

EUG XI



Symposium PCM6

Physicochemical Behaviour of
Accessory Minerals: Crystallisation,
Transformation, and Technological Applications

Convenors

Franck Poitrasson
Urs Schaltegger
John M. Hanchar

PCM6

Physicochemical Behaviour of Accessory Minerals

Wednesday PM Session

PCM6 : WEpm26 : G6 Thorite-Zircon-Coffinite-Xenotime Solid Solutions: Composition and Origin

Hans-Jürgen Förster (forhj@gfz-potsdam.de)
GeoForschungsZentrum Potsdam, Telegrafenberg, 14473
Potsdam, Germany

The extent of miscibility is among the fundamental compositional parameters determining the stability relations of REE- and actinide-bearing accessory minerals. Precise knowledge of their susceptibility to alteration is essential not only for solution of basic scientific problems, but also has a major impact on practical purposes in terms of nuclear waste disposal. In this respect, considerable progress has been achieved for the monoclinic monazite group of minerals comprising the three endmembers monazite, brabantite, and huttonite. Here, composition of natural minerals suggests a continuous solid solution between monazite and brabantite, whereas phases intermediate between brabantite and huttonite are almost unknown to date. The monazite-huttonite join is occupied only sporadically and, hence, complete miscibility between them has yet to be demonstrated.

In contrast, a comparatively minor effort has been spent on thorite (ThSiO₄); an accessory phase that occurs preferentially in evolved I- and A-type igneous rocks and may account for more than 50% of the whole-rock Th budget. Moreover, comprehensive electron-microprobe investigation of accessory mineral assemblages in evolved granites revealed significant solid solutions between thorite and its tetragonal isotyps zircon, coffinite, and xenotime. On the contrary, the LREE entered the thorite structure only in maximum amounts of a few wt%. Thorite from these granites may contain up to 16.1 wt% ZrO₂ (0.42 apfu Zr, normalized to 4 oxygen atoms), 23.3 wt% UO₂ (0.29 apfu), and 26.5 wt% (Y,HREE)₂O₃ (0.59 apfu). Zircon incorporated up to 32 wt% ThO₂ (0.31 apfu), 8.7 wt% UO₂ (0.07 apfu), and 13.1 wt% (Y,HREE)₂O₃ (0.26 apfu). Finally, xenotime could substitute up to 41.8 wt% ThO₂ (0.48 apfu), 13.4 wt% UO₂ (0.15 apfu), or 12.1 wt% ZrO₂ (0.29 apfu).

Compositions strongly deviating from those of the endmembers typically refer to grains that are distinguished by low analytical totals (suggestive of the presence of substantial water); increased contents of P, Ca, Fe, Al, and F; depletion in (radiogenic) lead; and petrographic textures suggesting significant alteration. Formation of compositional extremes in the thorite-zircon-coffinite-xenotime system took place primarily in connection with processes of metamictization and severe fluid-mineral interaction. They may have grown from water- and F-rich granitic residual melts or from the volatile-rich metasomatizing fluids.

In the light of the few previous experimental solubility studies, the extreme compositions are unlikely to be thermodynamically stable. Instead, they rather represent metastable phases produced by residual melts or fluids containing unusually high abundances of Th, U, Zr, Y, and other elements, probably mobilized during decomposition of other accessory phases usually observed in the vicinity of the "metastable" phases. However, more experimental studies covering broad ranges in pT are required to better infer the degree of miscibility (complete or limited) between the four accessory phases.

PCM6 : WEpm27 : G6 Non-Linear Behaviours in the Apatite-Britholite Solid-Solution

Roberta Oberti (oberti@crystal.unipv.it)¹,
Luisa Ottolini (ottolini@crystal.unipv.it) &
Giancarlo Della Ventura (dellaven@unica.it)²

¹ CNR-CSSC, Pavia, I-27100 Italy
² Dip. Scienze della Terra, Univ. della Calabria, I-87030
Italy

Britholite is isostructural with apatite, and is crystal-chemically related to apatite by the exchange vector (REEs, actinides) Si Ca₂P₄. Structure refinement of several britholite samples shows ordering of cations with different charges and ionic radii in the Ca sites of apatite. This results into a lowering of the symmetry (from *P6₃/m* in apatite, to *P6₃* in britholite, and thus into an increase in the number of sites (REE1, REE1a and REE2) and also into significant structural adjustments. For instance, rotation of the Si tetrahedra in britholite increases the coordination of the REE2 site from 7- to 8-fold.

Structural characterisation of a sample with 0.84 (Th + U) pfu (Oberti et al., 2001) and re-examination of the structural and chemical data available in the apatite-britholite join show that there is a strong structural constraint toward REE incorporation into the structure. In apatite, the allowed range of the aggregate ionic radii at the REE sites is 1.10-1.13 Å, whereas in britholite it is 1.03-1.21 Å. This information explains the peak in REE uptake on Nd (i.r. 1.11 Å) observed in chloro-, fluoro and hydroxyapatites (Fleet et al., 2000) and may also be useful to design compositions to be used for toxic waste disposal. Along the apatite-britholite join, the unit-cell volume does not show any simple relation with <r> at the tetrahedral sites, whereas there is a clear sigmoidal relation with <r> at the REE sites. This suggests that the response of the britholite structure to changes in the intensive parameters may be different from apatite, in which, however, the Ca₂-Ca₂ distance is the most affected by P variations (Comodi et al., 2001).

Oberti R, Ottolini L, Della Ventura G & Parodi GC, *Amer. Mineral.* **86**, (2001).

Fleet ME, Liu X & Pan Y, *Amer. Mineral.* **85**, 1437-1446, (2000).

Comodi P, Liu Y, Zanazzi PF & Montagnoli M, *Phys. Chem. Minerals*, (2001).

PCM6 : WEpm28 : G6 Trace-Element Incorporation in Titanite: Constraints from Experimentally Determined Solid/Liquid Partition Coefficients

Massimo Tiepolo (tiepolo@crystal.unipv.it)¹,
Roberta Oberti (oberti@crystal.unipv.it)²,
Elio Cannillo² &

Riccardo Vannucci (vannucci@crystal.unipv.it)¹
¹ Dipartimento di Scienze della Terra, Università di Pavia,
via Ferrata 1, Pavia, Italy

² CNR-CSSC, via Ferrata 1, Pavia, Italy

Titanite is a common accessory mineral in many magmatic and metamorphic rocks. Much attention has been paid to the displacive phase transition occurring both as a function of T and of composition (e.g., X_{Al}). However, systematic studies on trace-element partitioning between titanite and silicate liquids at different P, T and X conditions are rare, and limited to few elements of petrological relevance (Nb, Ta and REE). Reliable and representative sets of titanite/liquid partition coefficients would allow understanding its effects on the trace-element signature of magmas during fractional crystallisation and partial melting processes; moreover, modelling of trace-element incorporation as a function of the physical-chemical conditions in titanite might help to identify possible uses for technological materials or for radioactive-waste disposal.

Titanite crystals coexisting with silicate melts were synthesised at upper-mantle conditions (T = 1000°C; P = 1.5 GPa) from compositions around high-Ti lamprophyres, after doping with a large number of trace element including Large Ion Lithophile (LILE), High Field Strength (HFS), Rare Earth (RE) and selected transition elements. Major- and trace-element compositions of titanite crystals and of equilibrium glasses were determined by EMP and by Laser Ablation ICP-MS, respectively.

The euhedral habitus of the crystals and the absence of significant major-element zoning confirmed that the assemblages were at equilibrium, and thus allowed calculation of solid/liquid partition coefficients. With the exception of LILE (Rb, Ba, Cs), Pb and actinides (U, Th), all analysed elements were found to be compatible in titanite. S/LD >10) were observed for Ta⁵⁺ at the octahedral site and for middle REE at the Ca site, showing a strong structural control on the uptake of trace elements. These elements are in fact most similar in ionic radius and charge to the major constituents (Ti⁴⁺ and Ca²⁺, respectively). Trace elements become progressively less compatible with increasing differences in ionic radii. At similar ionic radii, incompatibility increases with the difference in ionic charge. At the octahedral site, Ti⁴⁺ and Ta⁵⁺ have nearly the same compatibility, whereas V³⁺ is slightly less compatible. At the Ca site, the partition coefficients of MREE are about 2 times lower than that of Ca. These preliminary results indicate that titanite may be a good repository of HFS, RE and transition elements, whereas it is not capable to incorporate large amounts of U, Th and Pb.

