns on free surfaces of calcite single-crystals using 'wet' Atomic Force Microscopy. Samples were stressed in the AFM by means of bending. Thin-sections (80 µm) of Iceland Spar crystals were prepared on a microscope cover glass (200 µm) and glued into a concave holder with constant curvature. Stress-distributions in the elastically bend doubly-layer were calculated by numerical modeling. Calcite samples were curved to a degree close to the elastic limit in compression, i.e., just below the critical curvature at which first mechanical twins were observed. The initial sample surface was ultrapolished, either parallel to (10-14) cleavage planes or, to increase the number of initial reaction sites, inclined to these crystallographic planes by 5 degrees. Experiments were carried out in freshly deionized water and ran for up to 3 hours.

The surface patterns of the 22 studied samples (12 stressed, 10 stress-free) showed significant variation, making it difficult to determine whether an effect of stress on pattern formation existed. Sample surfaces polished parallel to (10-14) showed dissolution by etch-pit formation, both with and without stress. Sample surfaces inclined to (10-14), both with and without stress, dissolved along parallel steps not originating from dislocation, but (like etch-pit walls) with a preferred orientation parallel to one of the cleavage plane direction. After strong initial (~30 minutes) bunching of dissolution steps, an apparent steady state pattern was usually reached with only minor variation across a single sample surface. From sample to sample much variation existed in the length an width of terraces in between bunched dissolution steps. Compared to stress-free samples, stressed samples showed more heterogeneous dissolution patterns on the micron scale and, on average, a higher number of growth features, preferably at elevated (stress-free) sites on the roughening sample surfaces.

**Modelling localized volume changes: Application to pressure solution and stylolites**

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A newly developed two-dimensional elasto-plastic numerical model is used to study the evolving interaction between stress distribution in a soluble elastic matrix and a resulting pressure solution (PS) distribution. Spatial distributions of PS resulting from different dominant PS mechanisms are compared (e.g. thin-film and undercutting). The model is used to study growth of a single stylolite, as well as stylolite interactions under a variety of boundary conditions. Results suggest that 1) Other PS mechanisms in addition to (or instead of Thin-Film PS take place in stylolites. 2) Spacing between stylolites might be controlled by elastic mechanisms and rock heterogeneity, similarly to controls on spacing between cracks and compaction bands.

![Initial hole](image1.png)

**Figure 1.** PS evolving around a compressed crack. Gray shading indicates rates of dissolution in non-dimensional units (here white is used for the highest dissolution, black for the lowest one; white area with grid in the middle of the picture corresponds to area where there is no dissolution occurs). a) Dissolution resulting from PS dominated by normal stress (thin-film) is concentrated at the crack tips. b) PS controlled by strain-energy (undercutting) is concentrated both at the tips and the walls of the initial crack.
Modelling the formation of stylolites as a competition between elastic forces, surface tension and noise

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Stylolites are rough dissolution seams in natural rocks. They are a very common feature with a roughness on a large range of scales. Stylolites are usually used to identify the orientation of the largest compressive stress and the maximum amplitude of their peaks is used to estimate compaction in sedimentary basins. Why and how the stylolite roughness develops in detail is still debated. We present a new numerical model that is used to study the roughness development of stylolites in time and 2D space. A particle model is used with a linear elastic spring network where particles dissolve as a function of elastic and surface energies as well as normal stress on reactive interfaces. An initial quenched noise on the dissolution constants of particles is used to initiate the roughness. The initial configuration in the model is a perfectly flat dissolution surface that represents an initial heterogeneity in the rock. This surface remains flat when no initial noise is used in the system indicating that elastic and surface energies as well as the normal stress on the surface smoothen the interface and prevent roughness development. Systems with an initial noise, however, develop a significant roughness within a relatively short time. Over time the mean position of the stylolites remains fixed whereas their mean and maximum amplitude scale as a function of the square root of time. Elastic energy, normal stress and surface energy influence the roughness growth and thus the scaling properties of the stylolites. Fast Fourier Transforms of time and space series indicate that the stylolites may show self-affinity in both, time and space. We compare the results of the numerical model with natural systems and discuss the implications of our study.

Physical chemistry of replacement: Consequences for petrology and reaction-transport modeling

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Mineral replacement, characteristically preserving both volume and morphological features of the host, is widespread in rocks of all kinds. Crystal aggregates that grow in a rock exert a local stress on adjacent mineral grains as they grow. This induced stress depends on the kinetics of crystal growth that causes it, the shape of the aggregate, the pre-existing macroscopic stress, and the host rock's response to the growth (Fletcher & Merino, 2001). Possible responses are pressure-solution, deformation, and fracturing of the host rock.

I. Replacement takes place where the A growing crystals are accommodated only by pressure-solution of adjacent B-host grains. The induced stress between A and B forces the crystal growth rate of A and the pressure solution rate of B to become equal. This is why replacement is always isovolumetric. Adjusting the replacement of B by A on volume often provides unsuspected insight. Adjusting the weathering replacement of feldspar by gibbsite on volume provides the thread to grasp the feedback (between the leaching and the accumulation zones) at the core of all weathering (Merino et al, 1993). It is thanks to this feedback that the two zones remain associated as they dynamically “eat” their way into parent rock, as confirmed by dynamic modeling (Wang et al, 1995), and as observed.

II. If the B host rock has low strength and/or a low dissolution rate constant, then the growing crystal(s) of A are accommodated by local deformation of the B host rock. If A grows as dispersed crystals or nodules their aggregate mechanical effect is to overpressure a large volume of host rock, on a scale much larger than the size of each nodule.

III. If A grows in a host rock subjected to unequal principal stresses, then A grows as displacive veins. Vein-shaped growth injects the least strain energy into the host, compared to spherical and rod-like growths. Displacive vein examples: septarian concretions; zebra veins in dolomites, evaporites, serpentinitized gabbros; veins normal to stylolites.

Dynamic reaction-transport modeling including the growth-induced stress and its consequences – replacement or displacive growth – can better integrate modeling and petrology (Merino & Dewers, 1998).

References
Pore-scale coupling of dissolution, diffusion, and crystallization forces during alteration of vesicular lavas

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Time-progressive infilling of vesicular pore space by secondary minerals is a common textural feature of zeolite facies metabasalts. For instance, individual vesicles are often rimmed by one or more generations of mafic phyllosilicates and silica phases, with later infillings of one or more generations of zeolites and other silicates. Infilling of pore space is due to formation of secondary mineral phases that are considerably less dense than the basalt. Digital analysis of pore geometries and mineral parageneses at the thin section scale show that the thickness of phyllosilicate linings is independent of pore size within a sample leading to an increased percentage of phyllosilicate occlusion of porosity as pore size decreases. However, the preservation of residual pore space after alteration is a function of pore size, with larger pores being more likely to retain porosity after alteration. In rare instances, alteration aureoles are observed around pores. We propose a model to explain these observations that involves coupled diffusion of water into the matrix of the lavas and ions into the vesicle that is governed by the amount of available open volume necessary to accommodate new mineral formation. Mass balance calculations indicate that the volume of mafic phyllosilicates formed during alteration is smaller than that of the lava dissolved. However, reaction path modeling indicates that at low degrees of reaction, mafic phyllosilicates form first with an early net gain in solid volume. Further reaction leads to stabilization of zeolites along with mafic phyllosilicates, which leads to a dramatic increase in total solid volume of up to ~30 % for complete reaction of the lava. Paragenetically late infilling of vesicles by zeolites without phyllosilicates suggests that phyllosilicate formation during zeolitization is restricted to pseudomorphic replacement of primaryphases, consistent with petrographic observations. The fact that the progressive infilling textures are consistent from vesicle to vesicle, and that mineral volumes are not averaged between vesicles, indicates that these processes are controlled by local scale diffusion and volume availability at the scale of individual pores. Temporal variations in mineral stability and net volume changes during reaction thus drive net transport of components between vesicles and the lava matrix in response to restrictions on the space necessary for authigenic mineral formation.

Dissolution-precipitation creep under cyclic stress

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Dissolution-precipitation creep DPC is one of the main deformation mechanisms in natural systems. Common models for DPC assume a steady state process in a closed system consisting of three steps: i) dissolution at the grain-to-grain interfaces of non-hydrostatically stressed surfaces, ii) transport of the solute in interfaces, iii) precipitation at grain-to-pore interfaces or at hydrostatically stressed crystals. The deformation is ultimately driven by the potential energy of the system (Weyl, 1959) and the kinetics of DPC is assumed to be transport controlled. However, recent investigations (He et al., 2003; Lohkämper et al., 2003) show that open systems, capillary forces, or temperature variations can significantly affect the rate of DPC. Here, we investigate the influence of cyclic stress on the deformation rate of halite crystals in contact with silica. In low stress periods, transport within the interface is noticeably enhanced in comparison to high stress periods. Therefore during low stress periods, material, which was plastically deformed in previous high stress periods, can be quickly removed and transported out of the interface.

Regardless of the interface morphology, reducing the load enhances material transport. Therefore, cyclic variations of stress provide an efficient deformation mechanism by remanently increasing the internal energy of the crystal via plastic deformation in high stress periods and reducing the energy via dissolution and transport in low stress periods.

As evident from seismic activities, cyclic variations of stress are common in geological systems. Therefore, we expect from our results that cyclic build up and release of stress can become key factors for fluid assisted deformation of rocks.

References
The importance of plastic flow in the deformation of a sodium chloride indenter undergoing pressure solution

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We conducted experiments to study the deformation of a loaded single crystal sodium chloride indenter immersed in saturated solution. The contact between the indenter and an inert silicate window was viewed with a confocal microscope. The indenter exhibits two stages of deformation: The first involves rapid inward dissolution of the contact (undercutting) accompanied by slow vertical convergence caused by the elastic response to the shrinking contact and vertical (“thin-film”) dissolution. The second stage consists of rapid vertical convergence by plastic flow and removal of the flowed material by strain-energy driven inward dissolution. The transition from stage 1 to stage 2 occurs when the contact stress is 75MPa on average, which indicates that the indenter undergoes significant strain hardening to this point. During the second stage we observe oscillations in the rate of convergence, which are closely related to oscillations in the area of the contact. These oscillations reflect the counteraction of plastic flow and inward dissolution.

3D microtomography of a salt aggregate during pressure solution

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Pressure solution creep is one of the possible processes of mechano-chemical deformation that controls porosity and permeability variations in the upper crust. The three-dimensional geometry of the porous network of halite aggregates was imaged during compaction driven by pressure solution creep using X-ray synchrotron computed microtomography. With this technique the whole aggregate textural changes during deformation (Fig. 1a) as well as individual grain contacts (Fig. 1b) were imaged at several stages of the deformation. By reconstructing subvolumes, the 3D porosity of the aggregates was extracted. The time-resolved decrease in permeability during porosity reduction was calculated by solving the Stokes equations. The permeability remained isotropic and decreased from 2.1 to 0.15 Darcy after 18.2% compaction. Two microscopic mechanisms can explain the permeability reduction: grain indentation and pore connectivity reduction by precipitation on the free surface of pore throats.

Figure 1: a) X-ray tomography of a salt aggregate during compaction in the presence of a saturated brine. Individual grains appear in light gray, whereas the pores are dark. b) Zoom on two salt grains before (left) and after compaction (right).
EARTHTIME: A community-based effort towards high-precision calibration of earth history

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Geological time is customarily treated as an "independent variable"; deductions and conclusions are made assuming that the geological timescale as given is precise and accurate. Current geological timescales are based on data of variable quality, commonly averaging dates obtained by different techniques, with differing (though often ignored) absolute uncertainties. Consequently, the greatest uncertainty in most analyses of geologic and evolutionary rates is the timescale itself. Recent advances in geochronology and correlation methods now allow us to reframe research into the timing and rates of geological and biological processes in deep time, producing a newly calibrated geological timescale with significantly improved accuracy and precision standards commensurate with new and emerging geochronologic and chronostratigraphic methodologies. To address these issues the EARTHTIME initiative has been proposed as a new community-based effort to focus attention on the calibration of at least the last 800 million years of earth history. This will allow earth scientists to address a whole new series of questions that rely on knowledge of precise rates of biological, geological, and climatic change. Two EARTHTIME workshops have been held, the first to discuss the need for better integration of geochronology and paleontology and the second, on intercalibration of the U-Pb and Ar-Ar chronometers. As an outgrowth of these two meetings we have proposed the production of a mixed ²⁰⁶Pb-²⁰⁸Pb-²³⁵U-²³⁸U spike for distribution to the international community and the sponsorship of a community wide intercalibration experiment using standard material (see Heizler et al., and Condon et al., this session). Community support is growing and we expect that this effort will fundamentally change our knowledge of the distribution of time in the rock record and give us unprecedented insight into the rates of geological, biological, and climatic processes in deep time. The EARTHTIME concept has wide application to all parts of the geological record and the Earth Sciences.

Intercalibration of astronomical and radioisotopic time

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Geological time scales (GTS) may be chronometrically calibrated using a variety of absolute dating techniques. In a recent version of the GTS (Gradstein, 2004), the entire Neogene is calibrated on the basis of astronomical ages, while the older part of this timescale relies on radioisotopic ⁴⁰Ar/³⁹Ar and U/Pb methods. In order for the timescale to remain accurate and consistent throughout, it is crucial that astronomical and radioisotope dating methods produce identical results when the same geological event is evaluated. The Mediterranean Neogene provides an excellent opportunity to compare these different dating methods through direct isotopic dating (⁴⁰Ar/³⁹Ar, U/Pb) of volcanic ash layers intercalated in astronomically tuned marine successions. We will present ⁴⁰Ar/³⁹Ar ages for many of these tephra from parallel determinations in two laboratories (BGC and VU). These results allow the calculation of an astronomically calibrated age for the widely used FCT sanidine standard. A major advantage of an astronomically calibrated FCT age against a K/Ar calibrated standard is twofold: 1) consistency with Neogene timescales which increasingly are based on astronomical ages, and 2) a much smaller error in the absolute age due to absence of uncertainties in absolute ⁴⁰K and radiogenic ⁴⁰Ar content or ⁴⁰K/K in the primary standard, and a smaller error contribution of the decay constants because the branching ratio of decay to ⁴⁰Ca and ⁴⁰Ar is not required. A next step would be the introduction of a directly astronomically dated standard, eliminating the ca. 0.1% typical intercalibration error for unknown samples within the appropriate age range of the standard.

We will discuss all potential uncertainties in the astronomical ages of ash layers, as we have determined for ash layers in astronomically calibrated Mediterranean sections. This approach may be extended to other (U/Pb, U/Th) techniques and to older time intervals.

Reference
Dating erosion events using $^4\text{He}/^3\text{He}$ thermochronometry

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The timing of rapid erosion events, e.g., induced by river incision or by glaciation, can be determined using chronometric systems sensitive to low temperatures provided that a sample was cooled from above the system’s bulk $T_c$ to the point of quantitative retention. Even in the case of apatite He ages this requires cooling by more than 60°C, or more than a few km of erosion. Thus for all but large magnitude erosional events, traditional thermochronometry is not useful.

Determination of the $^4\text{He}$ spatial distribution by the $^4\text{He}/^3\text{He}$ method may provide an alternative approach. An apatite residing at a temperature where significant diffusion occurs will develop a diffusive $^4\text{He}$ distribution decreasing to zero at the grain edge. If this apatite then rapidly cools to Earth’s surface temperatures and thereafter remains cold, the concentration profile increases uniformly across the grain and the concentration at the edge is a direct reflection of the age of the event, the U+Th concentration, and $\alpha$ ejection. The local “age” at the edge of the grain constrains the timing of the cooling event. Depending on timescale, the temperature at which these outermost few microns have a zero effective concentration is in most cases ~30°C, i.e., the “edge age” can be measured and constrains the timing of erosion events or paleoclimatic responses.

Preliminary results and challenges with this technique will be discussed with reference to ongoing studies in the Sierra Nevada. Additional results will be presented by Shuster et al. (this volume).