PCM6 : WEpm29 : G6 The Substitution of Al and F in Titanite at High Pressure and Temperature

Peter Tropper (peter.tropper@uibk.ac.at)¹,
Craig E. Manning² & Eric J. Essene³

¹ Institute of Mineralogy and Petrography, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

² Department of Earth and Space Sciences, University of California at Los Angeles, Geology Building, 595 N. Circle Drive, Los Angeles, CA 90095-1567, USA

³ Department of Geological Sciences, University of Michigan, C.C. Little Building, Ann Arbor, MI 48109-1063, USA

Experimental studies were carried out to evaluate phase relations involving titanite-F-Al titanite solid solution in the system CaSiO₃-Al₂SiO₅-TiO₂-CaF₂. The experiments were conducted at 900 - 1000°C and 1.1 - 4.0 GPa with various proportions of anorthite, fluorite, titanite, kyanite, quartz, and rutile. The F-Al content in the resultant titanite ranged from 0.51 ± 0.02 to 0.91 ± 0.05 mole percent. The average F/Al ratio is 1.01 ± 0.06, consistent with the substitution [TiO²⁺]₁[AlF²⁻]₁. Titanite compositions and coexisting minerals in the experiments constrain the locations of the equilibria

Titanite + Kyanite + Fluorite = F-Al Titanite + Rutile (TAFT)

and

Anorthite + Fluorite = F-Al Titanite (AFT)

The TAFT assemblage is stable only at high pressure (>1.5 GPa) at temperatures above 900°C, and XAl in titanite of 0.46 - 0.60. The temperature and pressure dependence of titanite composition in the TAFT assemblage is minor at the conditions investigated. The AFT assemblage is stable at low pressures (<2.0 GPa) and is stable over a wide range of titanite compositions, pressure, and temperature. Analysis of the phase relations indicate that titanite solid solutions coexisting with rutile are always low in XAl, whereas the maximum XAl of titanite solid solution occurs with fluorite and either anorthite or Al₂SiO₅. The results of this study indicate that the F-Al substitution in titanite depends on the nature and variance of the coexisting assemblage.

PCM6 : WEpm32 : G6 Apatite and Phosphorus Geochemistry of the Granitic Rocks of the Western Carpathians

Igor Broska (geolbros@savba.sk)¹,
Alexandre Aubin (etchouta@hotmail.com)² &
Patrik Konecny (konecny@gssr.sk)³

¹ Geological Institute SAS, Dubravská cesta 9, 842 26
Bratislava, Slovak Republic

² Unité d'enseignement en sciences de la terre, UQAC,
555 Blvd de l'Université, Chicoutimi, QC G7H 2B1,
Canada

³ Geological Survey, Mlynska dolina 1, 817 04 Bratislava,
Slovak Republic

Character of apatites significantly contributed to the recent granite typology of the Western Carpathians where the granites are divided into (1) orogenic group comprises Meso-Variscan (Late Devonian to Lower Carboniferous) mainly S- (less I-type) granites and Late-Variscan (Upper Carboniferous) I-type tonalites to granodiorites and (2) anorogenic group which is represented mainly by specialised (rare-element) S-type granites in Gemicic superunit. The phosphorus geochemistry deeply reflects the composition of the felsic magmas. The Meso-Variscan crustal granites which have mostly the S-type affinity show low correlation in the variation of SiO₂ vs P₂O₅ and usually there is a typical increasing of P in the late differentiation products. The monazite, xenotime and apatite control the distribution of P in those melts together with the late K-feldspars and alkali feldspars in their differentiated rocks. The albite in the pegmatites (differentiated products) of Meso-Variscan S-type granites contains 0.2 wt.% of P₂O₅ and K-feldspar locally up to 0.6 wt.% of P₂O₅. In these genetic group of granites the black pigmented (dusky) apatites are sometimes very common (90 vol.% of apatites are dark). The normalized REE patterns show a distinct Eu-negative anomaly with higher content of HREE - (Ce(ppm)/Yb(ppm)) = 257). On the other hand, the Late-Variscan I-type granitoids show the fractionation of apatite which is indicated by high correlation between SiO₂ and P. Fractionation of precipitated apatite as an early magmatic phase regularly decreases P in the felsic melts. Apatite from this point of view is the only accessory mineral phase controlling the distribution of the phosphorus in the I-type granites. The P, besides in early apatite, is in the I-type

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granites incorporated only to the late K-feldspars and the contents of P_2O_5 reaches locally 0.2 wt%. The REE normalized patterns in apatites is without Eu-negative anomaly. The specialized rare metal Permian anorogenic S-type granites show completely different relations. Their alkali feldspars are richer in P and only small amount of apatite is usually present in these rocks. The albite of these specialised granites contain 0.3 wt.% P_2O_5 and K-feldspar 0.5 wt.% P_2O_5 in average. Alteration of granites due to the exsolution of the P and formation of new generation of tiny apatites in the alkali feldspars is observed. Apatite contain maximum of fluorine regarding stoichiometry. The C bearing granites and the Eu-negative anomaly found in apatite of granites with S-type affinity indicate the lower fugacity of oxygen or water activity in comparison with I-type granites. The apatite composition of S-type granites indicate that the original melt contained in average 30% more fluorine than I-type granites. The highest fluorine content in the melt was found in Permian S-type granites which contain F saturated apatites.

PCM6 : WEpm33 : G6 Towards a Better Understanding of Rare Earth Element Partition Coefficients in Zircon

John M. Hanchar (jhanch@gwu.edu)¹,
Robert J. Finch (finch@cmt.anl.gov)²,
E. Bruce Watson (watsoe@rpi.edu)³ &
Paul W. O. Hoskin (papanui@xtra.co.nz)⁴

¹ Dept. of Earth & Env. Sci., The George Washington Univ., 2029 G St., NW, Washington, DC, USA

² Argonne National Laboratory, CMT/205, 9700 S. Cass Ave., Argonne, IL 60439, USA

³ Dept. of Earth & Env. Sci., Rensselaer Polytechnic Inst., Troy, NY 12180, USA

⁴ Dept. of Geological Sciences, The Univ. of Canterbury, Private Bag 4800, Christchurch 8020, New Zealand

Over the past twenty years, there have been several studies concerning REE partitioning in zircon in geological systems. As would be expected from crystal-chemical size constraints, the results obtained from these studies revealed that the Heavy REE (HREE) are more compatible than the Light REE (LREE) in zircon. This is primarily a result of the decrease in ionic radius of the $3+$ REE from La to Lu as they approach ionic radius of Zr in zircon. On a plot of partition coefficients versus ionic radius, the general shape of the REE partition coefficients in zircon, for all of the previous studies, curve is convex upward, and there is a flattening of the partition coefficient curve at the HREE end of the curve.

A strain elasticity model was recently proposed (Blundy & Wood, 1994) in which partition coefficients may be calculated for minerals by assuming that the primary constraint on an element partitioning into a mineral is the strain caused by that element "fitting" into the site of interest. For zircon, depending which known partition coefficient is used in the model (e.g., La or Lu), the model predicts that either the LREE are much more incompatible in zircon, or the HREE are much more compatible in zircon, than what is observed in previous studies. One severe potential limitation in applying this model to zircon, is that charge-balancing of the trivalent REE in zircon (e.g., the xenotime substitution $Zr^{4+} + REE^{3+} Si^{4+} + P^{5+}$) is not taken into account.

We have recently experimentally measured the extent of $3+$ REE incorporation in synthetic zircon crystals, and determined the extent of the xenotime-type substitution. We determined that, as expected, there is an increase in the compatibility of the $3+$ REE from La to Lu; however, strain caused by P^{5+} substituting for Si^{4+} in the Si site eventually exceeds strain caused by $3+$ REE substituting for Zr^{4+} in the Zr site. Strain at the Si site caused by the small P^{5+} ion effectively limits the amount of REE $^{3+}$ that can be incorporated into zircon. This may explain the flattening of the partition coefficient curve in the HREE region of the curve in our results and in many of the previous studies, and the lack of flattening of the HREE in the results obtained using the strain elasticity model (Blundy & Wood, 1994). Thus, P^{5+} required for charge balancing limits the amount of REE $^{3+}$ that can be incorporated in zircon. When evaluating partition coefficients in zircon charge balancing of the REE $^{3+}$ for Zr^{4+} must be taken into account in order to better understand the system.

Blundy J. & Wood, B. *Nature*, **372**, 452-454, (1994).

PCM6 : WEpm34 : G6 Diffusion in Zircon Under Crustal UHT Metamorphic Conditions?

Andreas Möller (amoeller@mail.uni-mainz.de)¹,
Patrick J. O'Brien², **Allan Kennedy**³ &
Alfred Kröner¹

¹ Institut. f. Geowissenschaften, Geologie, Universität Mainz, 55099 Mainz, Germany

² Institut. f. Geowissenschaften, Universität Potsdam, 14415 Potsdam, Germany

³ Dept. of Applied Physics, Curtin University, Bentley, WA 6102, Australia

Results of experimental studies on the diffusivity of trace elements in zircon (Lee et al. 1997; Cherniak et al. 1997a, b; Cherniak & Watson, in press) indicate that ultra high temperature (UHT) crustal conditions affect zoning patterns of trace elements. This may be evident from blurring of back scatter electron and cathodoluminescence images. The experimentally derived diffusivities suggest that pure thermal diffusion may cause Pb-loss and disturb U-Pb systematics under such UHT crustal conditions. According to Cherniak & Watson (in press), 1000°C maintained over 100,000 to one million years should cause 10-30% Pb-loss in zircon of 100 micron diameter.

Natural zircon from ultra-high temperature (UHT) granulites which has been subjected to high temperatures for long time periods can provide a test for the experimentally derived data. Our field-based study centres on the regional metamorphic aureole of Rogaland, SW-Norway, where metamorphic conditions vary along a field gradient from amphibolite facies (about 600°C) to UHT granulite facies (>1000°C). Two pre-UHT and one UHT zircon age population can be distinguished, however, each age population occurs in the medium T as well as the UHT rocks, with no tendency of Pb-loss in the UHT rocks. There is also no correlation between U-Pb discordance and distance from grain rims. Metamorphic as well as pre-metamorphic grains preserve their age information and remain concordant despite metamorphic temperatures in excess of 1000°C. Our ion-microprobe results on UHT granulites from Rogaland thus do not show evidence for diffusive Pb-loss affecting the geochronological results in these rocks. Backscatter electron and cathodoluminescence images do not indicate blurring or extinction of trace element zonation in the most heated metamorphic rocks. Trace element profiles measured with electron- and ion-microprobe across zones with strongly contrasting concentrations are carried out to back up the information gained from U-Pb dating and imaging.

Thermally driven diffusion does thus not appear to be a viable and important mechanism for the mobility of Pb in natural, non-metamict zircon under even the most extreme crustal conditions.

Cherniak DJ & Watson AB, *Chemical Geology*, (in press).

Cherniak DJ, Hanchar JM & Watson AB, *Contrib. Mineral. Petrol*, **127**, 383-390, (1997a).

Cherniak DJ, Hanchar JM & Watson AB, *Contrib. Mineral. Petrol*, **134**, 289-301, (1997b).

Lee JKW, Williams IS & Ellis DJ, *Nature*, **390**, 159-162, (1997).

PCM6 : WEpm35 : G6 The Physical Behaviour of Radiation Damages in Apatites and Zircons under Pressure, Temperature and Stress

Anke S. Wendt (anke@dstu.uni-montp2.fr)¹ &
Olivier Vidal (vidal@ens.fr)²

¹ Laboratoire de Géophysique, Tectonique et Sédimentologie, Université Montpellier 2, Place Eugène Bataillon, 34095 Montpellier, France

² Laboratoire de Géologie, Département TAO, Ecole Normale Supérieure, 24, rue Lhomond, 75005 Paris, France

The physical behaviour of fission tracks in zircons and apatites is studied by imposing geologically relevant parameters such as pressure, temperatures, stress and fluid supply experimentally on monocrystals of both mineral phases. In a first step, fluid confined externally heated horizontal autoclaves are used for investigating the influence of pressure, temperature, time, fluid supply and chemical composition of the minerals on the physical behaviour of the fission tracks. Wet experiments are performed at pressures of 100 MPa to 350 MPa and temperatures from 250°C to 500°C for the zircon and from 100°C to 500°C for the apatite. The crystals are exposed to these conditions for

time spans ranging from 140 hours to 500 hours. In a second step, pressure, temperature, time and mineral composition were investigated using an internally heated gas confined autoclave at pressures of 600 MPa and temperatures of up to 500°C for several hundred hours. In a third step, triaxial constant load deformation experiments are performed at confining pressures of 300 MPa and temperatures of up to 500°C on both types of crystal phases. This allows us to study the influence of pressure, temperature and stress on the fission track stability. Microscopical observations of the experimentally induced changes of the fission tracks are done on spontaneous tracks using TEM, SEM, optical microscopy and the micro-probe.

The first PT experiments on apatites of various compositions revealed that fission tracks are stable at temperatures of 250°C without less than 5% fading when pressure of 300 MPa are applied for a time span of 160 hours. According to this, fading was slightly stronger for the same temperatures and the same time span at lower pressures (100 MPa). Fading becomes nearly 40% for the same temperatures at ambient pressure. This clearly demonstrates that restoring radiation damages in the crystal lattice of apatite is dependent on temperature and pressure (and time) and not on temperature alone. We expect the same results for the restoring of radiation damages in zircons.

The results of this study will contribute to the understanding (1) of the physical behaviour and the structure of radiation damages in crystals and the mobility of Uranium in crystalline/metamict structures and (2) to define diffusional processes in crystalline structures as a function of pressure. It will allow us (3) to redefine the stability field of fission tracks in zircon and apatite (of given compositions) as a function of pressure, temperature, time, stress and supply of fluids. Both issues are important for any further quantitative theoretical analysis of Uranium doping of minerals as well as for the characterisation of exhumation paths and the determination of the age of young particular geological events (e.g. low grade shear zones) based on the FT method.

PCM6 : WEpm36 : G6 Structural Healing of a Radiation Damaged Zircon Under High Pressure

Petra Simoncic (petra@kristall.erdw.ethz.ch)¹,
Martin Kunz (kunz@kristall.erdw.ethz.ch)¹ &
Urs Schaltegger (urs.schaltegger@erdw.ethz.ch)²

¹ Laboratory of Crystallography, ETH Zurich, Switzerland

² Institute for Isotope Geochemistry and Mineral Resources, ETH Zurich, Switzerland

Zircon is a common accessory mineral in igneous, metamorphic and sedimentary rocks. For earthsciences, this mineral is of great importance because of its use for U-Th-Pb age determination. The presence of uranium and thorium, however, causes considerable radiation damage of the crystal lattice through alpha decay. This radiation damage leads to a progressive amorphization of the crystal structure. It is therefore of great interest to learn about the behavior of zircon under different pressure and temperature conditions as a response to different geological environments. The sample of our study is a zircon in an early stage of metamictization (350 Ma, 500 to 900 ppm U). This can be seen by the enlarged unit cell and the still sharp but less intensive x-ray diffraction peaks (Murakami, 1991), indicating only a minor part of the structure to be damaged. Defects are thus presumed to be local without any coherent amorphous regions.

The metamict zircon was investigated by powder synchrotron X-ray diffraction, which was performed at the SNBL beamline of ESRF in Grenoble. Maximal pressure attained during this experiment was 6 GPa. Le Bail profile refinements were applied to the diffraction pattern in order to determine the unit cell parameters. As a comparison an identical experiment was performed on a synthetic, nonmetamict zircon.

The volume of the U-bearing zircon before the experiment was determined as 265.24(9) Å³. The decrease of the unit cell for the U-bearing sample shows a conspicuous step-wise collapse-behavior, with a very soft behavior at low pressures and increasingly stiff ranges between the collapse-regions. Therefore, no reasonable bulk modulus can be calculated for the metamict zircon on the compressive branch. During decompression, the increase of the volume is continuous and returns to an ambient pressure value of 264.41(8) Å³, i.e. significantly smaller than the starting value. The P-V curve on decompression can be

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modeled with a Birch-Murnaghan equation of state with values of $K_0 = 244(1)$ GPa, $V_0 = 264.185(8)$ Å³, K' fixed at the value of 6.5. These results are very similar compared to the values of the synthetic zircon ($V_0 = 261.16(4)$ Å³, $K_0 = 236(1)$ GPa)

Weber (1990) reports the annealing of radiation defects in zircon over geologic times under ambient conditions. We interpret the stepwise compression behavior and the volume decrease after a compression experiment as an indication for a partial healing of defects in the zircon structure. This indicates that the application of pressure may provide the necessary activation energy to accelerate a healing of structural defects in low metamict zircons. These results may have implications for the behavior of a zircon stored under lower crustal conditions over geological times, as the diffusivity of lead is governed by the presence of defects in the crystal lattice.

Murakami T, Chakoumakos B, Ewing EC, *Am. Mineral.*, **76**, 1510-1532, (1991).

Weber WJ, *J. Mater. Res.*, **5**, 2687-2697, (1990).

PCM6 : WEpm37 : G6 Control of Substitution on Apatite Fission Track Annealing

Jocelyn Barbarand (j.barbarand@ucl.ac.uk),
Andy Carter & Anthony J. Hurford
Department of geological sciences, University College
London, Gower street - London, WC1E 6BT, United
kingdom

Apatite fission track thermochronology is a valuable tool used by geologists to constrain low-temperature thermal histories. Apatite (Ca₅(PO₄)₃(F,Cl,OH) fission track (FT) annealing corresponds to the progressive shortening of ²³⁸U derived fission fragments. Whilst temperature and time have a first order control on annealing, other factors such as crystallographic orientation and apatite composition can also have an influence. Crystallographic variation is reduced by measuring tracks only on prismatic sections. At present our understanding of the compositional-based effects is incomplete. The role of anion substitution has been well documented: tracks present in chlorapatite are more resistant to annealing than those in fluorapatite (Green et al., 1986). However, Cl/F control does not explain all of the observed variation. Attempts to define the role of substitution into the calcium site on FT annealing have so far been unsuccessful (Carlson et al., 1999).

We reassess the role of chlorine and fluorine on FT annealing and consider other P- or Ca-substitutions. New laboratory isothermal annealing experiments (10-, 100-, 500- and 1000-hours), have been undertaken using 13 apatite samples of different origin and composition. Electron microprobe and ICP-MS as well as X-ray diffraction have been used to characterise each apatite sample. Induced horizontal confined track lengths are used to monitor fission track annealing with each sample being measured by several analysts.