Calibration of a Pleistocene geomagnetic instability time scale (GITS) using $^{40}\text{Ar}/^{39}\text{Ar}$-dated lavas

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Advances in the measurement of paleomagnetic intensity recorded by marine sediments, as well as $^{40}\text{Ar}/^{39}\text{Ar}$ dating of paleomagnetic directional recordings in Pleistocene lava flows, offer a powerful means of calibrating a global magnetostratigraphy for the last 2 myr. This involves moving beyond the classic geomagnetic polarity time scale (GPTS) and resolving temporally not only the undisputed polarity reversals, but also the many short-lived geomagnetic “events,” or cryptochrons that are thought to signal periods of instability in the geodynamo. Some cryptochrons may be best described as geomagnetic excursions, others aborted reversals, and still others, rapid successions of back-to-back reversals. Even the shortest events are now revealed as distinct paleointensity minima in global stacked sediment records (e.g., SINT-800; GLOPIS-75). When the degree of stability of the geodynamo is considered, rather than lengths of polarity intervals, an alternative approach to the study of the GPTS is appropriate.

Hence, a challenge is to calibrate a Geomagnetic Instability Time Scale (GITS) via $^{40}\text{Ar}/^{39}\text{Ar}$ dating of transitionally-magnetized lava flows. As an example, the Laschamp event—expressed as a sharp paleointensity minimum in the GLOPIS-75 marine sediment stack—was dated by matching O-isotope variations in North Atlantic sediments to those recorded in annually counted layers of the GISP2 ice core. By matching a few $^{14}\text{C}$ ages from the sediments to specific varves in the ice core, the paleointensity minimum was found to span ~1500 years between 41 and 39 ka. $^{40}\text{Ar}/^{39}\text{Ar}$ incremental heating and unspiked K-Ar dating of two lavas that record the event at Laschamps, France yield an age of 40.4±1.1 ka (2σ, analytical uncertainty). Thus, despite systematic uncertainty in the $^4\text{K}$ decay constant, both the accuracy and precision of the K-Ar clock—carefully applied to basaltic lava flows—can be remarkably good, i.e., better than 2% for the entire Pleistocene. A GITS based on intercomparison of several $^{40}\text{Ar}/^{39}\text{Ar}$-dated geomagnetic events will contribute further to quantifying: (1) astrochronologic age models based on O isotopes and orbital tuning, (2) long-term correlations of marine sequences, (3) the long-term behavior of earth’s geomagnetic vector field, (4) production of cosmogenic isotopes, including $^{14}\text{C}$, and (5) paleoclimate records at sub-orbital time scales.
Evaluating intercomparability amongst several $^{40}$Ar/$^{39}$Ar laboratories

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The Earthtime initiative seeks to achieve a highly precise (ca. ±0.1%) geologic timescale as a basis for reaching a heretofore-unavailable record of several geological and biological processes. To reach this goal, calibration of standards within individual geochronological methods and amongst different methods must be improved. As an outgrowth from the Earthtime I meeting, fifteen $^{40}$Ar/$^{39}$Ar laboratories organized an effort to each analyze five common fluence monitors in a blind, full disclosure, experiment. A list of participating laboratories can be found at http://www.earth-time.org. No specific protocol was mandated except that each laboratory would run a split of the sample provided using Fish Canyon Tuff sanidine (FC-2) as the base neutron fluence monitor. The samples chosen include Alder Creek sanidine (~1.1 Ma); Taylor Creek sanidine (~28 Ma); GA1550 biotite (~99 Ma); and PP20 (equivalent to Hb3gr) hornblende (~1071 Ma). In addition, a sanidine separate from a Mid-Tertiary ignimbrite (TS-1a) was provided as a voluntarily unknown. Thus far 8 labs have contributed and until all data are received no rigorous compilation will be presented. The present results confirm that the standards are homogeneous and $^{40}$Ar/$^{39}$ArK values relative to FC-2 at 0.05-0.2% (1σ) precision was achieved. Perhaps somewhat surprising, but gratifying, is that intercomparability between labs (with minor filtering) was at better than 0.2% for all samples. As expected, each laboratory fought various instrument problems throughout the year and anomalous data could generally be attributed to poor analysis conditions. These experiments indicate that the $^{40}$Ar/$^{39}$Ar community is well positioned to produce data that will be intercomparable at a level that corresponds to the goals of the Earthtime initiative. Further refinement and standardizing of protocol for Earthtime research should be considered. For instance, narrowing the number of reactors used for Earthtime samples would allow a concentrated characterization effort. Also, using the standards characterized in this effort would help eliminate errors involved with calibration of in-house standards. Continuing communication efforts and open sharing of ideas and data that have begun through the Earthtime workshops is essential to success.

The role of U-Pb TIMS dating in resolving the causes of mass extinction events

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The P-Tr and K-T boundaries mark the two largest mass extinction events in the rock record. While there is widespread acceptance of a meteorite impact origin for the K-T extinctions, the trigger for the P-Tr extinctions is considerably less certain, but with Siberian flood basalt volcanism generally regarded as a leading suspect, and the case for meteorite impact recently gaining momentum. A new U-Pb TIMS zircon age of 251.7±0.4 Ma for a volcanic bed immediately below the P-Tr boundary, near Heshan, S. China, provides a robust maximum estimate of the boundary age that is identical to previously published U-Pb ages from Siberian flood volcanic rocks (251.1±0.3 and 251.7±0.4 Ma; [1]) and the Noril’sk I intrusion (251.2±0.3 Ma; [2]). These ages provide a rigorous temporal link between the time of the most devastating mass extinction event and the largest Phanerzoic volcanic event.

The resolving power of the U-Pb dating method is widely accepted as unsurpassed, but to maximize its potential requires rigorous assessment of geological and analytical details that can potentially bias data. Small but significant age discrepancies reported by different U-Pb labs for the P-Tr boundary [3-5] emphasize the need for the EARTHTIME inter-laboratory calibration project, which seeks to understand and minimize sources of bias. Our data for the P-Tr boundary and Siberian flood volcanic events have been obtained from the same laboratory, thus circumventing any inter-laboratory calibration biases.

Meteorite impact has also been suggested as the primary trigger to the P-Tr event [e.g. 6], but the evidence presented is controversial [e.g. 7-9]. As in the case of the Deccan volcanism and the Chicxulub impact at the K-T boundary, precise time relations are essential for establishing the feasibility of such theories as large impacts initiating a chain of events leading to massive volcanism, rapid atmospheric-environmental changes, and mass extinction.

References
U-Pb inter-laboratory calibrations using zircon samples: Application of the new CA-TIMS technique

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U-Pb inter-laboratory calibrations using natural zircon standards are perhaps the most useful and meaningful type of inter-calibration, but also the most demanding: they test not only isotopic tracer calibrations, but also sample homogeneity and analytical techniques, especially complete removal of all zircon domains with Pb loss.

A new zircon U-Pb geochronology method, CA-TIMS, combines pre-dissolution high-temperature annealing of natural radiation damage followed by multi-step dissolution. Early partial dissolution steps preferentially remove domains that have lost Pb. Later partial dissolution steps sample zircon that has behaved as a perfect closed system with respect to U and Pb. This yields highly precise and accurate crystallization ages for zircons that lack any inheritance, and also is very sensitive to detecting the presence of inheritance or any other isotopic complexities.

CA-TIMS was applied to two recent, but widely used zircon standards: R33 and TEMORA-2. An aliquot of each zircon standard was annealed in air at 1,000°C for 48 hrs, then digested in 16 partial digestion steps of gradually increasing intensity. In each case, the first 4 steps removed disturbed zircon. Both samples showed perfect closed-system behavior for the remaining 12 steps, each yielding a set of statistically identical 206Pb*/238U ages and defining a plateau on a plot of age versus 238U released. The plateau for R33 yields an age of 419.96 ± 0.15 (MSWD = 0.96); TEMORA-2 yields an age of 417.82 ± 0.06 (MSWD = 0.52).

In terms of mass balance, the plateau for R33 was reached after removal of 15% of the total U, but only 5% of the zircon mass. The plateau for TEMORA-2 was reached after removal of 31% of the total U, but only 3.4% of the zircon mass, reflecting the strong U zoning of the zircons, and also demonstrating the high selectivity of the CA-TIMS steps.

Both samples yielded 207Pb*/206Pb* ages for the plateau steps that are concordant with the 206Pb*/238U ages within analytical and decay constant uncertainties.

The CA-TIMS analyses demonstrate that both R33 and TEMORA-2 have “clean” isotopic systematics, and that only a very small volume of high-U rim material has Pb loss; both are excellent standards for U-Pb calibration purposes.

Progress report on the U-Pb interlaboratory experiment

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Uncertainty in the Pb/U ratio of tracer solutions utilized in U-Pb isotope-dilution thermal ionization mass-spectrometry (ID-TIMS) geochronology, typically estimated at 0.1 to 0.25%, is one of the largest sources of uncertainty in the comparison of data from different laboratories. In order to better assess the degree of agreement among the various ID-TIMS U-Pb laboratories, an interlaboratory experiment involving natural zircon standards (R33 and TEMORA) and common mixed U-Pb gravimetric solution(s) is now underway as an outgrowth of the EARTHTIME project (http://www.earth-time.org/). Published ID-TIMS data sets for these two standards indicate that concordant and equivalent clusters of data can be obtained with uncertainties in the 206Pb/238U date of ca. 0.1-0.2% [1]. These studies also demonstrate that techniques employed to minimize Pb-loss (e.g., air abrasion) are critical for producing equivalent datasets. Initial datasets from TEMORA and R33 zircons that were presented at the EARTHTIME II workshop indicate up to 1% scatter in the U-Pb dates between various laboratories. However, given variation in pre-treatment techniques (i.e., degree of air-abrasion etc.) and variability in blank contribution, it is impossible to assess how much of the variation is attributable to tracer solution calibration. In order to minimize such effects, batches of uniformly pre-treated zircons (both air-abraded and annealed/leached) were prepared and distributed. Such high-n ID-TIMS data sets, combined with tracer solution calibrations against multiple mixed U-Pb gravimetric solutions, offers the potential for interlaboratory calibration at the 0.1% level or better. Data on these standards and solutions will be presented. Elimination of interlaboratory biases is a crucial first step before the geochronology community will be able to systematically (1) compare and/or integrate U-Pb and 40Ar/39Ar data sets from multiple labs and, (2) assess systematic variation between 206Pb/238U and 207Pb/235U dates and uncertainties in the 235U and 238U decay constants.

Reference
High-precision Re-Os shale geochronology

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The 187Re-187Os system has been known to yield depositional ages for organic-rich clastic sedimentary rocks like black shales for some time. However, only with improved analytical methodologies for digestion and optimal sampling strategies have “high-precision” Re-Os ages (precision better than ±1% 2σ) been routinely attained. In addition, we have shown that the Re-Os geochronometer in shales remains undisturbed through hydrocarbon maturation and in some cases chlorite-grade metamorphism, which together with “organic-selective” dissolution techniques, allows precise depositional ages to be determined from a greater range of shales than previously thought possible, even with TOC contents as low as ~0.5%. Accuracy of our Re-Os shale dates is best illustrated by comparison to units or boundaries for which precise U-Pb age determinations also exist. For example, our recent study of directly dating black shale at the Devonian-Carboniferous boundary in Western Canada, has yielded a Re-Os age of 361.3 ± 2.4 Ma (2σ, including λ uncertainty), in accord with the most recent interpolations of the DC boundary age using U-Pb zircon age determinations. This result, and other high-precision results for Jurassic units, demonstrate that the Re-Os shale geochronometer has a role to play in timescale calibration research, especially in sections with limited potential for ashbed dating. In another application, precise (<±1% 2σ) Re-Os shale dates have been determined for several shale units associated with Neoproterozoic glaciations which have resulted in a more detailed understanding of the timing of these glacial event(s). Limitations of the method include the restriction to < chlorite-grade metamorphism, and accuracy, intercalibration and decay constant issues related to uncertainties in Os standard compound stoichiometry.

Triassic-Jurassic time scale and mass extinction: Current status and new constraints

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The Triassic-Jurassic (Tr-J) boundary coincides with one of the most profound mass extinctions known in the history of life on Earth. A number of potential causes for the biotic crisis have been proposed but most constraints for the timing are restricted to terrestrial sequences which have been studied in detail in eastern N America as well as NW Africa. Recent research presented geochronological evidence supporting a link between the Tr-J biotic crisis and the CAMP (Central Atlantic Magmatic Province) volcanism. 40Ar/39Ar ages from CAMP magmas cluster around 199.9 Ma and have been documented to coincide with an abrupt change of both fauna and flora on land.

In contrast, the preserved marine geologic record is scarce. The only recent radio-isotopic age, a U/Pb zircon date of 199.6 ± 0.3 Ma (Palfy et al., 2000), was obtained from a volcanic ash predating the Tr-J boundary. Although in apparent agreement with the 40Ar/39Ar age for the CAMP volcanism, recent results from several studies applying U/Pb and 40Ar/39Ar analyses to minerals from the same rocks show that there is a systematic bias between the two isotopic systems, with 40Ar/39Ar ages being ca 1% younger than U/Pb ages. Accounting for this discrepancy consequently shifts the expected U/Pb age for the main pulse of the CAMP volcanism to 202 Ma and therefore predates the U/Pb age for the marine extinction by more than 2 Ma. Additional constraints come from a preliminary age of 198.0 ± 0.6 Ma (single-crystal IDTIMS U/Pb analyses) applied to a volcanic layer within early Sinemurian marine sediments in S Hungary, which suggests that the Tr-J boundary is older than 199.6 Ma, unless the lowermost stage of the Jurassic (Hettangian) is extremely short.

A number of potential scenarios arise, none of which can be unambiguously accepted from the currently available database, and therefore await a rigorous test. Among them is the possibility that the extinction on land and in the ocean was diachronous, or that the biotic crisis was synchronous in both environments and the geochronology, particularly in marine environments, needs significant improvement.

Reference
The Manicouagan impact melt rock: A proposed standard for the intercalibration of U-Pb and \(^{40}\)Ar/\(^{39}\)Ar isotopic systems

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A source of uncertainty in the high-precision intercalibration of U-Pb and \(^{40}\)Ar/\(^{39}\)Ar geochronology using magmatic minerals is protracted crystallization in complex magma chambers. This has been demonstrated in felsic plutonic and pyroclastic rocks, where magma chamber residence times of >0.3 Myr have been documented. One approach is to find rapidly formed and cooled, homogeneous, magmatic rocks, for which impact melt rocks appear to be an ideal candidate.

The central island of the 65-km-diameter Manicouagan crater in east-central Quebec, Canada is underlain by a sheet of melt rock with an apparent thickness of 230 m. The melt sheet overlies, and is locally mixed with, brecciated basement lithologies of Proterozoic age. The texturally stratified, upward coarsening, melt sheet is marked by an upward reduction in impact-derived clast content. Its chemistry is suggestive of extensive homogenization prior to solidification [1]. Thermal modelling indicates a maximum crystallization duration of about 1600 yr at the core of the melt sheet [2].

Single, 160 to 300 µm-size, zircons from the highest levels of the melt sheet analysed so far by ID-TIMS have consistently produced \(^{206}\)Pb/\(^{238}\)U dates of ca. 215.5 Ma. No indications of inheritance from older zircon have been detected. These results are in agreement with previously reported U-Pb zircon dates of Hodych and Dunning [3]. Ar systematics are complex but a preliminary \(^{40}\)Ar/\(^{39}\)Ar sanidine plateau age of ca. 215 Ma by Shepard [4] is encouraging. We propose the demonstrably melt-derived zircon and sanidine in Manicouagan as new potential standards for the high-precision intercalibration of the U-Pb and \(^{40}\)Ar/\(^{39}\)Ar isotopic systems. In addition, this study confirms the conclusions of Hodych and Dunning [3] that the impact does not coincide with the Triassic-Jurassic extinction at ca. 200 Ma.