Cl substitution is associated with greatest resistance to FT annealing, but the relationship between Cl content and level of annealing is not linear: apatites with 0.4-0.6 Cl atom per formula unit (apfu) show longer tracks than apatites with a Cl content of > 1 apfu. For fluorapatite, samples show a large range in response to annealing; for example, using the same annealing conditions, mean confined track lengths can range between 0 and 10 µm. The different controls on fission track annealing will be discussed.

Carlson WD, Donelick RA & Ketcham RA, *Am. Mineral.*, **84**, 1213-1223, (1999).

Green PF, Duddy IR, Gleadow AJW, Tingate PR & Laslett GM, *Chem. Geol. (Isot. Geosci. Sect.)*, **59**, 237-253, (1986).

PCM6 : WEpm38 : G6 Case Study of Metamorphic Zircons from Alpine HP/LT Metamorphic Rocks from Syros, Cyclades, Greece

Frank Tomaschek (ftom@nwz.uni-muenster.de)¹,
Allen Kennedy (ikennedy@info.curtin.edu.au)²,
Igor M. Villa (igor@mpi.unibe.ch)³ &
Chris Ballhaus (chrisb@nwz.uni-muenster.de)¹

¹ Institut für Mineralogie, WWU Münster, Corrensstrasse
24, 48149 Münster, Germany

² CEMS, Curtin University of Technology, Kent St.,
Bentley 6102 WA, Australia

³ Isotopengeologie, Universität Bern, Erlachstrasse 9a,
3012 Bern, Switzerland

We investigated zircons from a HP/LT-metamorphic terrane, combined imaging, mineral chemical and isotopic analysis and obtained new information on how zircon can respond to metamorphism.

Complex zircon populations were separated from meta-acidic rocks [jd+pa+qtz] prevailing, which have undergone Alpine HP/LT-conditions (ca. 500°C / 15 kbar). In addition to euhedral, clear pristine zircons, turbid inclusion-packed grains of the same simple medium- to short-prismatic morphological type and skeletal zircons were examined from the same samples. Imaging (SE, BSE, CL) often reveals corrosive pits or channels intruding from the grain surface accompanied by various degrees of internal alteration. Pristine zircon grains often show pronounced or weak oscillatory zoning parallel to crystal faces. This pattern gives way to irregularly curved altered patches, which are characteristically rich in xenotime and fluid inclusions. EMPA elemental mapping was carried out on individual zircon grains that contain both relict and altered domains. These measurements reveal that trace elements, except Hf, which substitute in the crystal lattice of zircon are redistributed. Particularly, P, Y, REE and Th are enriched in relict zircon-1 but low in zircon-2, where these elements are now stored in (Y, REE, Th)-phosphate phases instead. U-Pb-ages and Th/U-ratios were determined using SHRIMP. In samples from Grizzas locality e.g., pristine zircons and relict domains yield Cretaceous age (ca. 80 Ma, medium-high Th/U). Several younger spots (ca. 70-55 Ma, variable Th/U) may be geologically meaningless, resulting from incomplete resetting or sampling multiple domains within a single analysis spot. However, a cluster with low Th/U-ratios (< 0.1) forms a well defined group at 53 ± 1 Ma. This age agrees with both, an Ar-Ar-paragonite step heating age of 52 ± 1 Ma from the same rock and the established regional white mica age pattern. Additionally, zircon and paragonite indicate another event at < 30 Ma. It is therefore possible to correlate the formation of metamorphic zircon with the petrological evolution of the rock, pointing to the importance of fluid-driven recrystallization towards the end of Eocene HP/LT-metamorphism. Recrystallization via solution-precipitation provides a fast and effective mechanism and is consistent with the observed zircon characteristics, eventually resulting in complete "pseudomorphic" replacement of preexisting zircon-1 by the inclusion-packed grains of zircon-2. Due to the short time span between primary zircon formation and recrystallization, radiation-damage seems unlikely to be the main controlling factor. The total α -doses calculated from most enriched relicts are $D < 0.1 [10^{16} \alpha\text{-decays/mg}]$, insufficient to reduce the zircon to metamict state. The physicochemical environment or trace element content plays a more important role for the zircon recrystallization process. Zircon-1 corresponds to Cretaceous zircons from Syros which have previously been interpreted as metamorphic (Bröcker & Enders 1999); this seems supported by Lu-Hf whole rock ages (Lagos et al. 2001).

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Wednesday PO Session

PCM6 : WEpo01 : PO Replacement of Monazite by Florencite during Hydrothermal Alteration

Franz Bernhard (bernhard@egam.tu-graz.ac.at)
Institut für Technische Geologie und Angewandte
Mineralogie, Technische Universität Graz,
Rechbauerstraße 12, A-8010 Graz, Austria

Monazite, ideally CePO₄, is a wide-spread accessory mineral in igneous, metamorphic and sedimentary rocks. It is highly stable during weathering and also often during metamorphism up to granulite facies conditions and migmatization. The stability of monazite during metamorphism, however, appears to depend on rock type and associated fluids. Monazite grows in pelitic rocks from ca. 450°C onwards, whereas in metamorphosed granitoids, primary magmatic monazite can be partly or totally replaced by apatite, allanite and epidote at the same metamorphic conditions (Finger et al., 1998). This kind of monazite alteration requires addition of Ca through metamorphic fluids.

A different type of fluid-assisted monazite replacement is observed in alteration zones adjacent to Permo-Triassic hydrothermal lazulite(MgAl₂(PO₄)₂(OH)₆)-quartz veins in polymetamorphic metapelites and metapsammities of the Lower Austroalpine Grogneis complex, Styria, Austria (Bernhard et al., 1998). The alteration zones are composed of quartz, muscovite, Mg-rich chlorite (XMg = 0.70-0.85), rarely kyanite and chloritoid, apatite, zircon, rutile, xenotime and monazite/florencite. Preliminary mass-balance calculations for an alteration zone in quartzitic mica schists at Höllkogel indicate a significant loss of Fe, Mn, Na and a ca. three-fold enrichment of Mg, based on the assumption of Ti- and Zr-immobility during hydrothermal alteration.

In the proximal parts of the alteration zones (0 to ca. 0.5 m away from the veins), primary metamorphic monazite is largely replaced by florencite, ideally CeAl₃(PO₄)₂(OH)₆. Up to 0.2 mm large, anhedral to subhedral florencite crystals typically enclose several up to 0.03 mm large relics of primary, corroded monazites. A significant fractionation of REE between monazite and florencite is not observed. Assuming constant REE, addition of Al, P and H₂O is necessary for the transformation of monazite to florencite. This would result in a ca. three-fold volume increase compared to the precursor monazite. Aluminum and P are major elements of lazulite-quartz veins, and breakdown of monazite to florencite in the alteration zones can be most probably related to the hydrothermal fluids associated with vein formation. This interpretation is supported by the occurrence of accessory florencite as the sole LREE-bearing mineral in the lazulite-quartz veins itself, suggesting instability of monazite, and stability of florencite, in the vein-forming fluids.

Distal parts of the alteration zones (> 0.5 m away from the veins) are enriched in Mg, but lack the replacement of monazite by florencite. Unaltered metapelitic country rocks contain monazite with ages between 340 and 250 Ma, belonging to a Variscan amphibolite facies and Permian HT-LP event (Bernhard et al., 2000). This monazite is usually fresh or can be partly replaced by apatite and REE-bearing epidote. This replacement can be related to the Eo-Alpine greenschist to lower amphibolite facies metamorphic overprint of the area.

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PCM6 : WEpo02 : PO
Formation of Zircon and Srilankite during High-Grade Metamorphism of Mafic Rocks. Example from the Caledonides of W Norway and Implications for Zircon Geochronology

Bernard Bingen (bernard.bingen@ngu.no)¹,
Håkon Austrheim

(hakon.austrheim@toyen.uio.no)²,

Martin Whitehouse (martin.whitehouse@nrm.se)³

& **Joakim Mansfeld** (joakim.mansfeld@ngu.no)¹

¹ Geological Survey of Norway, 7491 Trondheim, Norway

² Mineralogisk-Geologisk Museum, University of Oslo,

0562 Oslo, Norway

³ Swedish Museum of Natural History, SE 104 05

Stokholm, Sweden

The Proterozoic Lindås Nappe is situated in the Caledonides of W Norway. It was affected by penetrative Sveconorwegian granulite-facies metamorphism, followed by a fluid-driven eclogite- and amphibolite-facies Caledonian overprint. This overprint is spatially restricted along fractures and shear zones. In mafic granulites and amphibolites, a luminescent anhedral zircon overgrowth which gives an average age of 924 ± 58 Ma (Th/U = 0.52; SIMS data) surrounds a magmatic zoned core with an age of 952 ± 32 Ma (Th/U = 1.27). In the granulites, a continuous rim of zircon or a discontinuous corona of ca. 10 μ m rounded to flat zircon crystals is observed at the outer margin of ilmenite grains. Baddeleyite (ZrO₂) and srilankite (Ti₂ZrO₇) blebs are reported around ilmenite included in feldspar or pyroxene. Baddeleyite is interpreted as an exsolution product from magmatic ilmenite. Srilankite was formed as a reaction product between ilmenite and baddeleyite during granulite-facies metamorphism in silica deficient subsystems. The zircon corona around ilmenite and the luminescent zircon overgrowth were also formed as a reaction product during granulite-facies metamorphism where silica was available at grain boundaries. Textures suggest that magmatic ilmenite was a main source of Zr to form metamorphic zircon. LA-ICP-MS analyses of ilmenite are in progress to test this hypothesis. In massive amphibolites, relic ilmenite grains are surrounded by a corona of titanite and a discontinuous corona of micro-zircons. Amphibolite-facies overprint is not associated with any significant growth or dissolution of zircon. An unshattered eclogite displays a zircon population with an euhedral oscillatory zoned overgrowth giving an age of 455 ± 29 Ma (Th/U lower than 0.13). A corona of micro-zircon grains is observed at some distance around rutile, and locally these zircons show a prismatic overgrowth. A specific low-Th zircon growth event is related to eclogite-facies forming reactions, involving breakdown of a two-pyroxene + garnet + plagioclase + ilmenite assemblage to form a garnet + omphacite + rutile assemblage in the presence of a fluid. The low Th content of this zircon probably stems from the coeval precipitation of clinzoisite. This oscillatory zoned zircon records fluid infiltration and coeval Caledonian eclogitization in the crust.

PCM6 : WEpo03 : PO
Relationship between the Microstructure and the Retention Properties of Apatite

Fatima-Zahra Boujral¹, Nicolas Menguy², Guillaume Morin², Georges Calas² & Rajaa Cherkaoui El Moursli³

¹ Laboratoire de Physique Nucléaire, Fac. des Sci., BP. 1014, Av. Ibn Battouta, Rabat, Maroc, Depart. de Phys. Appli., Faculté des Sciences et des Techniques, B.p. 523, Beni Mellal, Maroc

² Laboratoire de Mineralogie Cristallographie, Case 115, 4, Place Jussieu, F-75 252 Paris Cedex 05, France

³ Laboratoire de Physique Nucléaire, Fac. des Sci., BP. 1014, Av. Ibn Battouta, Rabat, Maroc

Sedimentary phosphates contain 50 to 200 ppm of uranium in partial radioactive equilibrium and therefore are radon emanation sources. These contain 60 to 80% of apatite (Berrada et al., 1995 and Boujral et al., 1999), the actual nature of which not yet well understood. The aim of this study is to examine the parameters which influence the radon diffusion processes and the contribution of the microstructure to the apatite retention properties. We have paid a special attention to the influence of thermal annealing on radon retention. The emanating efficiency has been examined before and after heating at temperatures comprised between 100 and 900°C, for two hours. The radon content was determined by gamma-ray spectrometry (Berrada et al., 1995). As defined in our recent studies (Boujral et al., 1999 and 2000), the heat treatment has been involved: 1) in a short term to the release of the radon

existing prior sample heating, 2) in a long term to the retention of the radon formed after heating. The structure of apatite and texture of phosphate have been studied by X-ray diffraction (Rietveld structure refinement and diffraction peak profile analysis) and transmission electron microscope (TEM). The form and the size (MCD) of apatite crystals measured by MET were in close agreement with data of coherent domain derived from X-ray diffraction analysis. This study confirms the relation between the radon release and retention and the microstructure of the apatite. Indeed, the radon release is related to the associated annealing processes and kinetic of crystalline growing, whereas the radon retention is only related to the texture (specific area). During annealing, the specific surface decreases as crystal size increases, which explains the observed radon release. According to this understanding, the second effect of heat treatment is a consequence of the first one.

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PCM6 : WEpo04 : PO
Nuclear Wastes Conditioning: How to Increase the Stability of Apatites?

Jöelle Carpéna (carpe@bahia.cad.cea.fr)¹ & **Jean Louis Lacout²**

¹ CEA/DCC/DESD/SEP/Bât.307, Cadarache, 13 108 Saint Paul lez Durance cedex, France

² Laboratoire Matériaux, ENSCT, 38 rue des 36 Ponts, 31 400 Toulouse, France

Apatites form a large family of isomorphous minerals with the general formula Me₁₀(XO₄)₆Y₂ that generally crystallize in the hexagonal system (spatial symmetry group P6₃/m). The most encountered natural apatite is the phospho-calcic fluorapatite, however, this stoichiometry is not able to incorporate significant amount of cationic dopant. As a matter of fact, and based on natural analogy, britholites (silicated apatites) have been identified to be potential host phases (Carpéna et Lacout, 1997). Various apatites (natural and synthetic) have been studied to test different substitutions: - substitutions on the Y anion site : F, Cl, OH, O²⁻, - substitutions on the (XO₄) anionic groupment: the complete solid solution between the full-phosphated apatite and the full-silicated apatite, - substitutions on the Me cationic site: La, Nd, Eu, Gd, U, Cs To investigate the apatitic structure behaviour in the aim of High Level Wastes immobilization, a pluridisciplinary study has been performed (Carpéna, 1998; Boyer et al., 2000; Senamaud et al., 1999 ; Soulet et al., 2000 ; Meis et al., 2000) displaying now: - the cristallography of the different britholites, - the effect of the different substitutions on the thermal annealing of amorphized zones, - the effect of substitutions on the balance between creation and annealing of damages in the structure, - a computational study of the structure. The different data obtained give a good approach of the different substitutions which allow to obtain a stable material. Our study let us to valid the stoichiometry which, in natural analogs, had demonstrated its stability. The study is going on.

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PCM6 : WEpo05 : PO
Zircon and Zircons: Unveiled by the Stepwise Leach Experiment

Fukun Chen (fukun.chen@uni-tuebingen.de),
Wolfgang Siebel

(wolfgang.siebel@uni-tuebingen.de) &

Muharrem Satir (satir@uni-tuebingen.de)

Institut für Mineralogie, Petrologie und Geochemie,

Universität Tübingen, Wilhelmstraße 56, 72074

Tübingen, Germany

In order to obtain more concordant U-Pb ages, zircon grains usually are abraded using the Krogh method (1982) or are leached stepwise in HF-acid, before complete digestion. For zircon grains with a complex internal heterogeneity, e.g. irregular metamict domains, the chemical method should be a better way to achieve this aim (e.g. Mattinson, 1994). But, an artificial U-Pb fractionation causing reverse discordance and/or artificial too-high ²⁰⁷Pb/²⁰⁶Pb ratios have been reported after chemical treatment (e.g. Corfu, 2000). Of interest in the behaviours of Pb and U of chemically and structurally homogenous zircons during the extraction by the stepwise leach method, zircons from the Palaborwa complex, South Africa, and from Kuehl Lake, Canada, are leached in HF-acid to read the information.

Fragments of the Palaborwa zircon have been well dated at 2052 Ma by the evaporation method (e.g. Kröner & Willner, 1998). U-Pb dating on one fragment without any treatment yield discordant ages of 1961 ± 2 Ma (²⁰⁶Pb/²³⁸U) and 2006 ± 2 Ma (²⁰⁷Pb/²³⁵U). After leached with HF-acid at different temperatures and different pressures, residue of another fragment yield obviously older but highly concordant ages of ca. 2068 \pm 2 Ma. About 23% of total radiogenic Pb and 24.5% of total U were extracted in the four leach steps. At the first leach step, 11% of Pb but only 7% of U were extracted and so a reverse discordance is yielded. Solutions of three successive leach steps give discordant ages in different degrees and have higher radiogenic ²⁰⁶Pb/²⁰⁶Pb ratios than the zircon residue.

Two fragments of the Kuehl Lake zircon were evaporated and dated at 1063 ± 2 Ma and other two fragments without chemical treatment yield nearly concordant U-Pb ages of 1066 ± 2 Ma. The results agree with the reported U-Pb ages of 1065 Ma (Wiedenbeck et al., 1995). Three fragments were leached in HF-acid by employing the same procedure above. Only 1% of the total radiogenic Pb was extracted by the leach steps. But, the zircon residues yield more discordant and older ²⁰⁷Pb/²⁰⁶Pb ages (1072 ± 1 , 1079 ± 2 , and 1082 ± 1 Ma), indicating artificial ²⁰⁷Pb/²⁰⁶Pb ratios, as no inherited core has been detected.

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PCM6 : WEpo06 : PO
Combining Microscopic (SEM-BSE), Microanalytical (EMP+SIMS) and X-Ray Diffraction Techniques in the Study of Igneous Rock Samples for Geochemical Modelling

Giancarlo Della Ventura

(dellaven@uniroma3.it)¹,

Roberta Oberti (oberti@crystal.unipv.it)²,

Luisa Ottolini (ottolini@crystal.unipv.it)² &

C. Terry Williams (t.williams@nhm.ac.uk)³

¹ Largo S. Leonardo Murialdo 1, Roma, Italy

² CNR-CS per la Cristallografia e Cristalochimica, Via

Ferrata 1, Pavia, Italy

³ Dept. of Mineralogy, The Natural History Museum,

Cromwell Road, London, SW7 5BD, London, United

Kingdom

Understanding the mobility, complexation, and transport of elements (e.g., light and/or RE) that are commonly used as petrogenetic indicators is still a challenge in mineralogy and geochemistry. Recent studies (e.g., Oberti et al. 1999; Della Ventura et al. 1999) done combining X-ray single-crystal diffraction, micro-analytical (electron microprobe for medium-Z and ion microprobe for light- and heavy-Z elements) analyses, high-resolution electron (SEM and BSE, TEM) microscopy, and spectroscopic (IR) techniques, showed that several igneous (volcanic and sub-volcanic) rocks contain dispersed REE- and actinides-bearing accessory phases with size at the micron

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Physicochemical Behaviour of Accessory Minerals

or sub-micron scale. Some of these phases possibly originated from late-stage fluids linked to residual magmas and enriched in incompatible elements. However, other phases can be related to late-to-post-magmatic processes, such as the assimilation of country rocks. These mineralisations can be easily overlooked using standard petrographic techniques. An important consequence is that great care should be exerted when using bulk-rock trace-element data for geochemical modelling.