References

Intercalibration of the U-Pb and \(^{40}\)Ar/\(^{39}\)Ar geochronometers: Status, prognosis, and proscription

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The \(^{40}\)Ar/\(^{39}\)Ar method is comparable to U-Pb in terms of precision and possession of internal reliability criteria. Intrinsic limitations favor U-Pb in the pre-Mesozoic, and \(^{40}\)Ar/\(^{39}\)Ar for the Cenozoic. Nonetheless, the substantial overlap in routine applicability dictates that these two geochronometers be well intercalibrated in order to achieve an accurate and highly resolved time scale. Existing uncertainties (e.g. in decay constants and \(^{40}\)K/\(^{40}\)Ar data for standards) in calibration of the \(^{40}\)Ar/\(^{39}\)Ar method yield ab-solute age uncertainties of approximately 2%, roughly an order of magnitude worse than for U-Pb. While independent improved calibration of the \(^{40}\)Ar/\(^{39}\)Ar method is worth-while, it is equally valid and in some ways more desirable to effectively normalize the \(^{40}\)Ar/\(^{39}\)Ar to the U-Pb system. Such a program has been ongoing at BGC for 7 years, and has produced 15 data pairs for volcanic rocks of Cenozoic-Proterozoic age. Volcanic rocks are critical to avoiding decoupled isotopic systems due to slow cooling. From this data set, complemented by several U-Pb data from MIT, approximately –1% bias (\(^{40}\)Ar/\(^{39}\)Ar relative to U-Pb) is evident. Under the stimulus of EARTHTIME, more such data are likely to be generated in the future. The statistical methods of Kwon et al. (2002) permit simultaneous derivation of both the \(^{40}\)K total decay constant and the age of a standard. Values determined by this approach are already better than 0.5% in 1σ precision and will improve with increased data input. It will be critical in going forward that data used for this purpose be of the highest possible quality for both systems. Obviously, both systems must be applied to minerals separated from the exact same rock. Data from intrusive rocks, though perhaps illustrative, are inappropriate for quantitative use. \(^{40}\)Ar/\(^{39}\)Ar data must have rigorously controlled neutron fluence relative to a well-intercalibrated standard (e.g., FCs) and be demonstrably free of effects due to alteration, secondary degassing, recoil, and excess argon. U-Pb data must be free of Pb-loss and inheritance effects, as best deduced from ID-TIMS analysis of single zircons using the annealing/chemical abrasion technique.

Reference
U-Th/He dating of basalt
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Determining ages and/or time scales for Quaternary (<1.8 my) basaltic eruptions still remains a challenge. Despite considerable progress in the fields of C-14, Ar-Ar, and cosmogenic nuclide dating, no single method with wide applicability has emerged and those methods that have been used often do not overlap in time or type of applicable material. We have investigated the use of the U-Th/He system as a method for dating the eruption age of volcanic rocks. Our first step was to assess the viability of using this dating technique on young samples (Aciego et al, 2003). The second step is to apply this technique to a system that has some age constraints, but that could benefit from direct age measurements. For this purpose we have chosen to focus on two areas: (1) a set of basalt samples from the Snake River Plain of Idaho and (2) a suite of post-shield alkalic basalts from the Big Island of Hawaii. Both sets of samples have upper and lower bounded age constraints, but individual flows have not been dated. One of the drawbacks associated with using the U-Th/He technique on olivine has been the different sources of error. First, the olivine typically has low U,Th concentrations, making measurement of U,Th and He difficult. In the absence of improvements in mass spectrometer sensitivity, one way to overcome this is to measure larger amounts. The low concentrations of parent and daughter products also necessitates measuring the parent and daughter on the same aliquot, as small variations in parent or daughter between separate aliquots would produce large errors in the calculated age. For this purpose, a furnace was designed capable of heating 1-2 g of sample then retrieving the melted sample for U, Th determination. Second, the basalt matrix has more U and Th than the phenocrysts leading to a He implantation effect. Modeling of the injection-ejection effects indicate that the corrections are small. Ages have been measured for several basaltic lavas ranging from 100 to 350 kyr. The ages are consistent with geological constraints and have 1-sigma errors of ±6%.

Reference

Study of the $^{40}$Ar/$^{39}$Ar age and Ar isotope distribution of phengite in high pressure orthogneiss (the surrounding rock of the Qinglong-shan eclogite, East China)
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The conventional $^{40}$Ar/$^{39}$Ar ages of phengite in high pressure metamorphic orthogneiss, the surrounding rock of the Qinglongshan eclogite, East China, are from 211.4Ma to 219.5Ma. This ages range is not only in concordance with the $^{40}$Ar/$^{39}$Ar age (217.9Ma) of K-feldspar which is extracted from the same rock sample, but also identical with the Rb-Sr age (219Ma) and Sm-Nd (224Ma) of eclogite [1]. We use laser spot-fusion technique to analyze the $^{40}$Ar/$^{39}$Ar age in a single grain of phengite. The minimum age is 218.2±2.3Ma and the biggest one is 220.4±4.3Ma. These ages are concordant with the classical $^{40}$Ar/$^{39}$Ar ages of bulk-sample of phengite, which shows that the argon isotope has been fairly well-distributed in the phengite. Therefore the fundamental conclusion is: (1) phengite in the high pressure metamorphic orthogneiss does not contain excess argon and can be used as the object of $^{40}$Ar/$^{39}$Ar dating. (2) phengite in Qinglongshan eclogite contains large amounts of excess argon [1] while phengite in its surrounding rock, high pressure orthogneiss, does not contain excess argon. This fact proves that the excess argon of phengite in the eclogite does not come from its country rock but from its inheritance.

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Reference
Precessional climatic signal in the Plio-Pleistocene Chemeron Formation, Central Kenya Rift

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The Chemeron Formation (4.5–1.6 Ma) is exposed within the Tugen Hills, a tilted horst block within the central Kenya Rift. The formation typically consists of fluvial-lacustrine and alluvial fan sediments, with volcaniclastic interbeds. Near the Barsemoli River, the formation includes a series of five prominent diatomite beds (2.7–2.5 Ma) intercalated in the terrigenous sequence. The diatomite units, up to 12m thick, document intermittent, significant lake systems within the axial portion of the rift.

40Ar/39Ar dating of anorthoclase-bearing tephra horizons within the section permit precise determination of chronometric tie points to evaluate the sedimentation history of the sequence. Sedimentation rates are remarkably linear through the sequence that includes the diatomite horizons. By interpolation, we are able to estimate the absolute ages of the individual lakes (as represented by the diatomites). The regular temporal spacing of the lake sequence (ca. 25 ka periodicity) matches very well with the periodicity of the Earth’s precessional curve for this interval. Given that there is a 1:1 match of diatomites to precessional peaks for five successive precessional cycles, we deem it highly probable that the lake systems are a climatic response to changes in insolation accompanying precession of the Earth, rather than a response to tectonism.

The Gauss/Matuyama paleomagnetic transition occurs just above one of the diatomites of this precessional sequence. This relationship to a paleomagnetic boundary allows us to compare the phase relationship of a wet period in the central Kenya Rift to the Mediterranean sapropel record; they appear to be in phase to within one quarter of a precessional cycle, if published astronomical ages for paleomagnetic boundaries can be relied upon.

Quartz hydration dating: A new mineral geochronological technique

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New Geochronological Technique for Direct Dating of Minerals

The new Quartz Hydration Dating (QHD) technique relies on the phenomenon of water diffusion into quartz leading to the formation of a hydration layer that can be measured by a hydrogen profiling technique, based on the resonant reaction 1H(15N,αγ)12C, and diffusivity data connecting the layer thickness with the hydration time.

We have obtained such data by induced-hydration experiments in the temperature range 60 to 200 °C and derived a general equation for calculating diffusion coefficients which was validated by results from dated artifacts. The main factors influencing the diffusivity are temperature, the crystallographic orientation, measured as the angle between surface of hydration and crystal c-axis, and initial H content of the quartz.

The effective time range of QHD is 100 ya to over 100 kya. The error of age determination is 35%, but may be reduced to 20% by controlling for material variability. QHD is applicable to single-crystal specimens and aggregates of single crystals. QHD serves as an example of silicate mineral dating. A range of geological applications is discussed.

Reference

Estimating $\lambda^{(40)}K$ by U-Pb and $^{39}$Ar-$^{40}$Ar dating of the peralkaline Ilímaussaq complex, Greenland

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The Mesoproterozoic Ilímaussaq igneous complex comprises an extraordinary diversity of peralkaline rock types formed in three distinct magmatic events. The first one, augite syenite, was followed by alkali granite and, finally, nepheline syenites. Such extreme differentiates require a fast ($<$ 0.1 Ma) differentiation process. Solidus temperatures reach down to 450 °C; intrusion depths were 3-4 km. Water activity was very low and no metamorphic overprint occurred. Therefore, all mineral ages are magmatic crystallization ages.

Baddeleyite is an early phase in the augite syenite: it occurs as euhedral inclusions in olivine, cpx, feldspar and Fe-Ti-oxides. U-Pb dating on 4 replicate baddeleyite fractions from stage 1 augite syenites gave 1160 ± 5 Ma. This agrees with the zircon age of 1166 ± 9 Ma from stage 2 alkali granite [6].

Seven amphiboles were dated by $^{39}$Ar-$^{40}$Ar: Ca-rich members from early augite syenites (ferro-edenite, ferro-pargasite) and Na-dominated arvedsonite and nyböite from late agpaitic rocks. Very importantly, the Ar mass spectrometry was performed with the Faraday cup only, avoiding potential problems with multiplier nonlinearity. K-Ar dating of the peralkaline rocks, which is unreasonable. This indicates that the best agreement between K-Ar and U-Pb ages is present so far has to be re-examined (see also [1]).

Simultaneous optimization of the K-Ar monitor age with $\lambda$ was proposed by [3]. Calculating the ages of our amphiboles using the values in [3], 28.27 ± 0.13 Ma and 5.476 ± 0.034 x $10^{-10}$ a^{-1}, respectively, makes them ca. 7 Ma older than the U-Pb ages calculated ages with the 40K decay constant of Steiger & Jäger [5], $\lambda = 5.543 x 10^{-10}$ a^{-1}, and relative to an MMhb-1 age of 523.1 Ma (i.e. an FCT age of 28.02 Ma [4]), are ca. 1145 Ma. In this case, one has to postulate a differentiation history with a gap of 15 Ma between the augite syenite and the other agpaitic rocks, which is unreasonable. This indicates that the $\lambda$ used so far has to be re-examined (see also [1]).

The best agreement between K-Ar and U-Pb ages is obtained by reducing the FCT age to 28.15 Ma and increasing $\lambda$ to 5.490 x $10^{-10}$ a^{-1}, in marginal agreement with those proposed by [3]. If one considers the FCT age as fixed at 28.24 ± 0.01 Ma [2], then the resulting $\lambda$ is 5.503 x $10^{-10}$ a^{-1}.

References

Calibration of the early Triassic biotic recovery: New U/Pb zircon ages from South China

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Calibration of the Early Triassic biotic recovery is presently only constrained by two zircon ages obtained for the Permian-Triassic boundary (252.6 ± 0.2 Ma, Mundil et al., 2004) and the Anisian-Ladinian boundary ($\approx$ 241 Ma, Mundil et al. 1996, Palfy et al. 2003). The respective durations of the four Early Triassic stages (Griesbachian, Dienerian, Smithian, Späthian) and of the Anisian remain to be established. Preliminary new zircon ages obtained from ash beds intercalated with ammonoid faunas in the Luolo Fm (Early Triassic) and the overlying Baifeng Fm. (Anisian) in northwestern Guangxi (South China) lead to first estimates of the durations of the Späthian and of the Anisian.

Zircons were dated by precise isotope-dilution U-Pb techniques of mechanically abraded single-grains. In the upper carbonatic unit of the Luolo Fm., zircons from the lower ash bed (basal Späthian) yield a crystallization age of 250.7 Ma, whereas those from the upper ash bed (Haugi Zone, latest Späthian) yield an age of 247.1 Ma. Zircons from an ash bed at the very base of the Baifeng Fm. (early Anisian) point to an approximate age of 246.4 Ma. Increased precision will be achieved by applying annealing-leaching procedures.

Hence, the Späthian/Anisian boundary is bracketed between 247.1 Ma and 246.4 Ma, which leads to a duration of the Early Triassic comprised between 5.5 and 6.2 my if adopting a P/T boundary age of 252.6 Ma. As the duration of the Späthian is no less than 3.6 my, this stage accounts for at least half of the duration of the Early Triassic. The duration of the Anisian is comprised between 5.4 my and 6.1 my when taking a 241 Ma Anisian/Ladinian boundary. Our new ages constrain the very high recovery rate of ammonoids, which had a first diversity peak during the Späthien.

References
New high precision zircon ages from the Carboniferous of Scotland and their implications for the systematic bias between U-Pb and $^{40}$Ar/$^{39}$Ar dating techniques

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Several samples have been precisely dated by using either U-Pb or $^{40}$Ar/$^{39}$Ar methods in the Midland Valley of Scotland. While high quality sanidine and zircon have not yet been dated from the same sample, we have dated samples in close proximity where the stratigraphic relationships are well established. The U-Pb results on concordant abraded zircons range in age from 335 to 344 Ma with 2$\sigma$ uncertainties of ±0.7 to ±0.9 Ma. $^{40}$Ar/$^{39}$Ar ages from related samples have uncertainties of approximately ±1.5 Ma but are systematically younger. The minimum bias between the dating techniques can be quantified because the U-Pb ages from stratigraphically higher samples are between 0.50±0.33% and 1.34±0.48% older at the 95% confidence level than $^{40}$Ar/$^{39}$Ar ages from samples lower down in the same succession. The U-Pb and $^{40}$Ar/$^{39}$Ar ages are relative to ages of 418.2 Ma for Temora zircon and 98.79 Ma for GA1550 biotite using well characterised mineral standards and U-Th-Pb metal reference solutions. Magma chamber residence time between dated crystal separates is unlikely to explain a bias of this size, given the Carboniferous absolute age. The amount of systematic bias is smaller than that documented from some other studies yet important when using the dates for numerical timescales or regional correlations. Together the data suggest that the minimum bias between the two methods is between 0.5%-1.0%. The results support the need for further work on fundamental argon concentration measurements that underpin K-Ar and $^{40}$Ar/$^{39}$Ar age determinations and/or the $^{40}$K decay constant, and to a lesser extent refinements in the U decay constants and U-Pb intercalibration experiments.

Paleocene timescale miscalibration: Fact or fiction?

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In the absence of an accepted global stratigraphic section, the Paleocene/Eocene (P/E) boundary is currently a c. 1 m.y. interval within magnetic polarity chron C24r which includes the NP9/NP10 nanofossil boundary, the planktonic foraminifera P5/P6a boundary, a seawater carbon isotope excursion, and the -17 through +19 ash layers in Denmark. Early, unpublished Ar/Ar ages suggested that the -17 ash was c. 55 Ma. The late Paleocene thermal maximum [LPTM] is older than the -17 ash, but younger than the base of C24r.

Based on a correlation of the palynoflora found within the base of the Mull Plateau Group lavas with the LPTM, Jolley et al [2002, 2003] suggested that there is a previously undetected problem with the Paleogene time scale, concluded that the LPTM is older than the Mull lavas, placed the LPTM within the early phase of widespread North Atlantic igneous province volcanism, and even suggested of that the onset this volcanism at 60 Ma was the cause of ocean-floor methane hydrate release thought to be responsible for the LPTM.

Below we present new Ar/Ar ages on the +19 and -17 ashes which, combined with our previous results constraining the duration of British Tertiary volcanism, conclusively show that the Danish ashes and P/E boundary are indeed 55-56 Ma, there is no general problem with P/E time as previously calibrated, and the LPTM is no older than 56-57 Ma. As the main extrusive phase of British Tertiary volcanism was complete by 59 Ma, the thermophilic palynoflora found within the base of the Mull lava pile simply cannot be correlated with late Paleocene thermal maximum time.

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<th>Paleocene/Eocene Ashes:</th>
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<tr>
<td>+19, Denmark</td>
<td>55.26</td>
<td>±0.24 Ma</td>
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<tr>
<td>-17, Denmark</td>
<td>55.44</td>
<td>±0.08 Ma</td>
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<th>Late Stage British Tertiary Volcanism:</th>
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<tr>
<td>Mull, Late Stage dikes</td>
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<tr>
<td>Mull, Loch Ba Ring dike</td>
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<tr>
<td>Skye, Loch Ainort granite</td>
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<tr>
<td>Eigg, Sgurr of Eigg rhyolite</td>
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<th>Early Stage British Tertiary Volcanism:</th>
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<tr>
<td>Mull, basal lava</td>
</tr>
<tr>
<td>Muck, basal tuff, zircon U-Pb</td>
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<tr>
<td>Muck, basal tuff, sanidine</td>
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Cretaceous/Tertiary Boundary
Beloc, Haiti, tektite | 65.78 | ±0.06 Ma |

Ages relative to FCs @ 28.02 Ma $^1$ or TCs @ 28.34 Ma $^2$
Determination of the $^{87}$Rb decay constant by $^{87}$Sr accumulation

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We are currently re-determining the decay constant of $^{87}$Rb ($\lambda_{87}$) with improved accuracy by measuring $^{87}$Sr accumulated in RbClO$_4$ prepared by Davis in 1976 from a high purity salt with a known initial Sr isotopic composition. Results from 14 aliquots give a preliminary value of $1.421 \pm 0.001$ (MSWD=0.88), and are shown in Figure 1. $^{87}$Sr* accounts for between 82-97% of all $^{87}$Sr.

Figure 1 shows results of the Sr accumulation experiment and includes a reference line at 1.402. First eight measurements were taken on VG354, last six on Triton. (Error bars are 2$\sigma$).

This value agrees with that of Davis et al. (1977): 1.419 \pm 0.012. However, it is higher than the age-comparison values suggested by Minster et al. (1982), Shih et al. (1985), and Amelin and Zaitsev (2002) of 1.402, Kossert's (2003) counting experiment value of 1.395 \pm 0.009 and the value recommended by Begemann et al. (2001). Six additional aliquots await isotopic analysis and we are undertaking duplicate spike calibrations on pure samples of SrCO$_3$ (SRM-987) and SrCl$_2$.

References
Davis et al. (1977) $GCA$, 41: 1745-1749.

New ID-TIMS U-Pb zircon ages for the Carboniferous-Permian boundary sections of the southern Urals – Russia, Kazaskhstan

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Abundant interstratified volcanic tuffs within a detailed multi-taxa biostratigraphic framework for Late Pennsylvanian-Cisuralian (Early Permian) stratotypic marine sections of the southern Urals provide the opportunity to calibrate the absolute ages and durations of the global stages and biozonal subdivisions of this geological transition, which holds one of the Phanerozoic’s major climate regime changes.

New ID-TIMS U-Pb zircon ages (weighted mean $^{206}$Pb/$^{238}$U dates of equivalent annealed and chemically abraded single zircons with no rejected outliers) have been obtained for ash beds above and below the Pennsylvanian-Permian boundary at the Usolka and Dal’ny Tulkas sections, spanning the Upper Moscovian to Upper Sakmarian stages. Two ash beds separated by 2.3 meters in the Upper Moscovian at Dal’ny Tulkas yield ages of 307.3 ± 0.2 Ma and 305.4 ± 0.2 Ma, in stratigraphic order. At Usolka, an ash bed in the Lower Sakmarian yields an age of 290.0 ± 0.4 Ma. In concert with refined bracketing ages for the Pennsylvanian-Permian boundary at Usolka, these data anticipate the fine scale to which an accurately correlated, composite reference section for the Pennsylvanian-Cisuralian can be constructed and calibrated.

With this high-resolution framework we can anticipate unprecedented temporal constraints on: the rates of sedimentation and sea-level change in various locations around the world; accurate reconstructions of the full range of variability of the Late Paleozoic climate systems; the relations between marine and terrestrial geologic records; spatial and temporal patterns of extinction events and the rates of ecological recovery and biodiversification following such events; and the timing, duration, and synchronicity of tectonic activity associated with the final assembly and early modification of Pangaea.
Characterising and U-series dating (TIMS) of travertine from Hungary

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Introduction
Terrestrial carbonate formations, such as travertine, speleotherm and lake sediments, are important archives of terrestrial climate forcing. At the sections at Süttö in Hungary, a complex sequence of travertine is covered by loess and palaeosols indicating at least an OIS 7 age for the travertine. The Süttö travertine is a high resolution continental archive of interglacial palaeoenvironmental change.

Analytics
As the growth of travertine is a very complex mechanism and pore cements may cause serious problems for precise dating (e.g. Mallick and Frank 2002), we utilized microscopic, mineralogical and geochemical methods to determine the abundance of primary calcite phases. The state of alteration of primary spar and micrite was characterized by cathodoluminescence and microprobe analyses. Absolute ages were determined by TIMS $^{230}$Th/U.

Results and Discussion
In contrast to travertines from Weimar-Ehringsdorf, Germany, travertines from Süttö showed homogenous phases of primary calcite, minor micropores and rare pore cements. For U-series dating the samples were prepared from areas with mainly micrite and spar, avoiding pores. We determined $^{230}$Th/U isochron ages with an isochron approach using the leachate/leachate method (Kaufman 1992). Travertines from Süttö show Mid Pleistocene ages which are supported by results from luminescence dating of the overlying loess sequence.

Conclusions
The absolute age determination of travertines at Süttö, Hungary yields a more reliable chronological frame to reconstruct both climate and environmental change for the time period of the Mid Pleistocene more precisely.

References

On the $^{40}$Ar/$^{39}$Ar age of biotite in Green River Formation ash:
The advantages of incrementally heating single crystals with a laser

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Some distal ash fall tuffs in the Eocene Green River Formation either lack sanidine, or the small proportion of sanidine crystals yield heterogeneous ages unsuitable for precise $^{40}$Ar/$^{39}$Ar-based age stratigraphy. Thus, we have on occasion turned to biotite, mindful that it is far more prone to alteration, argon loss, and $^{39}$ArK recoil. For example, we determined the age of biotite in the 6th tuff using a CO$_2$ laser to fuse 26 small aliquots, each comprising three ~500 µm diameter crystals, to be 49.70 ± 0.17 Ma [1] based on 22 of the measurements [2]. A second laser fusion study of biotite from the same tuff measured smaller (>354 µm) and fewer (1-2) crystals per aliquot, with the result that only 11 of 31 apparent ages were considered concordant and gave a mean age of 49.12 ± 0.39 Ma [1], ~580 kyr younger than our fusion age [3].

To resolve this age discrepancy, and investigate the problems presented by biotite, we incrementally heated large (~1000 µm), hand-screened, euhedral crystals, or groups of three such crystals together with a laser. Twenty-three of twenty-six such experiments yield reproducible, concordant plateau ages that give a grand weighted mean age of 49.62 ± 0.17 Ma [1] (MSWD = 1.02). The three excluded experiments exhibit discordant spectra with young initial steps, plateau ages ~500 kyr older than the mean age, and integrated ages both older and younger than the mean. This pattern suggests that microscopic alteration along crystal edges and internal cleavage planes promoted subtle $^{40}$Ar*-loss and $^{39}$ArK recoil from these domains in ~10% of studied grains. Such open-system behavior may explain much of the variance attributed to xenocrystic contamination in previous fusion-based studies, particularly given the smaller crystals used [2,3]. Our new age fits well into the sanidine-based $^{40}$Ar/$^{39}$Ar accumulation rate profile for the Green River Formation [2]. Should biotite be the only available chronometer for a distal ash, incremental heating of large crystals is recommended.

References
[1] ages relative to 28.34 Ma TCs standard; ±2σ intercalibration uncertainty.
Ar-Ar and SHRIMP U-Pb age evidence of the Daohugou fossil-bearing beds in Ningcheng, Inner Mongolia, NE China

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A new set of fossil-bearing beds, Daohugou fossil-bearing beds, was found in Daohugou area, Ningcheng, Inner Mongolia, NE China. This Biota is the key of researching the Yanliao Biota’s extinction and the origin of the Jehol Biota. Before, there exist two representative opinions on the age of the Daohugou fossil-bearing beds. Some specialists suggest that it should belong to the Middle Jurassic and others believe that it should belong to the early Cretaceous. Their difference on the age is over 30 million years but both of them did not provide accurate isotope geochronological data. We dated the trachyte and trachytic welded tuff structurally overlying the Daohugou fossil-bearing beds using Ar-Ar and SHRIMP U-Pb method.

The plateau age of the sanidine from the trachytic welded tuff is 164.2±2.5Ma and the mean ²⁰⁶Pb/²³⁸U age of the zircon from the same sample is 164.6±2.4Ma. The mean ²⁰⁶Pb/²³⁸U age of the zircon from the trachyte is 165.2±1.8Ma. Based on these data, we can draw the following conclusions: (1) the age of the intermediate-acid volcanic rocks overlying the Daohugou fossil-bearing beds is about 164-165Ma; and (2) the age of this fossil-bearing beds is over or equal to 165Ma. Therefore we suggest that the age of Daohugou Biota is tens of millions years earlier than that of the Jehol Biota and it should belong to the Yanliao Biota or belong to the Biota between the Yanliao and Jehol Biota.

Acknowledgement

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The effect of organic ligands on the mobility of the PGE in soils and natural waters: Implications for exploration and the environment

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The PGE have become a potential environmental concern owing to attrition from catalytic converters and other industrial emissions. There is evidence that the PGE are both bioavailable and toxic. The degree to which the PGE are bioavailable and/or toxic depends to a large extent on their mobility in aqueous media. The degree of mobility of these elements also has implications for the use of geochemistry in the exploration for new PGE resources.

In most natural waters, the predominant inorganic PGE species are hydroxide complexes such as Pd(OH)$_2$$^2$-, yielding relatively low solubilities. Naturally occurring organic ligands such as simple carboxylate anions (e.g., acetate, oxalate, etc.) and humic and fulvic acids have been implicated in PGE mobility in the surface environment in many published field-based studies. We also suggest that siderophores (natural organic ligands secreted by microbes and plants to solubilize nutrient iron) may increase the mobility of PGE, based on published Linear Free Energy Relationships which indicate that siderophores may bind Pd as strongly as Fe. Solubility and spectroscopic investigations show that monocarboxylate anions such as acetate are not likely to increase significantly the mobility of PGE. However, dicarboxylate anions capable of bidentate chelation, such as oxalate, phthalate and salicylate, form much stronger complexes and can increase PGE solubility significantly. Amino acids have been shown to be important Pt species in seawater. Even more important in PGE mass transfer are multidentate ligands such as humic and fulvic acids. Experimental studies show that fulvic acid can increase the solubility of palladium hydroxide by orders of magnitude over a wide range of pH.

We have conducted solubility and spectroscopic studies on the interaction of two siderophores, desferrioxamine B (DFO-B) and ferrichrome, with Pd, Pt, Rh and Ir. These studies confirm strong complexation of PGE by siderophores, and show that there are significant differences in binding between different siderophores. Much more data are required to quantify fully the extent to which siderophores may increase PGE mobility in natural environments. However, they do indicate an important role for siderophores.

Effect of the trihydroxamate siderophores desferrioxamine-B and ferrichrome on the mobility of Pd, Pt, Rh and Ir

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Trihydroxamate siderophores are strong chelators for a variety of metals in near-neutral pH waters. We established that the solubility of amorphous Pd(OH)$_2$ is greatly enhanced by the presence of desferrioxamine-B (DFO-B) at pH 8. Experiments involving the dissolution of metallic Pd, Pt, Rh and Ir in solutions containing DFO-B (106 to 2000 micromolal) or ferrichrome (68, 200 micromolal) at pH 8 and a ionic strength of 0.14 indicate that the dissolution rates of Pd, Pt and Rh increased with increasing DFO-B concentrations up to 300 micromolal, remained independent of DFO-B concentrations between 300 and 1000 micromolal for the first 4500 hours, and then were increased again for a DFO-B concentration of 2000 micromolal. Increased dissolution of Ir only took place in the presence of 2000 micromolal DFO-B. Equilibrium was not achieved even after 6245 hours of reaction. After this time, the Pd concentration in the 2000 micromolal DFO-B solution was 0.62 mg/kg H$_2$O (Pt 0.29 mg/kg H$_2$O, Rh 0.02 mg/kg H$_2$O). This value is 1.5 order of magnitude higher than that for the solubility of amorphous Pd(OH)$_2$ in the absence of the siderophore. By comparison to Pd(OH)$_2$, however, Pd metal dissolves between 2.5 (100 micromolal DFO-B) and 3.5 (1000 micromolal DFO-B) times more slowly. Before 4500 hours, no difference was observed in the rate of dissolution of the individual PGE between the 68 and 200 micromolal ferrichrome solutions. After this time, Pd dissolved slightly faster in the 68 micromolal than in the 200 micromolal ferrichrome solution. Pt and Rh showed similar dissolution rates between DFO-B and ferrichrome solutions, whereas the Pd concentration in the 200 micromolal ferrichrome solution attained a value 3.5 times more elevated than that in the 200 micromolal DFO-B solution after 6245 hours. Ferrichrome is much more effective in dissolving Ir than DFO-B. Whereas the Ir concentration after 3196 hours in the 200 micromolal DFO-B solution was only marginally above that in the solution without siderophore, its concentration was increased by a factor of six in the 200 micromolal ferrichrome solution. These results clearly indicate that siderophores may play an important role in the solution transport of anthropogenic or naturally occurring PGE in the environment.
Economic Pt and Pd in amagmatic settings?

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Experimental data on the solubility of Pt and Pd under various hydrothermal conditions suggest that transport and deposition of high levels of these elements could occur in several geological environments without the need for mafic magmatic fluids or heat.

In intracratonic rift environments, oxidized brines generated by surface evaporation and/or halite dissolution circulate to depth through a preponderance of oxidized lithologies and precipitate Pt and Pd in association with U and Au (unconformity-type U deposits) or Cu (sediment-hosted Cu deposits). Pt and Pd are likely to transported as chloride complexes in such oxidised brines. The best known product of this process is the Coronation Hill deposit in Australia.

In deformed passive margin sequences rich in carbonaceous and pyritic metasedimentary rocks, hydrothermal fluids are most likely to be reduced and have elevated sulfur content. Under these conditions Pt and Pd would be transported as bisulfide complexes. Potentially economic levels of Pt and Pd have been reported in numerous orogenic gold deposits of the former Soviet Union (notably the Sukhoi Log deposit) and in sediment-hosted Ni and Mo deposits of southern China and north-western Canada.

Oxidized low-salinity waters in surface environments buffered by atmospheric oxygen could also lead to mobility of Pt and Pd as hydroxyl complexes. Anomalous but sub-economic levels of Pt and Pd have been reported in low-temperature hydrothermally altered rocks of the Semail ophiolite and in laterite developed on ophiolitic rocks.

These examples suggest that high grades of Pt and Pd occur in a wide range of deposit types, although there is clearly a problem in some cases with quality of analysis. A crucial question is whether there is the potential for both high grades and large tonnages of Pt and/or Pd-bearing ore in these settings. This question can be answered in part by routine analysis for Pt and Pd by exploration geologists and by further research into transport and depositional processes.

The hydrothermal Ni-Cu-PGE sulfide ore of the Fortaleza de Minas deposit, Brazil

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The hydrothermal Ni-Cu-PGE massive ore of the Fortaleza de Minas deposit

The Fortaleza de Minas Ni-Cu-PGE sulfide deposit is hosted by Archean komatiite rocks (Brenner et al., 1990) in the southwestern margin of São Francisco craton. The deposit contains 6 million tons at the average grade of 2.2%Ni, 0.4%Cu, 0.05%Co and 1.2ppm PGE+Au (Brenner et al., 1990) and comprises metamorphosed-magmatic and hydrothermal ore bodies. The former is cut by N-S and NE-trending late faults that host the hydrothermal ore. The hydrothermal ore is characterised by thin, discontinuous and irregular lenses and veins of massive sulfides hosted by serpentinite and talc schist (Almeida, 2003). It is composed mainly of pyrrhotite, pentlandite, chalcopyrite, magnetite and carbonates, with minor cobaltite-gersdorffite, sphalerite, ilmenite, serpentine and chlorite, and rare maucherite, tellurides (Pd-bearing melonite, tsumoite, tellurobismuthite and hessite) and PGM (omeiite, irarsite, testibiopalladite, Ni-bearing merenskyite and RuTeAs unknow phase). Late pyrite, chalcopyrite and carbonate fill fractures and violarite replaces sulfides. The PGM occur either included or associated with sulfides, silicates and oxides or filling fractures in pyrrhotite and chalcopyrite, indicating they started to precipitate with these minerals and continuous to precipitate after the sulfides were formed.