Here we present two examples of such mineralisations. One is from a syenitic volcanic ejectum from Latium (Italy), which contains several accessory phases including zircon, fluoro-apatite and britholite, and REE- and actinide-bearing silicophosphates with compositions close to cheralite-brabantite plus bastnaesite. The rare borosilicate hellandite is also present, and is typically associated with britholite; SEM-BSE observations suggest that it originated from britholite after reaction with boron-rich late-stage fluids. Accurate SIMS and SEM-BSE investigations showed that most hellandite crystals are very strongly zoned in (Li, Be) vs. (REE, actinides) contents.

The second example is from a pegmatitic rock-fragment from the Evans-Lou quarry (Quebec, Canada) that contains fergusonite, kanoite, tenerite, xenotime, wakefieldite and hellandite. Detailed SEM-BSE and SIMS data show that late-stage fractures crossing the specimen are filled by micro-crystals of an Y-silicate with extreme inter- and intracrystalline zoning of REE and actinide contents. An high amount of B, corresponding to hellandite-composition, was found in a microarea of the same thin section that also contains dispersed and small (50-100 µm) crystals with high relief. EMP and SIMS microanalyses indicate that this latter phase is an hydrous silicate extremely enriched in actinides (ThO₂ + UO₂ summing up to > 57 wt%) and REE (Y₂O₃ + REE₂O₃ up to > 16 wt%), and depleted in CaO (~ 1 wt%). Special SIMS procedures were developed with the scope of complete quantification, and the excellent agreement between ion- and electron-probe data (where possible) provides another example of the extreme flexibility of SIMS for the analysis of trace, minor and even major elements in chemically complex matrices. The composition of this mineral is definitely unusual when compared to those of the (Th, Y)-silicates known so far.

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PCM6 : WEpo07 : PO Hydrothermal Alteration of Accessories in Carbonatites from the Kola Carbonatite Province, NE Russia

Ruslan Liferovich (rlife@mail.ru)¹,
Elena Balaganskaya
(balagan@geo.kolasc.net.ru)¹,
Kauko Laajoki (kauko.laajoki@oulu.fi)² &
Seppo Gehor (seppo.gehor@oulu.fi)²

¹ Geological Institute of KSC RAS, 14 Fersmana Street, Apatity, 184200 Russia

² Institute of Geosciences, Oulu University, PL-3000, 90014, Oulu, Finland

High-temperature alterations touched big volumes of carbonatites and phoscorites occurring within alkaline-ultramafic massifs of Kola carbonatite province and caused both in-situ replacement of major silicates and late generations of accessories. Local tectonism coupled with circulation of alkaline carbohydrotherms [1, 2, 4] affected mostly late carbonatites intruded along faults. The intensity of alteration is higher in those rocks showing more cataclasis. Minor and accessory pyrrhotite, fluorapatite, zircon, baddeleyite and pyrochlore were being altered with solutions. Under moderate fluid:rock ratio minerals were being replaced or corroded, under the fluid-abundant conditions pyrrhotite, brankite, probably fluorapatite were leached leaving cavities. The fissures and vugs in the late carbonatites bear the latest mineral assemblages composed of the elements released from altered accessories. Composition of pseudomorph after pyrrhotite in altered carbonatites depended on chemistry of solutions employed: pyrite formed under high log *f*H₂S, magnetite under high O₂ fugacity (the Kovdor, Vuorijarvi, Salmagora massifs), hydrous Fe-phosphates under P oversaturation (Kovdor), chlorite (everywhere). Siderite, crystallised under the same alterations in Khibina [4], was not formed in Kovdor, Vuorijarvi and Sebyavir indicating low CO₂ fugacity. It shows that temperature of the hydrotherms was below 270°C, which is the point of degassing of carbonatite-derived fluid [1]. Primary fluorap-

atite was corroded and replaced for carbonate-hydroxylapatite, which contains 2-2.5 wt% less P₂O₅. In the Kovdor, intense apatite alteration was probably the reason for oversaturation of solutions with P resulted in hydrothermal phosphate mineralization in vuggy carbonatites. Alteration of zircon took place in the carbonatites from Kovdor, where both intensive zircon dissolution or baddeleyite pseudomorphs after zircon appeared that agrees with experiments by Rizvanova et al. [3]. Moreover, baddeleyite as well as pyrochlore were corroded also (Kovdor, Vuorijarvi, and Sebyavir). The realised Zr formed in vugs calcapatite, Na₂ZrSi₃O₇·2H₂O which, in turn, was replaced with unknown Zr-hydrophosphate in Kovdor; in Vuorijarvi were also crystallized: komkovite (BaZrSi₃O₇·3H₂O), hilairite (Na₂ZrSi₃O₇·3H₂O), georgechaoite (KNaZrSi₃O₇·2H₂O) and gaidonnayite (Na₂ZrSi₃O₇·2H₂O). The hydrothermally mobilised Nb formed in altered carbonatites from Vuorijarvi and Sebyavir belkovite (Ba₃Nb₆(Si₂O₇)₂O₁₂), hochelagaite (ANb₂O₁₁·8H₂O, where A=Ca, Na or Mg); nenadkevichite and labuntsovite series minerals were also formed in Kovdor and Vuorijarvi. Abundant ancyllite-(Ce) pseudomorphs after brankite in altered carbonatites from Vuorijarvi and Sebyavir had been formed under REE low mobility, contrary to removal of REE under hydrothermal alteration of accessory fluorapatite in Kovdor's carbonatites. Hydrothermal alterations of accessories resulted in late mineralization of Zr and Nb related to altered carbonatites. Unstability of the accessories under influence of carbonatite-derived alkaline carbohydrotherms can be responsible for misleading with zircon- and baddeleyite-based geochronology of the phoscorites-carbonatites and host alkaline rocks.

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PCM6 : WEpo08 : PO Crystal Chemistry of Brabantites-Monazite Solid-Solutions

Jean-Marc Montel (montel@cict.fr)¹ &
Jean-Luc Devidal (devidal@opgc.univ-bpclermont.fr)²

¹ LMTG Minéralogie, 39 allées J. Guesde, 31000 Toulouse, France

² LMV, 5 rue Kessler, 63000 Clermont-Fd, France

The brabantite substitution (Ca²⁺ + Th⁴⁺ = 2 REE) is a way to introduce actinides in the monazite structure. We systematically studied the possible substitutions in brabantite CaTh(PO₄)₂. Synthesis were carried out by dry synthesis at 1 atm., flux-assisted crystallisation at 1 atm., and hydrothermal techniques at 2 kbar. The products were characterised by microprobe and XRD. The results can be summarised as follow. (1) CaTh(PO₄)₂, SrTh(PO₄)₂, PbTh(PO₄)₂, always yielded a typical monazite structure. CdTh(PO₄)₂ and BaTh(PO₄)₂ can also take the monazite structure. The evolution of unit-cell parameters of brabantites with the ionic radius of cations is very regular and mimics the evolution known for the REEPO₄ series (2) Cd-brabantite can be obtained only at 1 atm. Under pressure, a triclinic, slightly distorted polymorph is obtained (3) Ba-brabantite was obtained only hydrothermally at 2 kbar. At 1 atm. a monoclinic polymorph with an approximately doubled unit-cell volume is obtained. (4) Attempts to replace Ca by Ni and Co, or Th by Hf and Zr have been unsuccessful. (5) At 1 atm. the LaPO₄-brabantite solid solutions are continuous for the Ca, Sr, Cd and Pb. (6) In the Ba-brabantite-LaPO₄ solid solution there is a miscibility gap with about a maximum of 50% mole of Ba-Brabantite in LaPO₄. The presence of such an immiscibility gap indicates that the Ba-Brabantite-LaPO₄ solid solution is non-ideal. (7) The non-linear evolution of the unit-cell parameters with progressive substitution suggests that the LaPO₄-PbTh(PO₄)₂ is non-ideal. On the contrary, the unit-cell parameters of other brabantite-LaPO₄ solid solutions vary linearly with the degree of substitution. Monazite seems then to be a very soft structure, accepting in significant amounts ions with variable size and variable charge. As a consequence, we could expect natural monazite to contain a significant amount of Ba and Sr, and this could be used to determine the Sr isotopic ratios of monazite. We can also understand why monazite can accept very large amounts of radiogenic Pb, up to few weight percent for very old and very radioactive monazite.