Geochemical Results And Interpretations

The hydrothermal ore grades are 290–2180ppb Pd, 69–1180ppb Rh, 194–602ppb Ru, 156–447ppb Ir, 132–335ppb Os and 31–61ppb Au, being consistently higher than the metamorphosed, magmatic ore. In addition, the hydrothermal ore is strongly depleted in Cr when compared with the metamorphosed magmatic ore. The geological mineralogical and geochemical data suggest that the PGE were remobilized by carbonic-rich fluids and precipitated as tellurides and arsenides in the late faults.

References
On the hydrothermal origin of platinum-group element deposits in layered intrusions

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There are a number of lines of evidence suggesting that volatile-rich magmatic fluids have played a dominant role in the petrogenesis of platinum-group element (PGE) deposits in layered intrusions. These include footwall sections that are unusually enriched in Cl in the higher grade deposits, potholes, layered intrusions. These include footwall sections that are unusually enriched in Cl in the higher grade deposits, potholes and other fluid-escape structures, pegmatoidal textures, relatively abundant hydrous minerals, and the ease by which sulphur can be moved in hydrothermal systems.

Models of a solidifying and degassing crystal pile illustrate how magmatic fluids can give rise to zones of PGE-enrichment in layered intrusions. Cooling through the base of a crystal + liquid column leads to solidification age. This indicates that most measured ratios are equivalent to initial ones. Of the 28 samples studied, only two contain phases contaminated by young Pb. Plagioclase possesses a single composition, interpreted to represent that of the original magma was introduced into the rocks under conditions under which sulfide but not the plagioclase precipitated in the vapor-undersaturated interstitial liquids, producing a zone of relatively high modal sulphide that also migrates upward with time. This sulphide-enriched front can mimic a conventional sulphide-in horizon and appear as the stratigraphic level at which the magma became S-saturated, but it is secondary and hydromagmatic in origin.

Owing to their strong preference for sulphide, the PGE are not significantly mobile until all sulphide is resorbed. In addition, fluid migration can result in significant chromatographic separations of ore elements. These chromatographic "offsets" are characterized by a lower, typically S-poor, Pt- and Pd-enriched zone overlain by a zone enriched in the base metals, S and Au. The process can also produce high PGE/S ratios that mimic values conventionally interpreted as the result of high "R" values.

The fluid front and ore element transport may remain fully within the pile or it may reach the top of the pile where it can affect crystallization of the main magma body. For the former, metals may be trapped at compaction-induced porosity/composition discontinuities in the crystal pile (e.g., Great Dyke-type PGE deposits). The latter may result in significant degrees of incongruent melting of the solid assemblage due to volatile fluxing and form unconformity-type deposits (e.g., J-M Reef of the Stillwater Complex).

Tracing geochemical evolution of the Bushveld Complex with lead isotopes analyzed by LA-MC-ICP-MS

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A new investigation of Pb isotopic compositions of plagioclase and sulfide in the Bushveld Complex has been conducted to evaluate results of an earlier study, extend observations to the UG2 chromitite as well as Merensky reef, and characterize better the Pd components in the rocks. The PGE-rich UG2, like the Merensky reef, displays evidence of magmatic metasomatism and recrystallization. Analyses were obtained with the NuPlasma multicollector ICP-MS coupled with a NewWave DUV193 ArF Excimer laser. Helium was used as the carrier gas, spot sizes ranged from 80 to 150 μm and pulse rates 5 to 20 hz, and isotopic fractionation was controlled by external normalization.

Most plagioclase and sulfide analyses fall on the 206Pb/204Pb vs 207Pb/204Pb geochron of 2.06 Ga, which is the solidification age. This indicates that most measured ratios are equivalent to initial ones. Of the 28 samples studied, only two contain phases contaminated by young Pb. Plagioclase possesses a single composition, interpreted to represent that of the parent magma, of 208Pb/206Pb ≈ 15.00, 207Pb/206Pb ≈ 15.25, 206Pb/208Pb ≈ 15.00. The 238U/204Pb and 232Th/204Pb ratios of the source were 9.2 and 38.3, respectively. Sulfide compositions are commonly different than that of plagioclase in the same thin section, confirming the original results of Mathez and Waight (2003) and their interpretation that material with a Pb isotopic composition different from that of the original magma was introduced into the rocks under conditions under which sulphide but not the plagioclase compositions could be modified. The sulfides contain Pb from two different, old sources. Some possess 208Pb/206Pb and 207Pb/206Pb ratios distinctly lower than those of coexisting plagioclase. The Bushveld rocks are cut by a set of late magmatic veins, the plagioclase of which also displays anomalously low 206Pb/204Pb and 208Pb/206Pb ratios. Other sulfides contain Pb characterized by high 208Pb/206Pb and 208Pb/206Pb ratios, suggesting introduction of material from a Th-rich source substantially older than the Bushveld. The variability of Pb isotopes reflects a long and complex magmatic to subsolidus cooling history involving several episodes of melt/fluid infiltration.

Reference
The roles of fluid in the genesis and modification of reef-type PGE deposits in large layered intrusions

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Several hypotheses have been proposed for the origin of reef-type PGE deposits in large layered intrusions. These include: (1) alloy or immiscible sulfide liquid segregation from magma and (2) concentration by magmatic fluid. Our results of textural, mineralogic and isotopic studies indicate that fluids played important roles in the genesis and modification of the reef-type PGE deposits.

The Merensky Reef of the Bushveld Complex is a good example where magmatic fluid played a major role in the development of the reef. Abundant composite mineral inclusions are found in many chromite crystals in the basal chromite seam of the reef. Phlogopite and orthopyroxene are most abundant in the inclusions. The average compositions of the inclusions are characterized by higher MgO, Na$_2$O and H$_2$O, and lower CaO and FeO than the parental magma of the Merensky Reef. The chemical compositions of the inclusions are consistent with melts formed by hydration melting of orthopyroxene cumulate on the floor of the chamber in response to addition of fluid. Sulfide saturation in the Merensky Reef may have been induced by addition of S from the fluid.

In the J-M reef of the Stillwater Complex, replacement of braggite by the mixture of Pt alloy and base metal sulfides is found in unaltered ore samples from the Stillwater Mine. This is direct evidence for desulfurization of Pt-Pd sulfides by S-undersaturated magmatic fluid.

In the PGE-rich Main Sulfide Zone of the Great Dyke the base metal sulfides are variably replaced by actinolite, epidote and carbonates. PGM mostly occur within base metal sulfides, and to a much less extent in their replacement aureoles.

Our observations suggest that primary concentration of PGE in the reefs resulted from fluid-induced sulfide saturation and segregation whereas decoupling of PGE at sample scale was due to subsequent hydrothermal modification.

Re/Os isotopic and fluid inclusion studies of fluid-rock interaction in the contact aureole of the Duluth Complex, Minnesota

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Re/Os isotopic data from igneous rocks and massive sulfides from the Duluth Complex of Minnesota, along with sulfide-bearing Proterozoic (~1.85 Ga) country rocks of the Virginia Formation, indicate a complex history of assimilation and fluid-rock interaction. Sulfide-free troctolites plot along a chondritic 1.1 Ga reference isochron, and show little or no geochemical evidence for contamination by country rocks. Troctolites with disseminated sulfides and massive sulfides are variably anomalous with $\gamma_{Os}$ (1.1 Ga) values from 3 to 1200.

Sulfide separates from metasedimentary country rocks located outside of the contact aureole have Os isotopic values that are distinct from whole rock and kerogen values. The shale/siltstone is only slightly recrystallized, yet Re/Os isotopic values of sedimentary sulfide minerals indicate mixing at the time of emplacement of the Duluth Complex, and plot along a 1.1 Ga chondritic reference isochron. Quartz veins and stringers occur along pyrite beds in the sedimentary country rocks, and contain up to 15% of pyrrhotite, and lesser amounts of chalcopyrite, cubanite, bornite, pentlandite, and sphalerite. This assemblage is very similar to that found in the magmatic sulfide mineralization of the Duluth Complex.

Fluid inclusions found in the quartz veins homogenize at ~300° to 380°C, and with a minimum P correction suggest that a fluid of ~500°C reached the outer margins of the contact aureole along microfractures. Although the initial water content of the Duluth Complex magma is not considered to have been anomalous, water saturation would have been achieved in the melt interstitial to primocrystic olivine and plagioclase. The Re/Os isotopic characteristics of sedimentary sulfides in the country rocks are consistent with exchange and mixing between minerals and a Re-rich magmatic fluid characterized by a chondritic $^{187}$Os/$^{188}$Os ratio. This fluid appears to have been derived from uncontaminated mafic magma, rather than the contaminated magma that produced sulfide-bearing troctolites.
Re/Os isotopic studies of oxide minerals in the Birch Lake PGE prospect, Duluth Complex, MN

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The Birch Lake platinum group element (PGE) prospect is located along the western edge of the South Kawishiwi Intrusion (SKI) of the 1.1 Ga Duluth Complex in northeastern Minnesota. Country rocks include the Proterozoic Biwabik Iron Formation (BIF) and Archean-aged, greenstone belt-related plutonic and volcanic rocks. In the Birch Lake area the SKI consists of a layered troctolitic series that contains layers of semi-massive to massive oxides, as well as distinct inclusions of the BIF. Strong serpentinization of the oxide-melatroctolite rocks in the area is also distinctive. Zones of enriched PGE concentrations that are associated with Cr-rich oxides were detected during early mineralogical evaluations. Based on these associations, a hypothesis emerged which related PGE enrichment to areas of BIF assimilation. Further mineralogical and isotopic studies of the oxide minerals from the SKI and the BIF have aided in evaluating this potential relationship.

Three samples of unmetamorphosed BIF have Re/Os isotopic values that fall along a chondritic 2.23 Ga reference isochron. The values suggest that seawater Os isotopic composition was controlled by either leaching of young oceanic crust, potentially in a back arc environment, or by input of hydrothermal fluids with a near chondritic isotopic ratio. One sample of BIF from the contact aureole falls near the 1.1 Ga reference isochron, suggesting exchange between magnetite and a Re-rich magmatic fluid at the time of emplacement of the Duluth Complex. Most samples of both BIF xenoliths and layered massive to semi-massive oxides in the troctolites plot above the isochron formed by the unmetamorphosed BIF samples at $^{187}$Re/$^{188}$Os ratios less than 10. These values are suggestive of Re loss after a magma contamination event at 1.1 Ga. Oxygen and hydrogen isotopic values of serpentine suggest that the fluid involved in the serpentinization process was primarily of meteoric origin. Interaction with this fluid is thought to be responsible for the anomalously low Re/Os ratios of oxides in the metamorphosed BIF and melatroctolitic rocks in the Birch Lake area.

Reference

PGE mobility and PGM crystallization under hydrothermal conditions

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PGE-bearing associations from non-conventional geological occurrences (Kupferschiefer type shales; black shales; porphyry copper ores; hydrothermal ores; metamorphosed sediment and sediment-volcanic deposits, Cu-rich metamorphosed ores; metalliferrous coals; U-ores and oth.) are discussed. The list of PGM from these associations includes about 20 species with Pd, Pt, Te, S, Se, As, Sb, Au as characteristic elements of composition: Pd-Pt- sulfides, selenides, tellurides, (Pt,Fe), (Pd,Pt,Au), Pd- (Sb,As,Te,Sn) minerals etc. (Pashava J., Tarkian M., Jedwab J., Moralev G., Seredin V. and oth.).

These PGM are associated often with minerals characterized by layered structure, i.e. Fe-Mn oxides, hydroxides (goetite), “hybride” minerals (valleriite), clay minerals (halloisite, smectite), silicates (chlorite) etc. Tiny grains of PGM and “layered” mineral are closely intergrown forming specific aggregates. This is the reason of “strange” PGM compositions reported by some researchers.

According to the detail study PGM associated with clay minerals are presented by submicro- and nanoparticles often located on the surface or edges of layers. PGE are transported in nature by PGM precipitation could be reasoned by the non-equilibrated charge of structure layer surface, and by the composition of solution determining the decomposition of PGM-bearing complexes. The information on the composition of mineral-forming solution/fluids could be obtained due to the analysis of mineral composition and mineral associations as shown on some examples.

The morphology of PGM particles obtained during the hydrothermal experiments is analysed. Generally they are presented by dendrites or rounded grains. Using this fact and taking into account the composition of various complexes the mechanism of PGM crystal growth is proposed and discussed using data on PGM from other geological occurrences.
A magmatic end-member fluid at Sudbury, Canada?

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Veins and patches of granophyre are common in the brecciated/partially-melted footwall, and igneous sublayer of the Sudbury Igneous Complex. Cross-cutting relationships demonstrate that the granophyre veins in the footwall post-date the impact event and formation of massive sulfide ore along the footwall contact of the Sudbury Igneous Complex (SIC), but crystallized prior to the emplacement of Cu-PGE-enriched sulfide veins in the footwall. The granophyre veins are comprised of a sympletic intergrowth of quartz + orthoclase ± hornblende and preserve a primary, high temperature fluid inclusion assemblage derived from entrainment of an exsolved fluid phase. Trace element composition and structural considerations do not support the granophyre veins as forming in-situ (e.g., by host-rock melting). Rather, the granophyre may represent a K-enriched residua which was mobilized during the late stages of crystallization of the SIC. Brine inclusions within the granophyre phase homogenize at 543±55°C (n=82, 1σ), corresponding to a salinity of 66±8 wt% NaCl eq.

Microanalytical data (by LA-ICP-MS) show that the highest temperature, highest salinity brine inclusions contain a Na-Fe-K-Ca-Cl-rich fluid (up to 28 wt% K). All other brine compositions identified in the footwall environment fall on a mixing line between the high-temperature, Na-Fe-K-rich end-member and regional saline groundwaters. The range in brine inclusion compositions observed at Sudbury requires up to 90% (by mass) groundwater in the mixture. Base and precious metals (Cu – up to 1 wt%, Pt, Bi, Ag all in the 1-10 ppm range) were only detected in brine inclusions from granophyres occurring in close proximity to, or overprinted (replaced) by massive sulfide veins; this, along with cross-cutting relationships suggest that brines were in contact with sulfide liquids prior to the final crystallization of the sulfides in the footwall ore zones. Late secondary inclusions contain a saline fluid that is comparable in composition to the primary brine but contains much lower overall concentrations of major and trace elements. The late fluid may represent a cooled, diluted form of the primary, high-temperature brine. Ore metals were lost from the brine prior to entrainment of the secondary inclusions as the metal contents of the secondary inclusions are unremarkable.

High resolution LA-ICP-MS analyses of PGMs and sulphides, Marathon Pd-Cu deposit, Ontario

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The Marathon platinum group element (PGE)-Cu deposit is hosted by the 1108 Ma Coldwell intrusive complex. Three styles of mineralization occur in the deposit: (1) massive to net-textured Fe-rich sulphides in a massive, fine-grained gabbro (the Basal Zone); (2) disseminated, Cu-rich sulphides within variably-textured (medium-grained to pegmatitic) gabbroic rocks (the Lower Zone); and (3) magnetitite layers in layered olivine gabbro (the Upper Zone). PGE mineralization is Pd-rich and is principally associated with Cu-rich intervals in the Lower Zone, which generally occur several tens of metres stratigraphically above the sulphide-bearing, Basal Zone rocks. The magnetitites of the Upper Zone also host Cu-PGE mineralization.

Magmatic and hydrothermal sulphide textures exist within the different mineralized zones. LA-ICP-MS analyses of sulphides and platinum group minerals (PGMs) demonstrate stratigraphic chemical and mineralogical zonation. Basal Zone sulphides are As-rich and PGMs are Pb-poor, varying from arsenides to bismuth-tellurides to antimonides. The Lower Zone has As-poor and Te-rich sulphides and PGMs of extreme chemical variability. Upper Zone sulphides are Pb-rich as are the PGMs which are As-poor bismuth-tellurides and more Au-rich than PGMs in the other zones.

Strong zonation and a wide variety of PGMs is not unusual for PGE-rich mineral districts but this usually relates to lateral changes in footwall compositions while at Marathon it occurs within a single stratigraphic section of a few hundred meters.
A mixed message from U-series crystal ages

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To quantify the tempo of magmatic processes, the disparities between the different constraints on crystallization timescales must first be reconciled. When compared to crystal ages based on kinetic considerations (e.g., crystal size distributions, diffusional relaxation), U-series ages are generally an order of magnitude or more greater. Moreover, although limited in number, when both U-Th and Th-Ra ages are obtained for the same mineral aliquots (n=18), the ages are discordant in more than half the cases. In addition, those pairs of ages that are concordant are arguably too old in many cases to have simply crystallized from their host magmas, considering the magnitudes of Ra excesses in the hosts. Diffusion is likely a subordinate factor in producing these effects.

In situ dating of accessory phases in rhyolites has revealed evidence for refractory phases from crustal anatexis or contamination ( xenocrysts), crystals recycled from earlier genetically-related magmatic activity, and crystal cores that significantly predate eruption. Discordant and otherwise “old” U-series ages for mineral aliquots could similarly be explained as the product of variable degrees of mixing between such crystal populations. For contamination by xenocrysts to be largely responsible for the discordia observed, the average age of phenocryst growth would be >0.5 k.y in virtually all cases and xenocrysts would constitute a significant and therefore recognizable fraction of the crystal population (likely 10-30%). Alternatively, the U-series ages could reflect multiple episodes of crystal growth. Which are discordant require a significant fraction of the crystal population to be several tens of k.y old whereas those which are concordant may be explained by up to ~15 k.y of growth. The crystal ages cannot therefore be explained simply by remobilization of crystals near the solidification front. Very deep scouring of extensively mushy rinds of magma reservoirs, continuous or repeated exposure of crystals to melt, and/or stochastic intrusion and crystal re-entrainment in sill/dike complexes may be able to reconcile the U-series ages with kinetic constraints on crystallization. For the discordant ages, magma intrusion into earlier (co-genetic and mushy?) intrusive bodies may be required.

Time scales of chemically zoned magma chamber formation: U-series disequilibria in the Fogo trachyte deposits, São Miguel, Azores

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Fogo volcano, located on the island of São Miguel, Azores, has produced two chemically zoned trachyte deposits over the past 5,000 years, providing an excellent opportunity to investigate the time scales over which magma differentiation has taken place. Here we report high precision plasma ionization multicollector mass spectrometry measurements of 226Ra-230Th-238U disequilibria and Ba contents on pumices and glass separates from the Fogo 1563 A.D. (~0.14 km3) and the ~4.6 ka Fogo A (~0.7 km3) chemically zoned trachyte deposits. We suggest that continuous differentiation models may be more realistic than instantaneous models, and that they better explain the observed 226Ra-230Th variations within the deposits. These models suggest magma residence times prior to eruption of ~50 to 80 years for Fogo 1563, and ~2 to 4 ka for the larger volume Fogo A eruption. These time scales represent liquid residence ages rather than the crystallization ages documented in most previous magmatic time scale studies and allow constraints to be placed on the time scales necessary for the development of chemical zonation within the Fogo magma chamber. Our results indicate that calculated time scales are relatively insensitive to the precise nature of the continuous differentiation models. Meaningful magma differentiation time scales can be obtained despite open system behavior, because the 226Ra-230Th disequilibria are overwhelmingly controlled by feldspar fractionation. However, calculated time scales are extremely sensitive to Dba/Dra ratios. We emphasize the crucial importance of better constraints on the relative partitioning of Ra and Ba when employing 226Ra-230Th disequilibria data to constrain the rates and time scales of igneous processes.
The $^{226}\text{Ra}$ chronology and magma residence time of young lavas from Loihi Seamount, Hawaii

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We report measurements of $^{226}\text{Ra}-^{230}\text{Th}$ disequilibria in a suite of young lavas collected from the summit platform and south rift zone of Loihi Seamount using the Alvin, Pisces V, and Shinkai 6500 submersibles. These data are used to decipher the residence time of magma at Loihi and the relative post-eruptive ages of the samples. All analyses were performed on fresh, hand-picked glasses using high-precision plasma ionization mass spectrometry. The samples display a relatively large range in the amount of excess $^{226}\text{Ra}$ (~0-13%). Most of this variation probably reflects the decay of $^{226}\text{Ra}$ after these melts were extracted from the mantle. Model ages calculated from the $^{226}\text{Ra}-^{230}\text{Th}$ disequilibria imply a ~200-12,000 yr range in the time since melt extraction ($T_{\text{MEL}}$). Most of the $T_{\text{MEL}}$ variations are thought to reflect the post-eruptive decay of $^{226}\text{Ra}$, and thus, may be used as proxies for the relative eruption ages of the lavas. The eastern-central portion of Loihi’s summit appears to be one of the least active areas. Tholeiitic lavas from the wall of the East Pit at Loihi’s summit accumulated over a period of ~1200 yr. Residence time analysis of the fluctuations in the Th/Yb ratios of these lavas suggest that they were derived from a magma chamber with a residence time of ~530 yr, which is much longer than estimates for historical Kilauea Volcano using similar techniques (~30-180 yr). Assuming a magma supply rate of ~0.0058 km$^3$/yr for Loihi’s recent eruptive history (based on estimates of the age and volume of this volcano), these lavas may have tapped a chamber containing ~3 km$^3$ of magma. This is larger than might be expected for a pre-shield Hawaiian volcano, but is remarkably similar to the estimated volume of magma within Kilauea’s summit reservoir (~2-3 km$^3$).

Comparison of Th, Pb, Nd and Sr isotopes in oceanic basalts: Implications for mantle heterogeneity and magma genesis

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In principle, comparison of $^{230}\text{Th}/^{232}\text{Th}$, $^{238}\text{U}/^{232}\text{Th}$ and $^{238}\text{Th}/^{234}\text{U}$ with longer-lived radiogenic isotopes can provide first-order insight into the nature of the mantle source, and the styles of melt generation and magma transport. Despite several studies comparing Th isotopes with longer-lived radiogenic isotopes in oceanic basalts, only one of the four end member mantle components defining the mantle tetrahedron, DMM, is well represented. For the other three end member mantle components (HIMU, EM1 and EM2), there are no high precision measurements of Th isotopes for representative samples. Because of this lack of high quality Th isotopic data for the other three of the end member mantle components (HIMU, EM1 and EM2), the form and relative significance of the relationships between U-Th systematics and the other longer isotopic systems like Sm-Nd, Rb-Sr and U-Pb are not yet well defined.

Here we present new U-Th disequilibria data for a suite of young basaltic samples from the Samoan Islands representing the EM2 end member mantle component. These data are then compared with the MORB and OIB database for which U-series disequilibria and longer-lived radiogenic isotopes of Sr, Nd, and Pb have been measured by mass spectrometric methods. This data compilation shows that: 1) $^{230}\text{Th}/^{232}\text{Th}$ and $^{238}\text{U}/^{232}\text{Th}$ are correlated with $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$; 2) these correlations can, to a first-order, be approximated by two-component mixing; and 3) the functional form of these relationships are hyperbolic rather than linear, as has been previously suggested. The relationships of $^{238}\text{Th}/^{232}\text{Th}$ and $^{230}\text{Th}/^{232}\text{Th}$ with Pb isotopic composition are more complex and require multiple source components. Using a maximum likelihood non-linear inversion method we show that the correlations of $^{238}\text{Th}/^{232}\text{Th}$ with $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ are better defined than the correlations of $^{238}\text{U}/^{232}\text{Th}$ with $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$, suggesting that $^{236}\text{Th}/^{232}\text{Th}$ is a better estimate of the U/Th source ratio and that net elemental fractionation of U from Th plays an important role in establishing a basalt ($^{230}\text{Th}/^{238}\text{U}$) disequilibria. In addition we show that the extent and variability in $^{238}\text{Th}/^{238}\text{U}$ decreases as a function of source enrichment.
Producing U-series disequilibria through ultraslow crustal accretion

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238U-230Th-226Ra disequilibria measurements on 12 dredged glasses from between 9-25º E on the SW Indian Ridge show highly variable U-series systematics. The suite as a whole exhibits a large range in 230Th/232Th and 238U/232Th, covering nearly the entire extent of variability seen in the global MORB U-series database. Glasses from the oblique supersegment show the most enriched compositions (230Th/232Th = 0.8 and 238U/232Th = 0.76) of any MORB measured but have minor 230Th excesses (<9%) or small 238U excesses (~3.5%). In contrast, Th excesses in lavas from the orthogonal supersegment vary from 2–29%, but show no systematic trend and do not appear to be correlated with any other geochemical tracers. The same holds for (230Th/238U) on the oblique supersegment.

However, 230Th/232Th and 238U/232Th are correlated with Sr, Nd, and Hf isotopic compositions, indicating that Th isotopic compositions and U/Th reflect similar source heterogeneity. δSm/Nd and δLu/Hf are calculated trace element parameters used as proxies for total % melting and % melting in the garnet stability field, respectively. When plotted against Th excess, orthogonal supersegment lavas show variable but increasing (230Th/238U) with slightly increasing δSm/Nd and δLu/Hf. On the other hand, the oblique supersegment lavas show increasing (230Th/238U) correlated with decreasing δSm/Nd and δLu/Hf. This broadly suggests that the deeper the melting the lower the Th excess, and the larger the F the larger the Th excess.

Our data do not support the idea that Th excess is a function of spreading rate or axial depth, as initially proposed by Lundstrom et al., 1998 and Bourdon et al., 1996, respectively. However, SW Indian Ridge 230Th/232Th and 238U/232Th compositions do correlate with Sr, Nd, and Hf isotopic compositions, suggesting temporal equilibration of these isotopic systems.

Diffusive fractionation of 226Ra-230Th in oceanic basalts during shallow level interaction

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Complex melting and percolation models with a two-porosity system have been proposed to explain the high 226Ra excess in oceanic basalts and the observed inverse correlations of the 226Ra excess with the 230Th excess and with the trace element enrichment of MOR lavas [1]. We have offered an alternative hypothesis that interaction of primitive melts with MORB cumulates (troctolites or wehrlites) could be responsible for those geochemical signatures [2]. However, our previous model considered the interaction of a melt with only one solid phase (plagioclase or clinoxyroxene). Here, we present the results of a more realistic model that considers the diffusive interaction among a melt and multiple solid phases (plagioclase and clinoxyroxene) [3]. Our calculations suggest that diffusive interaction between gabbros and basalts can explain the observed inverse correlation of the (226Ra/230Th) ratios with the (230Th/238U) ratios in MORBs, and with the trace element enrichment of oceanic basalts. Furthermore, in contrast to the two-porosity model, our model gives a simple explanation for the lack of high 226Ra excess (generally < 1.7) observed in oceanic island primitive melts.

References


References

210Pb-226Ra-230Th disequilibria in very young Mid-Ocean Ridge Basalts

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We report the common occurrence of 210Pb-226Ra radioactive disequilibria in <20-year-old oceanic basalts. The 22-year 210Pb half-life requires significant 210Pb-226Ra fractionation within the past half to full century. This study on deep sea floor volcanoes, where eruption histories are largely unknown, was possible because each of our samples was collected by manned submersible from well-characterized and known or presumed age recent sea floor eruptions. Normal Pacific Ocean MORB were analyzed from 3 sites spanning a range of erupted volume, spreading rate (moderate to superfast) and compositional variation (Rubin et al., 2001). Multiple samples were analyzed from each young flow and all contain 210Pb deficits. (210Pb-226Ra)=1 in 2 older flows. By contrast, young Axial Seamount lavas display 210Pb excesses and Loihi Seamount tholeiites contain slight deficits. The largest deficits occur in the most primitive basalts and (210Pb/226Ra) activity ratios correlate with (226Ra/230Th), MgO and compatible trace element ratios in manners that preclude magma differentiation or daughter isotope (222Rn) degassing (e.g., Gauthier and Condomines, 1999) in crustal magma chambers as a primary cause of the 210Pb deficits. Thus the disequilibria were likely present before magmas entered crustal magma bodies. Observed 210Pb-226Ra-230Th disequilibria can be simulated with a common (analytically-solvable) instantaneous melting model (McKenzie, 1985) for a broad range of melting conditions and solid-melt partition coefficients, but the combined duration of subsequent melt transport and magma chamber residence must be on decadal timescales to preserve the observed disequilibria. Two important implications are that a major component of MORB magma transport at shallowest mantle and crustal levels is by rapid, presumably non-porous flow mechanisms and that crustal magma differentiation can occur in tens of years.

References

Degassing and crystallization time-scales implied by 210Po-210Pb-226Ra activities for lavas from Anatahan, Arenal, and Mount St. Helens

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Minerals and melts erupted from arc volcanoes are commonly marked by disequilibrium between 238U-series nuclides with half-lives ranging from days to 75 ka. These data imply time-scales of crystallization, melting, and degassing occurring over multiple time frames stretching back as far as hundreds of millennia before eruption. This presentation will focus on the magmatic processes occurring within during the century leading up to eruption by reporting activities of 210Po, 210Pb, and 226Ra in whole rocks, groundmasses, and plagioclase mineral separates. The volcanoes under investigation are Anatahan, Arenal, and Mount St. Helens, which have explosively to effusively erupted lavas ranging from basaltic andesite to dacite.

Basaltic andesites erupted from Analeen have relatively normal 210Po degassing levels [(210Po)/(210Pb) x 100] of about 95%. In contrast, silicic andesites from Anatahan are 85% degassed of 210Po, and 2004–2005 dacites from Mount St. Helens are variably degassed with values ranging to less than 40%. The low values for Mount St. Helens dacites can be explained by the principal degassing occurring during the 1980s as the magma rose to a relatively shallow storage site. An alternative explanation is that Po degassing efficiency changes with temperature and perhaps magma composition. Most lavas and tephras erupted from Analeen and Anatahan have near-equilibrium (210Po)/(226Ra) ratios reflecting a time period of rise to the surface and degassing from magma reservoirs of less than about two years. Exceptions include Arenal lavas erupted in the early 1970s and mid-1990s, which had 210Po excesses of 100 % and 20 % respectively. The 210Po excess in the early 1970s lava resulted from 222Rn fluxing associated with the arrival of recharge magma in the system. The excess in the 1990s may have resulted from a slowing of the magma velocity. Plagioclase from Arenal lavas have (210Po)/(226Ra) ~ 2 disequilibrium, indicating that a significant proportion of the crystals grew within years or decades of eruption. Plagioclase erupted in November from Mount St. Helens have unusually high (210Po)⁸ values, suggesting that at least a portion of these crystals also may be young.
Magma differentiation and storage at Katmai-Novarupta 1912: Comparing U-series time scales with thermal models

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Time scale constraints have the potential to distinguish between paradigms used to explain origins and evolution of compositionally-zoned eruptive deposits. We test these models using the canonical compositionally-zoned eruption, Katmai-Novarupta 1912. Following Reagan et al. (2003), we have undertaken a detailed stratigraphic Uranium-series study including 226Ra-disequilibria using representative samples from the base and top of each eruptive unit (layers A-D, F-G) and from the top of the dacitic system (layers C-D, F-G). The span the entire compositional range from 50 to 77 wt. % SiO2.

Our 230Th data show that variations between magma batches are small yet highly systematic, and strongly depend on bulk composition. Time scales inferred from 230Th systematics imply that differentiation from andesite to dacite took ~40 kyr, but that evolution to high-silica rhyolite required a further 300 kyr to have elapsed. 230Ra-excesses range from >200% in andesites to near-equilibrium values in dacitic batches. The Novarupta rhyolite lies within error of equilibrium, but at the base of Layer A, the rhyolite preserves a 20% 230Ra-excess.

In order to evaluate whether these time scales are thermally consistent with conductive cooling and closed system fractional crystallisation we used geological and experimental constraints to simulate cooling times for a single intrusive event. These show that cooling of the Katmai chamber to subsolidus temperatures should take 20 kyr or less, in the absence of thermal priming with successive intrusions.

Together with numerical models, the U-series data appear to favour the repeated influx of andesitic magma into the shallow crust in the recent past (<8 kyr).