PCM6 : WEpo09 : PO Zircon Trace Element Chemistry by LA-ICP-MS: A Monitor for the Magmatic-to-Hydrothermal Evolution of a Crystallizing Pluton?

Thomas Pettke (pettke@erdw.ethz.ch)¹,
Andreas Audetat (geomail2@vt.edu)²,
Urs Schaltegger (schaltegger@erdw.ethz.ch)¹ &
Christoph A. Heinrich (heinrich@erdw.ethz.ch)¹

¹ Isotope Geochemistry and Min. Resources, ETH

² Zentrum NO, CH-8092 Zurich, Switzerland

³ Dept. Geol. Sci., Virginia Tech, Blacksburg, VA-24061, USA

Zircon is most widely used for U-Pb dating of magmatic events, yet little is known about its minor to ultra-trace element chemistry, from magmatic to possibly hydrothermal stages of crystallization. Moreover, zircon is commonly argued to be resistant to post-crystallization overprint. The Sn-W mineralized Mole Granite in Eastern Australia hosts zircon populations that seem to have grown at several stages during its magmatic to hydrothermal evolution that is recorded over 2.5 Myrs by U-Pb systematics on zircon, monazite and xenotime (Schaltegger et al., 2001).

LA-ICP-MS analysis of major to trace elements revealed systematic differences between magmatic zircon in quartz phenocrysts, possible hydrothermal overgrowths in altered rock units, and zircon in free-grown quartz crystals from hydrothermal veins. All zircons are enriched in HREE up to 80000-times chondritic concentration and show a pronounced negative Eu anomaly. Magmatic zircon from unaltered rocks is characterized by fairly uniform trace metal contents that tend to decrease from core to rim, and by relatively high concentrations of Y, Fe and Mn. Chondrite-normalized REE patterns show Yb>Lu. Supposedly magmatic zircon affected by hydrothermal overprinting (occurring in alteration envelopes around hydrothermal veins) display a strong optical and chemical zonation. Virtually flat LREE sections (100-1000 times chondritic) and HREE enrichments (10000-40000 times chondritic), together with elevated Fe and Zr, and reduced Y, U and Hf contents are characteristic of core sections, whereas rims contain overall lower LREE contents with a variably pronounced, positive Ce anomaly. Zircon crystals within free-grown hydrothermal quartz are poor in Y, Fe and Mn, and show variable concentrations of trace elements. Chondrite-normalized REE patterns are HREE-enriched (<25000 times chondritic), show the typical negative Eu anomaly and are characterized by low La abundances (1 to 10 times chondritic). A progressively pronounced positive Ce anomaly is developed with decreasing absolute LREE content towards the rim of individual crystals.

The systematic changes in trace element contents and REE-patterns of zircon from various crystallization stages are tentatively interpreted to reflect chemical changes in the melt-fluid system during and after the crystallization of the Mole Granite. The oldest generation of zircon probably crystallized from fluid-undersaturated melts. Progressive fractional crystallization led to the exsolution of Cl-rich fluids, which resulted in major changes of the trace-element distribution in the system. Zircon as inclusions in free-grown hydrothermal quartz is chemically distinct from magmatic zircon, as are the rims of zircons from hydrothermally altered rocks. Our data suggest that zircon cannot be regarded as a closed system during hydrothermal overprint, and possibly may even crystallize from hydrothermal solutions. Clearly, the minor to ultra-trace element chemistry of Zr holds a great potential to distinguish magmatic from hydrothermal processes, once a more complete chemical characterization of such zircon populations becomes available.

Schaltegger et al., *J. Conf. Abs.*, **6**, (2001).

PCM6 : WEpo10 : PO On the Mechanisms of Allanite Alteration and their Geochemical Implications

Franck Poitrasson (franck.poitrasson@cict.fr)
Laboratoire de Géochimie, CNRS, 38, rue des 36 Ponts,
31400, Toulouse, France

Allanite is with monazite one of the main mineral hosts for REE in the continental crust and it has been shown to be a suitable mineral for Th-Pb magmatic geochronology (Barth et al., 1994). It is also well known that this mineral is prone to metamictization and not very resistant to alteration

PCM6

Physicochemical Behaviour of Accessory Minerals

(e.g., Ghent, 1972; Wood & Ricketts, 2000). We thus explored further the alteration mechanisms of this mineral, a monoclinic silicate of the epidote group with the general formula

$(Ca,Ce,La,Nd,Th)_2(F^{2+},Fe^{3+},Ti)(Al,Fe^{3+})_2(SiO_3)_2(OH)$, as well as the resulting behaviour of the lanthanides, actinides and Pb.

Various altered allanites from granodiorite (Pila-Canale) and hypersolvus aluminous granite (Mantelluccio) outcropping in Corsica (SE France) were studied. Observations by BSE-SEM revealed that alteration take mostly place along fractures penetrating the crystals, but certain allanite chemical compositions seem much more alterable than others within a given crystal. Electron microprobe analyses showed that two main alteration mechanisms occur in the mineral studied. In the allanites from the hypersolvus aluminous granite, alteration can be described by the substitution leading toward the epidote composition. In contrast, alteration of the granodioritic allanites are best represented by the chemical exchange $Al^{3+} + Ca^{2+} + REE^{3+} + Mg^{2+} \rightarrow Ti^{2+} + Th^{4+} + Fe^{3+}$, resulting in an overfilling of the M site with respect to the A site. This apparent structural discrepancy can be resolved if some of the iron goes in the rare earths crystallographic site (A) of allanite, or if crystallization of nanophases, structurally different from allanite and not visible by SEM occur.

Analyses by LA-ICP-MS show that these two alteration mechanisms are accompanied by contrasted REE behaviour. Whereas alteration in the granodioritic allanite results in the leaching of most rare earths, the alteration found in allanites from the hypersolvus aluminous granite are characterised by leaching of the middle rare earths and strong enrichment of HREE. This latter enrichment is compatible with the reduction of the lanthanide crystallographic site occurring during allanite to epidote transformation (Kumskova & Khvostova, 1964), as well as with the occurrence of HREE-rich fluids inferred from a Sm-Nd isotope study previously carried out at the mineral scale on the Mantelluccio granite (Poirasson et al., 1998). Nevertheless, the volumes of allanite affected indicate that these fluids with an exotic elemental and isotopic REE composition did not affect significantly the isotopic signatures of the bulk allanites and of the whole-rocks, in agreement with our previous isotopic investigations. Finally, these LA-ICP-MS analyses showed that for the U-Th-Pb systematics, allanite alteration seems mostly characterised by input of common lead. Hence, contrarily to monazite (Poirasson et al., 2000), dating of fluid-rock interaction through in situ analyses of allanite altered zones does not appear feasible.

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PCM6 : WEpo11 : PO Geochemical Heterogeneity of Zircons as a Criterion of Conditions of Metamorphic Rock Formation (An Example of the Urals)

Yulia Pystina (rmin@geo.komisc.ru)

Institute of Geology, 54, Pervomaiskaya St., Syktyvkar, 167982, Russia

Two types of zircons have been distinguished: terrigenous and metamorphogenic. Study of their microgeochemical composition has shown that: 1) separate morphological types of zircons from different metamorphic complexes in the Urals are comparable by U, Hf, Th, Pb, and Fe distribution; 2) U and Hf distribution in metamorphogenic zircons is normally non-uniform, indicating variation of physicochemical conditions at crystallisation; distinctions in U and Hf contents in the core and rims of metamorphogenic zircons suggest that the cores did not achieve complete homogenisation under metamorphic conditions; 3) terrigenous zircons are characterised by uniform U, Hf, Th, Pb, and Fe distribution, which can be explained by homogenisation of the terrigenous zircons, which failed to be trapped as "nuclei" for metamorphogenic zircon crystallisation; this suggestion is indirectly confirmed by similar isotopic ages of both the types; 4) according to the variations of the ZrO_2/HfO_2 value in zircons, their crystallisation could have occurred during both progressive and regressive stages of metamorphism.