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To evaluate the time scale of andesite differentiation at Arenal Volcano in Costa Rica, we have measured trace-element concentrations and U-series disequilibria in whole rocks and mineral separates (pyroxene, plagioclase, magnetite) from lavas of the current eruption (1968 to 2003) by ICP-MS, TIMS and PIMMS techniques. Whole rock and mineral separate analyses (n>20) show a small but measurable variation in \( \frac{^{230}Th}{^{232}Th} \) (1.10 to 1.18). In contrast, \( \frac{^{230}Th}{^{238}U} \) range from 0.91 to 1.04 reflecting the moderate spread in Th/U. Stage 1 (1968-1971) whole rocks and mineral separates have both higher \( \frac{^{230}Th}{^{232}Th} \) and \( \frac{^{238}U}{^{232}Th} \) in comparison to younger Stage 2 lavas (1971 to present), which have lower, nearly constant \( \frac{^{230}Th}{^{232}Th} \) and lower, slightly variable \( \frac{^{238}U}{^{232}Th} \). Stage 1 lavas have higher fluid-mobile over non fluid-mobile element ratios (e.g., U/Th or Ba/Th) and less steep REE patterns compared to Stage 2 lavas. \(^{226}Ra\) excesses exist in both whole rocks and mineral separates (n>18) and range between 1.1 and 2.3. Whole rock \(^{226}Ra\) excesses are largest in rocks of older eruptions (Stage 1; ~1.4), representative of older, previously emplaced material (Gill et al., 2004), and decrease in the younger eruptions (Stage 2; ~1.1), maximally influenced by newer recharge material. A positive correlation exists between \( \frac{^{226}Ra}{^{230}Th} \) and both \( \frac{^{238}U}{^{230}Th} \) and Ba/Th for whole rocks.

U-Th disequilibrium constraints on the origin of Holocene lavas from Jingbohu, Long-gang and Tianchi

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Holocene (<10,000 years) volcanic activity occurs at Wudalianchi, Jingbohu, Long-gang and Tianchi along northeast-southwest trending basins in northeastern China, possibly as a result of lithosphere rifting and asthenosphere upwelling or due to the subduction of the Pacific plate under the Eurasian plate. Short-lived U-Th disequilibrium along with long-lived Nd isotopes may provide insights into the origin of these young lavas and recent mantle geodynamical processes.

Strong (24-33%) \(^{230}Th\) excesses with enriched Nd isotopic compositions (\( \epsilon_{Nd} = -3.7 \) to \( -5.0 \)) in the historic Wudalianchi lavas have been previously documented [1]. Here we present data for chemically separated thorium from Jingbohu, Long-gang and Tianchi samples measured by a recently implemented technique using the UCLA Cameca IMS 1270 ion microprobe. Secondary ion mass spectrometry is advantageous due to its much higher ionization efficiency for thorium than thermal ionization mass spectrometry [2]. Jingbohu lavas display variable extents of \(^{230}Th\) excesses (7 to 28%) and moderately depleted Nd isotopic compositions (\( \epsilon_{Nd} = +1.5 \) to +3.3). Long-gang lavas have pronounced (20 to 35%) \(^{230}Th\) excesses and slightly depleted Nd isotopic compositions (\( \epsilon_{Nd} = +0.5 \) to +0.7). The Tianchi lavas display moderate (12%) \(^{230}Th\) excesses and slightly enriched Nd isotopic compositions (\( \epsilon_{Nd} = -1.0 \) to –1.1). Since \(^{230}Th\) enrichments in all these Holocene lavas are uncharacteristic of melts generated by subduction, recent subduction of the Pacific plate did not directly contribute subduction-related fluids to the source rocks for these basalts. Instead these basalts represent mixtures of melts derived from partial melting of enriched lithospheric EM1 mantle and depleted asthenospheric mantle in the deep garnet-stability field, as a result of the lithosphere rifting and asthenosphere upwelling.

References

**In situ biomolecules and isotopic signals from Clarkia plant fossils**

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Tertiary molecular paleobiology owes its rapid development to Clarkia plant fossils from which diverse ancient biomolecules have been reported. These claimed *in situ* biomolecules and compound specific isotope signals from identifiable fossils are critically reviewed; paleoclimatic signals derived from morphologically based methods and isotope approaches are compared.

Early work on the Clarkia biomolecules and biochemicals focused on flavonoids and their chemotaxonomic comparisons. Stable biomolecules such as lipids and lignin were found to be abundantly preserved but offer little taxonomic information. Recent studies confirmed the preservation of relatively labile polysaccharides and polar compounds, but they are relatively uncommon. Three reports claimed the retrieval of ancient DNA sequences of different genes from different fossil taxa, although extensive racemisation of amino acids were detected. Recent analyses of compound specific carbon and hydrogen isotopes of *n*-alkanes and *n*-acids from several plant taxa suggest the preservation of *in situ* molecular isotope signatures, opening up a new avenue of paleophysiology and paleoenvironmental studies.

Mean annual temperature for the Clarkia area during the Miocene time is reconstructed using the nearest living relative approach, leaf physiognomy method, compound specific D/H ratio of sediment carboxylic acids, and direct measurement of D/H ratio of sediment water. Discrepancies exist among values obtained using paleobotanical and geochemical methods, and such inconsistency may be due to preservational bias of plant megafossils and multiple origins of organic compounds that were used for isotope analysis.

**Morphological, anatomical, ultrastructural and macromolecular preservation of leaves from the Miocene of Clarkia, Idaho, USA**

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Leaves from Clarkia, are unusual – they have been claimed to exhibit ‘autumal colours of red, brown and blackish green’ and to preserve labile biomarkers, ancient DNA and organelles. Leaves can be lifted intact from the rock (Smiley 1985, Golenberg 1991, pers. obs.).

Insight of this ‘exceptional preservation’, the state of preservation of the least labile chemical entity, the leaf cuticle, has not been studied in combination with leaf morphology or ultrastructure. Fieldwork at Clarkia in summer 1999 revealed leaf fossil ranging from mere cuticle envelopes to opaque compressed leaves with thick internal organic material. Leaves of the conifers *Amentotaxus* & *Metasequoia* and the flowering plants *Quercus* & *Lithocarpus* reveal preservation of cuticle, leaf tissues, cells, and cell contents including ultrastructure of chloroplasts. *Amentotaxus* provides a natural experiment enabling us to link cuticle morphology and chemistry in two extreme preservation states. Cuticles of both lack ultrastructure and yield the highly aliphatic signature typical of leaf fossils. Exceptional preservation of leaf tissues, cells and organelles is not linked to exceptional chemical preservation in these fossils.

**Reference**

Tertiary *Metasequoia* leaves: A case example of paralleled preservation at biomolecular and morphological levels

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*Metasequoia* is an evolutionary conservative conifer genus with a continued fossil record widely reported in the Northern Hemisphere since Late Cretaceous. Three deposits, the late Paleocene-early Eocene Ellesmere Island deposit of Canada (~60Ma), the middle Eocene Axel Heiberg Island deposit of Canada (~45Ma), and the Miocene Clarkia deposit of the US (~15Ma) yield exceptionally preserved *Metasequoia* fossil leaves, offering a rare opportunity for a comparative and combined study at the morphological and biomolecular levels.

A sequence of biomolecular preservation is detected by Py-GC-MS analysis on solvent-extracted residues. Total ionic chromatographs show that the ~60Ma old material produces large amounts of polysaccharide moieties and detectable fatty acids, showing the best quality of preservation. The ~45Ma old material yields mainly lignin products but with lesser amounts of polysaccharide moieties. Fatty acids are hardly detected. The pyrolysis products of the ~15Ma old material are dominated by lignin products and a few polysaccharide moieties. Fatty acids are hardly detected. The pyrolysis products of the ~15Ma old material are dominated by lignin products and a few polysaccharide moieties with very low quantity are detected, indicating the lowest quality of biomolecular preservation.

SEM observation also exhibits a similar sequence of preservation at the morphological level. The ~60Ma old material is the best preserved with almost intact 3-dimensional epidermal cells and with distinct and continuous cuticular membrane layers. The cuticular membranes covering collapsed epidermal cells of the ~45Ma old material are still layered but layers are not readily recognizable. The ~15Ma old material is of the lowest quality of preservation with cuticle as the only structurally preserved part.

Such a comparative and combined SEM and geochemical approach makes it possible to detect the source of preserved structural labile biopolymers. These molecules might have played a significant role in the fossilization and preservation of exceptionally preserved fossil leaves.

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The preservation of cytoplasm in fossil plant cells

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Cytoplasm has been an object of paleobiological research only rarely because cytoplasm is labile in death of an organism and thus not incorporated into the fossil record. The plant cell walls that are relatively inert as well as plant parts covered with waxes, cutin or sporopollinin such as epidermal cells and spores or pollen are most often preserved. These are relatively stable and physiologically inactive parts of the plants and remain for some time after death of the plant while the cytoplasm in most extant plants usually is decayed shortly after death and certainly before fossilization. However, this decay process needs to be re-examined in light of new data that demonstrates the potential for the preservation of cytoplasm in fossil plants and the actual preservation of cytoplasmic cellular contents. Recent work on the ultrastructure of fossil plant cells suggests that the assumption of the rarity of the occurrence of cytoplasm in some fossil plant cells may be mistaken. The decay of cytoplasm is an organic reaction that needs time and the action of enzymes that are very sensitive to environment changes and only function at particular temperatures. Wildfires, that usually produce high temperatures that bake or burn original plant material, are not rare at all in modern or geological history. High temperatures of forest fires can stop the decay of cytoplasm and the right combination of temperature and occurrence of the fire can charcoalfy plant bodies, preserving cytoplasm within the plant cells. Charcoalified material is an inert material frequently seen in the sediments. Based on the above long-existing knowledge, it is conceivable that cytoplasm fossils should be more common objects for research than previously thought. In this paper, we will demonstrate the fine preservation and subcellular ultrastructures of cytoplasm never seen in fossil plants before. The fossil materials are charcoalified plant debrises from the early Cretaceous (the late Albian, about 100 m.a.) in Kansas, USA. Different preservation patterns suggest that at least lightning and wildfires are related to the production of fossil cytoplasm. Our conclusion is also favored by our experiments with the fixation of cytoplasmic contents of plant cells in modern plant materials by high temperatures.
Experimental simulation of organic fossilisation

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Pre-Tertiary arthropod and leaf fossils are comprised of recalcitrant aliphatic macromolecules, similar in composition to Type I/II kerogen. Typically, their extant counterparts lack any such resistant aliphatic precursor, precluding selective preservation of such a compound as a source for the fossil aliphatics. Instead, recent research reveals that fossil aliphatic macromolecules could be a product of lipid polymerisation. To understand this process, confined pyrolysis gold tube experiments were carried out on pure and chemically treated modern arthropod and plant tissues.

Artificially matured scorpion, shrimp and cockroach cuticle contains moieties related to phenols, pyridines, pyrroles and possibly indenes (derived from matured chitin), while straight-chain C16 and C18 fatty acyl moieties and C10 to C20 n-alkyl moieties indicate the presence of an aliphatic polymer. Cuticles matured after lipid extraction and saponification do not show the presence of these aliphatic components proving that they must derive from the extractable lipids of the cuticle/tissue. Similarly, pyrolysis of leaf tissue matured without any treatment yielded alkane/alkene homologues ranging from n-C10 to n-C34/35, whereas leaves matured after lipid extraction contained few long-chain n-alkyl moieties and leaves matured after base-hydrolysis apparently contain no aliphatic moieties. Thus, in the absence of cutan, other aliphatic components - cutin, waxes and internal lipids - contribute to formation of an aliphatic polymer.

The effect of a basalt flow on the chemical composition of sedimentary organic matter

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Thermal maturation is one of the most important controls on the preservation of fossil organic matter, but its effect is often difficult to separate from environmental or diagenetic controls due to the extended sedimentary sequences (>1000 m) through which thermally induced changes occur. The Enspel lacustrine deposit (Germany) is an ideal location to study the thermal imprint on sedimentary organic matter composition as it contains a sedimentary sequence abruptly terminated by a basalt flow but no subsequent deep burial. Thus, the sediments immediately underlying the basalt flow represent a compressed sequence of increasing organic matter thermal alteration – from highly immature (remarkably, sterols and hopanols are still present) to advanced catagenesis.

The thermal imprint is obvious in a range of bulk organic chemical and specific biomarker parameters. Among the parameters that decrease upsection are: total organic carbon and total nitrogen contents; degree of functionalization of both bulk organic matter and individual compounds; and the average chain length of n-alkanoic acids. Increasing upsection are the aromatic content of bulk organic matter and the extent of sterane and hopane stereochemical isomerization. Considered together, these records reveal how both algal and higher plant organic matter has changed in response to thermal alteration and will ultimately facilitate comparison of such pristine deposits as the Clarkia Formation to more ancient and thermally altered units.
A short story about preservation – from living organisms to fossils

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Fossil plants and animals are preserved in a number of different ways. These include impressions, permineralizations, and organically preserved structures. Most modern plants lacks biomineralized tissues, hence their survival in the fossil record relies on the preservation of organic remains. The fossil fauna is often biomineralized, however their cuticles can retain an organic signature.

Plant structures composed of both lignin and aliphatic macromolecules are the most likely to be preserved in the fossil record. However, the preservation potential of the aliphatic component itself is higher than that of lignin. Animal bodies are composed of biopolymers such as proteins, DNA, chitin and lipids, of which DNA and proteins are most susceptible to biodegradation and are thus rarely found in the fossil record. Despite degradation processes, chemosystematic information can often be obtained.

In both plants and animals, the physical and chemical properties of cuticles are responsible for their potential for preservation in the fossil record. However, the following factors also determine the extent of chemical and structural preservation, and subsequent survival into the fossil record:

1) type of the organism (terrestrial vs marine; degree of sclerotization or initial mineralization)
2) nature of the depositional environment (climate; oxic vs anoxic basin; terrestrial vs marine basin; pH of the environment; organic productivity; rate of sedimentation)
3) inhibition of initial biodegradation (microbial activity) and further diagenetic alterations

The role of temperature is not precisely known but time appears to be less important, but it can not be ignored completely. The preservation potential of major biopolymers (from DNA to lignin), in a variety of environments will be reviewed and discussed.

References

Diagenesis effects on specific carbon isotope composition of plant \( n \)-alkanes

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The stable carbon isotope composition of individual biomarkers in general, and of \( n \)-alkanes in particular, is often used to reconstruct palaeoenvironments. However, little is known about the evolution of such an isotopic signal through diagenesis. We have investigated the effect of diagenesis on the isotope composition of bulk leaves and individual \( n \)-alkanes from higher plant lipids. The effects of very early diagenesis were investigated by studying the evolution of the isotope signal in modern leaves degrading in soils. These results were compared with those obtained from related fossil plants originating from Mesozoic and Cenozoic deposits.

In agreement with literature, all the analyzed \( n \)-alkanes appeared \(^{13}\text{C}\)-depleted when compared with bulk leaves. Within a given extract, they exhibit variations in specific isotope composition, depending on carbon number. The \(^{13}\text{C}\)-depletion of \( n \)-alkanes when compared with bulk leaves and the distribution of their individual \(^{13}\text{C}\)-content with respect to chain length appeared variable among species, degradation stages and fossil vs modern plants. Such variabilities of specific alkane isotope composition reflect the multiplicity of factors influencing the isotope signal in plants and derived organic matter. In soil samples, the results tend to indicate that the isotope composition of individual \( n \)-alkanes may be more affected by degradation than that of bulk leaves.
The influence of C₄ photosynthesis during the Miocene

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The evolution of the C₄ photosynthetic pathway was driven by specific environmental conditions and thus reflects a record of global environmental change. Given the distinct stable carbon isotopic compositions (δ¹³Corg) of C₃ and C₄ floras, terrestrial δ¹³Corg can be applied to assess the relative proportion of C₄ plant input with time. Estimates of the C₄ plant biomass by this approach require an understanding of changes in the δ¹³C of atmospheric carbon dioxide (δ¹³CO₂) with time. In this on-going study, we evaluate the history of C₄ photosynthesis by measuring the δ¹³C of terrestrially-derived n-alkanes from a globally distributed set of oligotrophic and marginal DSDP/ODP marine sediments. Estimates of paleo-δ¹³C₀₂ are established from (1) the δ¹³C of C₄ plant organic matter from Paleogene-age sediments from the Isle of Wight, UK, assuming a constant carbon isotopic discrimination between CO₂ and bulk C₃ plant organic matter, and (2) from published δ¹³C records of planktonic foraminifera. From our data we model C₃ and C₄ δ¹³Calkane values and calculate the percent abundance of C₄ plant input for a given sedimentary δ¹³Calkane composition.

Our preliminary results from the Atlantic and Indian Oceans indicate that terrestrial C₄ photosynthesis was persistent during the Miocene (~25-5 Ma), constituting ~20 to 30% of aeolian-derived organic material. These results are broadly consistent with recent pCO₂ records that indicate a rapid decline in carbon dioxide between ~34-25 Ma, reaching near-modern levels by the latest Oligocene. Such low levels would have enhanced rates of photospiration, favoring the evolution and expansion of the C₄ pathway prior to the Miocene.

Using carbon and hydrogen isotope ratios of terrestrial organic matter to understand climate change at the PETM

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The Paleocene Eocene Thermal Maximum (PETM) is a period of abrupt and extreme warming (5-10°C) associated with a postulated catastrophic release of methane from gas hydrates. This event is marked by a large negative carbon isotope excursion that is twice as large in paleosol carbonates (6 to 8‰) as it is in marine carbonates (3 to 4‰). Organic carbon from paleosols demonstrates an excursion of intermediate magnitude (4 to 5 ‰) (This study and Magioncalda et al., 2004). One recent hypothesis for the greater magnitude of excursion in terrestrial than marine reservoirs calls for increased carbon isotope discrimination in plants resulting from a ~20% increase in available moisture, combined with an accelerated soil carbon cycle (Bowen et al. 2004). Using the carbon and hydrogen isotope signatures of plant lipids, we can test this hypothesis. The δD record of n-alkanes should record increases in available moisture, and their δ¹³C values should record plant carbon discrimination.

The compound-specific approach to characterizing the terrestrial carbon isotope excursion during this climatic event avoids the problem of preservational biases common to bulk measurements. In the Bighorn Basin, WY, we observe that the carbon isotope ratio of bulk organic matter in paleosols is variable and inversely correlated with the percent carbon by weight. This correlation may be the result of preferential removal of ¹³C-depleted carbon during decay, and/or depositional or preservational biases in different settings (oxic vs. anoxic conditions).

Leaf wax n-alkanes are preserved in organic-rich Paleocene and Eocene sediments from the Bighorn Basin, WY, and do not represent modern contamination. The carbon isotope ratios of n-alkanes are depleted relative to bulk organic carbon values by 3 to 5 ‰ and show considerably less short-term variation. Thus, the variability in bulk values reflects variable degradational or depositional conditions rather than variation in the carbon isotope signature of the vegetation input.
Hydrogen isotopic composition of
n-alkanes from leaf waxes:
An empirical evaluation of
environmental controls

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The primary objective of this work is to evaluate the environmental controls on the hydrogen isotopic compositions of n-alkanes from higher plant vegetation. Our goal is to establish the foundation of a new proxy that can be used to assess regional changes in evapotranspiration and effective moisture. We are in the process of collecting leaves from trees throughout strong climatic gradients in Hawaii, California, and the Yucatan Peninsula, Mexico. These data will be interpreted in the context of environmental parameters (such as precipitation, temperature, altitude, and the isotopic composition of precipitation) in order to assess their relationship with D/H ratio of leaf n-alkanes. δD and δ13C compound-specific measurements are being conducted on n-alkanes from 70 samples of *Metrosideros polymorpha* in Hawaii and 150 samples of *Quercus kelloggii* in California. Preliminary n-alkane isotopic data from *Quercus kelloggii* show a clear separation between leaves in the relatively wet northern California (δD -188 to -216‰) and leaves in the relatively dry southern California (δD -156 to -184‰). Differences in the amount of precipitation between these two regions could be one of the factors that resulted in these isotopic differences.

Furthermore, we are assessing the application of this methodology to paleorecords by using lacustrine sediment cores from three lakes on the Yucatan Peninsula. Initial results from isotopic measurements of D/H ratio of n-alkanes in lacustrine organic matter show enrichment/depletion patterns (δD variations up to 50‰) similar to those observed in δ18O of ostracod and gastropod shells (δ18O variations up to 5‰). This similarity indicates that regional changes in the paleohydrological balance had comparable effects on the isotopic composition of terrestrial and aquatic biota in or near these lakes.

DNA from fossils: Lake embedded plant and sediment remains

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About 20 years ago, DNA sequences were separately described from the quagga (a type of zebra) and an ancient Egyptian individual. What made these DNA sequences exceptional was that they were derived from ancient and extinct species. However, ancient DNA research, defined broadly as the retrieval of DNA sequences from museum specimens, archaeological finds, fossil remains, and other unusual sources of DNA, only really became feasible with the advent of techniques for the enzymatic amplification of specific DNA sequences. Today, reports of analyses of specimens hundreds, thousands, and even millions of years old are almost commonplace. Despite repeated claims of the isolation of DNA from lake embedded fossil remains, up to several millions of years old. None to date have been replicated independently, an essential criteria of authenticity for all ancient DNA research today. While million year old DNA from lake embedded plant remains has not be replicated, recent results from moderately aged beech and hemlock fossils from similar settings, appears to be reproducible. Thus the question remains, how old can one go in lake sediments? Theoretical and empirical results on this possibility will be discussed. I will also highlight some significant results and areas of promising future research.
DNA preservation in late Pleistocene materials from China

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During past few years, most of ancient DNA (aDNA) studies in China mainly focused on ancient human remains with ages ranging from several hundreds years to 6 Ka BP. Abundant Late Pleistocene mammalian materials distributing in vast areas in China with great potential significance for molecular evolution.

Biogeographically, taking the Qinling Moutains as the boundary, China can be divided into South China and North China regions during the Late Pleistocene.

South China is characterized by the giant panda–stegodon fauna. Because the humid and warm climate, the quality of aDNA preservation is very poor. Many DNA extraction experiments are performed on giant panda, stegodon materials collected from Hunan, Hubei, Guangxi, Sichuan and Yunnan Provinces in this region. But so far, no authentic DNA has been obtained from these materials. The study of aspartic acid racemization and bone or teeth histology on these fauna also indicates poor DNA preservation in these areas.

On the other hand, North China is marked by the mammoth-coelodonta fauna under dry and cold climate. The DNA preservation of a few sites in North China permits reliable ancient DNA sequences. So far, aDNA of mammoth collected from Inner Mogolia (Yang et Lai, 2003), bison from Harbin (Shapiro et al., 2004) have been reported. aDNA have been successfully extracted from horse, coelodonta, and mammoth from Harbin, Heilongjiang Province in Northeastern China.

DNA preservation in North China is better than South China. In addition to climate, pH value may also be a main factor influencing the ancient DNA preservation in these two areas.

References

The Miocene Clarkia deposit of Idaho: New uses for old molecules

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The investigation of ancient biomolecules is traditionally dominated by the search for biomarkers in petroleum geochemistry and in the investigation of the evolution of early life in Archaean and Proterozoic rocks. But research on the biochemistry of identifiable fossil remains also has an important role.

In situ biomolecules can provide chemosystematic and phylogenetic data and yield environmental indicators. Coupled with molecular isotope information (compound specific carbon and hydrogen isotope signatures) molecular analysis provides a powerful tool for investigating ancient CO₂ concentrations, temperature and precipitation patterns, and ancient physiological adaptations. In situ biomolecules are also an important resource for the calibration of degradation, and organic maturity and diagenetic processes, particularly where original composition can be inferred by comparison with equivalent living material.

Research on the biochemistry of individual fossils in Tertiary deposits was initiated largely on the Miocene Clarkia deposit in response to the spectacular preservation of the biota, not least the leaves. While the plant fossils from Clarkia are some of the best known in terms of their organic chemistry, they and other elements of the Clarkia assemblage provide a focus for investigating a range of other issues, particularly in comparison with other Tertiary biotas. These include: diagenetic alteration of macromolecules; the molecular context of the preservation of labile molecules; the influence of lithology, anoxia, hydrolysis, and other degradation agents on organic preservation and the fidelity of molecular and isotopic signatures; and contrasts in the preservation of plant molecules and those of insects and fishes.
Molecular records of northern California vegetation change

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During the late Pliocene and early Pleistocene, the northern California margin experienced major tectonic and climatic changes. A detailed record of these changes is preserved in two marginal marine sedimentary sequences tectonically uplifted and exposed along the California margin: the slope to outer shelf Rio Dell Formation, near Cape Mendocino, and the shelf to non-marine Merced Formation, near San Francisco. Portions of these two formations were analyzed at ~5000 year resolution through several apparent glacial-interglacial cycles for a diverse array of molecular fossils derived from terrestrial ecosystems: steroids, sesquiterpenoids, diterpenoids, triterpenoids, \( n \)-alkanes, and polycyclic aromatic hydrocarbons (PAH).

Context for this terrestrial marker data is provided by complimentary analyses of: sedimentary structure and texture, macrofossils, non-plant related molecular fossils, benthic foraminiferal assemblage, the stable isotopic composition of benthic foraminiferal carbonate, and palynology.

The combined analysis of these terrestrial molecular fossils allows the identification of distinctive and climatically sensitive elements of ancient California flora. For example, salt marsh floras -- abundant during marine transgressions -- are marked by systematic changes in the isotopic composition and relative abundance of different odd carbon number long-chain \( n \)-alkanes in sediment extracts, and Cupressaceae dominated floras are marked by a high relative abundance of tetracyclic diterpanes and isotopically light C\(_{33}\) and C\(_{35}\) \( n \)-alkanes. Glacial-interglacial cycles in PAH abundance and composition reflect dramatic changes in seasonal rainfall distribution, vegetation communities, and the frequency, magnitude, and nature of wildfires.

This multi-proxy study allows the interpretation of competing source and diagenetic effects upon the distribution of terrestrially-derived molecular fossils in the marine record. Observed diagenetic alterations are sometimes considerable and have implications for the use of terpenoid molecular fossils in other studies.
Grain-boundary fluids, chemical transport, and rheology: An Alpine perspective and resulting questions

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Experimental studies on wetting behavior of fluids have profound implications for understanding a variety of chemical and physical processes during synchronous metamorphism and deformation. The difficulty comes in determining how field and petrographic observations relate to the experimental data. Examples from the Eastern Alps will be used to document scales of fluid communication during metamorphism, to estimate wetting behavior of the fluids, and to explore effects on rock rheology: (1) Mineral and stable isotopic compositions in banded eclogites are homogeneous parallel to foliation but heterogeneous across foliation. Sharp interfaces rule out cross-foliation diffusion or fluid flow on a mm scale. Any interconnected porosity at high P was thus confined to layer-parallel networks. (2) Diffusive mass transfer during deformation of clast-bearing micaceous quartzites required an inter-connected fluid phase during amphibolite-facies shearing, but was ultimately self limiting. Rheologic cycling resulted from feedback effects between mass transfer and changes in deformation mechanisms. (3) Schists in the same shear zone contain carbonic fluid inclusions in graphitic layers vs. H2O inclusions in nongraphitic layers. Strain was accommodated by repeated fracturing in graphitic layers and by crystal plasticity in nongraphitic horizons. Non-wetting carbonic fluids in graphitic schists experienced significant volume expansion during decompression, causing fracturing (and possible seismonic faulting). (4) Preliminary rock-deformation experiments confirm the role of CO2 in promoting high-T embrittlement of quartz-rich rocks, and also show development of rheologic stratification in samples deformed in the presence of immiscible H2O-CO2 fluids.

These studies show that variations in fluid wetting behavior control both mass transfer and rock rheology. They also raise questions: How does deformation affect fluid wetting behavior? What role does fluid immiscibility play in controlling rheology during deformation? What data are needed from natural samples to infer paleo wetting behavior? Does wetting behavior play a role in the earthquake cycle? Closer collaboration between field and experimental scientists is needed to address these questions.

Garnet morphology and the kinetics of deep crustal reactions

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The kinetics of deep crustal reactions have important implications for rates of fluid release and the impact of fluids on rock strength and seismic hazard. We focus on growth textures preserved in garnets from two rock units within the Acadian Orange-Milford Belt, CT: meta-ultramafic rocks found in the Maltby Lakes Metavolcanics (MLM) and metapelitic rocks of the Wepawaug Schist (WepS).

And-Grs-Uv garnets of the MLM rocks nucleated on relic spinels and have rounded, “petal-like” shapes. Garnet to Kyanite zone garnets in graphic rocks of the WepS contain anhedral or “star-shaped” cores with relatively few inclusions. The cores abruptly give way to sub- to euhedral rims rich in inclusions of graphite and Fe-Ti oxides. Cores have larger Ca, Mn, and Fe/Mg than rims. Core-rim boundaries are marked by agglomerations of graphite. Similar features in graphic metapelitic rocks elsewhere define “textural sector zonation” (TSZ; Rice and Mitchell, 1991). Garnets with TSZ are found only in graphic WepS rocks, ruling out graphite precipitation events at core-rim transitions. Instead, the organic matter was present prior to garnet nucleation, but it was excluded from the garnet cores as they grew.

The garnet morphologies imply rapid growth and fluid release far from equilibrium at large delta G of reaction. Morphology diagrams (e.g., Xiao et al., 1988) suggest that the petal-like shapes of the MLM garnets represent the fastest growth rates farthest from equilibrium. The WepS garnet cores represent somewhat slower, but still highly overstepped growth that was followed by slower, more euhedral rim growth. We suggest that rapid growth coincided with rapid regional heating, consistent with recent geochronology (Lancaster et al., 2005).

References
Mineral dissolution kinetics at grain boundaries

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Mass transport of dissolved components in the shallow subsurface may often occur via a dissolution-reprecipitation mechanism, a process for which two decades of experimental study have provided substantial support. However, these studies were conducted in autoclaves at elevated temperatures and pressures. Direct observations of the mineral surfaces that constitute these reacting systems were prohibited, and thus kinetic mechanisms were not understood in any detail.

Figure 1: SEM photomicrograph of a dolomite quartz rock reacting to form dioide and CO₂ at 500 MPa and 680 °C (Luttge, 1995).

Recently, several researchers, e.g., Putnis (2004) and Baumgartner (2004), have revived interest in this research topic. While revisiting the mechanistic concepts they have highlighted in particular the importance of coupled mineral dissolution-precipitation kinetics.

In this context, our studies of crystal dissolution kinetics at lower temperatures (10 - 180°C) may help to shed some more light on this important problem. We employ a combination of direct observational techniques, i.e., atomic force microscopy (AFM) and vertical scanning interferometry (VSI) and computer simulations. Our research has led to a new model that emphasizes the importance of full incorporation of the three-dimensional crystal lattice into a fundamental kinetic treatment. Our stochastic approach is based on parameterized Monte Carlo techniques. Ab initio/DFT calculations are used for the parameterization.

Grain and phase boundaries and viscoelastic mechanical response

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The phenomenologies of creep and of seismic-frequency wave attenuation are intimately associated with the spatial distribution and structure & chemistry of grain and (solid-state) phase boundaries. My students and I pursue experimental research to quantify the relationships; the studies emphasize (i) state-variable analysis/description of dislocation-effected plasticity, (ii) phase- and grain-boundary effects on wave attenuation, and (iii) plastic-strain-effected phase separation in polyphase aggregates.

(i) Stress-relaxation experiments suggest that the dislocation rheology can be predicted in a strain-insensitive manner through use of a single microstructural state variable. It is the distribution of low-angle grain boundaries that corresponds to this state variable, and thus the physics of deformation is dependent on dislocation dynamics within those boundaries.

(ii) The power-law Q⁻¹ v. f spectrum (“attenuation band”) associated with the damping of seismic waves can result from a single loss mechanism having a non-exponential relaxation—specifically, one associated with chemical diffusion to relieve gradients in grain-boundary traction. Experiments scrutinizing the small anelastic strains involved in attenuation suggest that a threshold phenomenon related to electrochemical segregation to grain boundaries may be prevalent. Solid-state phase boundaries have been demonstrated as particularly strong mechanical absorbers, with implications, e.g., that hydrous-phase breakdown reactions in nature could produce rocks that combine high stiffness (fast velocities) with high attenuation.

(iii) Large-scale plastic strain in polyphase aggregates requires components of grain- and phase-boundary sliding. The relative sliding viscosities must result in solid-state phase separation (mineralogical layering) accompanying deformation. Discerning experimentally the scaling relationships could allow correlation of such natural structures with the thermodynamic conditions (σ, T) that produced them.

The energetics of grain/phase boundaries, modeled as arrays of lattice dislocations (for low-angle boundaries) or disclinations (for high-angle boundaries) are applied to understand the physical relationships uniting these observations.