PCM6 : WEpo12 : PO REE-Y-U-Th Rich Accessory Minerals in Topaz-Albite Granites of the Karlovy Vary Pluton (Czech Republic)

Milos René (rene@irms.cas.cz)

Institute of Rock Structure and Mechanics, AS CR, V Holešovičkách 41, Prague 8, Czech Republic

Topaz-albite granites of the Karlovy Vary pluton previously occur in Krudum massif that forms relatively independent magmatic body in the SW part of this pluton. Krudum massif has a markedly zoned internal structure with older porphyritic biotite granites in its central part and younger two-mica monzogranites and topaz-albite alkali feldspar granites on its periphery. In the area with occurrence of topaz-albite granites bonded are differently large ore deposits of Sn-W mineralisation of greisen type on these granites. The largest ore deposit was deposit Krásno-Horn Slavkov, where were Sn-W ores exploited from the 13th century till 1991. In this period, more than 30 000 tons of tin were extracted here. This ore district comprises more mineralized granite cupolas along the S and SE margin of the Krudum massif. The largest stocks of topaz-albite granites are those of the Schnöd and the Hub, which form complicated stock structure with well evolved inner structure. This inner structure comprises from the top pipes of gneissic breccia cemented by subvolcanic topaz-albite microgranites, irregular bodies of quartz-Li-mica-topaz greisens, greisenized, albitized and argillized topaz-albite granites, mica-poor aplitic topaz-albite granites with layers of feldspathites and unaltered topaz-albite granites. The topaz-albite granites underlying the whole cupola structure are rather homogeneous in mineralogical and chemical composition. Topaz-albite granites are mostly represented by medium-grained varieties locally accompanied by fine-grained porphyritic topaz-albite granites with characteristic snowball phenocrysts of quartz. K-feldspar forms porphyritic phenocrysts. Medium-grained equigranular topaz-albite granites contain quartz, albite (An0-10), K-feldspar, Li-mica and topaz. Accessory minerals are represented by apatite, fluorite, zircon, Nb-Ta-rutile, columbite-tantalite, monazite, xenotime, magnetite, uraninite, thorianite, pyrite, scheelite and cassiterite and by rare REE-minerals of As-crandallite-As-florenceite-As-goyazite group. Topaz-albite granites are strong peraluminous (A/CNK 1.10-1.63). These granites are also rich phosphorus (0.2-0.5 wt% P_2O_5). The high degree of magmatic fractionation of these granites is demonstrated by low Zr/Hf and Th/U ratios. In comparison with common Ca-poor granites the topaz-albite granites of the Krudum massif are poor in Ca, Fe, Mg, Sr, Ba, Zr, Sc and strongly enriched in incompatible elements such as Li, Rb, Cs, Sn, Nb and W. The REE contents are generally low. The chondrite-normalized patterns are relatively flat (LaN/YbN 1.6-4.8) having prominent negative Eu anomalies (Eu/Eu* 0.17-0.32). Optical cathodoluminescence allowed to distinguish three generations of apatite. All these apatites display intensive yellow CL indicative of significant Mn content in its lattice. Majority of analysed monazites are cheralite. For all analysed monazites is characteristic higher content of UO_2 (1.2-7.2 wt%). Content of UO_2 in analysed xenotimes is 2.0-5.2 wt%. This work is part of the KONTAKT project (No.ME-00-032).

PCM6 : WEpo13 : PO Dating of Magmatic and Hydrothermal Stages in a Mineralized Sn-W-Granite

Urs Schaltegger (schaltegger@erdw.ethz.ch)¹,

Andreas Audetat (geomail2@vt.edu)²,

Thomas Pettke (pettke@erdw.ethz.ch)¹ &

Christoph A. Heinrich (heinrich@erdw.ethz.ch)¹

¹ Institute of Isotope Geology and Mineral Resources, Federal Institute of Technology ETH, 8092 Zuerich, Switzerland

² Department of Geological Sciences, Virginia Tech, Blacksburg, VA 24061, U.S.A.

The Mole granite is a perfect field laboratory to study the sequence of magmatic to hydrothermal crystallization in a Sn-W-mineralized granite. This granite is part of the New England Batholith in NSW, Australia, and is considered as a post-collision A-type granite with elevated concentrations of Li, Rb, U, Th and F, intruded at a very shallow depth of only few kilometers.

The aim of this study is to resolve magmatic from hydrothermal processes, using high-precision U-Pb dating of: (1) zircon in quartz phenocrysts, representing the oldest stage of magmatic crystallization; (2) zircon, monazite and xenotime from the granite matrix; (3) zircon and xenotime

as inclusions in free-grown hydrothermal quartz; and (4) zircon and monazite from hydrothermal biotite-topaz veins. Crystallization temperatures can be estimated at 850-750°C for the magmatic minerals, and between >600°C down to 180°C for the hydrothermal minerals. The study is also a test for the existence of hydrothermal zircons, which is evaluated on the basis of trace and rare earth element concentrations in zircons (see Pettke et al., same volume).

From unaltered granite we found ages of 247.72 ± 0.49 Ma for monazite, and 247.74 ± 0.47 for zircon. Xenotime occurring within the same granite sample as well as in hydrothermal quartz yielded an age of 246.22 ± 0.50 Ma (all concordia ages with 95% c.l.). Tiny unabrased single zircon inclusions from subhedral quartz phenocrysts, as well as from hydrothermal quartz crystals gave discordant data and imprecise ²⁰⁷Pb/²⁰⁶Pb ages of 248 ± 60 and 245 ± 14 Ma, respectively, due to lead loss and contributions of common lead in analysis. Zircon and monazite from a hydrothermal biotite-topaz vein yielded slightly discordant data with an upper intercept age of 245 ± 3, with one monazite being concordant at 244 ± 1 Ma.

The results lead to the following preliminary conclusions: Magmatic and hydrothermal crystallization events seem to have occurred over a time span of 2.5 Ma. Formation of xenotime in vein-quartz and in the granite matrix were coeval and did not affect the U-Pb systematics of previously crystallized zircon and monazite. Biotite-topaz veins containing zircon and monazite crystallized up to 2.5 my. later. The time difference of 1.2 ± 1.0-0.5 my between zircon/monazite and xenotime crystallization translates to a cooling rate of 350°C/my, too slow for a granitic magma chamber in the upper crust. Possible explanations are: (1) heat supply from later magma batches to drive hydrothermal convection; (2) crystallization of some of the "magmatic" minerals prior to the final solidification of the granite; (3) later emplacement of the biotite-topaz veins, genetically unrelated to the intrusion of the main exposed Mole granite.

PCM6 : WEpo14 : PO An XRD and TEM Study of Experimentally Annealed Natural Monazite

Anne-Magali Seydoux-Guillaume

(seydoux@gfz-potsdam.de)¹,

Richard Wirth (wirth@gfz-potsdam.de)¹,

Jean-Marc Montel (montel@cict.fr)² &

Wilhelm Heinrich (whsati@gfz-potsdam.de)¹

¹ GFZ - Potsdam, Telegrafenberg PB 4.1, 14473 Potsdam, Germany

² LMTG-UMR 5563, Laboratoire de Minéralogie Université Paul Sabatier, 39 Allées Jules Guesde, 31000 Toulouse, France

The LREE-rich orthophosphate monazite is widely used in U-Th-Pb geochronology because of its high Th and U content. In an U-Pb concordia diagram, it is, in contrast to zircon, generally concordant, implying that it is either completely retentive or reset for Pb during any geological event. We can note that monazite and zircon are also very different, if we consider the effect of radioactive damages. Zircon is almost always metamict whereas monazite is not. Even old, strongly radioactive monazites are apparently crystalline, in spite of intensive radiation doses they were exposed to.

We experimentally studied the healing of radioactive damages in a natural, old monazite, using XRD and TEM. The starting material is a chemically (EMP) homogeneous monazite from a Brazilian pegmatite, concordant at 474 ± 1 Ma and showing nm-scale defects induced by radioactive decay. Two kinds of experiments were performed. First, dry monazite powder was heated at 500, 800 and 1000°C for 7 days and each sample were analysed with X-Ray diffractometry. The unheated starting material shows presence of two "phases", which could be interpreted as monazites with slightly different lattice parameters. The first one shows sharp peaks with high intensity and is interpreted as the perfect part of the monazite. The second "phase" shows very broad peaks with low intensity and may correspond to the defect domains of monazite. We observe that the latter progressively disappears with increasing temperature, thus showing gradual healing of defects. At 1000°C X-Ray diffractometry shows only one phase. Second, monazite grains were heated hydrothermally at different temperatures from 500 to 1200°C for about 10 days. TEM observations show that partial healing of the monazite lattice already occurs at 500°C and increases gradually with temperature, so that at 900°C and 10 days complete healing is achieved.

From the available Pb diffusion data, we can calculate that Pb loss by volume diffusion is only possible at very high temperature. From the present study, we conclude that Pb diffusion should proceed within a perfect crystal structure, by true volume diffusion. However this process is very sluggish and probably inefficient in most cases.

PCM6 : WEpo15 : PO
Arsenic: Distribution in Brown Coal Rich in Iron Disulfides

Zdenek Weiss (zdenek.weiss@vsb.cz)¹,
Milan Rieder (rieder@mbox.cesnet.cz)²,
J. C. Crelling³,
Ondrej Sustai (ondrej.sustai@vsb.cz)¹ &
Milan Drabek (drabek@cgu.cz)⁴

¹ Central Analytical Laboratory, Technical University
 Ostrava, 708 33 Ostrava, Czech Republic

² Institute of Geochemistry, Mineralogy and Mineral
 Resources, Charles University, Albertov 6, 128 43
 Prague, Czech Republic

³ Department of Geology, Southern Illinois University at
 Carbondale, Carbondale, IL 62901-4324, U.S.A.

⁴ Czech Geological Survey, Klárov 2, 111 11 Prague,
 Czech Republic

The brown coal studied comes from a sulfidic layer in the North Bohemian Coal Basin. It has a relatively high content of iron sulfides (11 wt.%). Thirty-three coal fractions (density between 1.0830 and 1.6902 g/ml) and the residuum were separated from pulverized coal by the density gradient centrifugation, weighed and analyzed for arsenic. The peak of the density distribution function (corresponding to the macerals) lies at the minimum of arsenic concentration, which indicates that arsenic cannot be bound in the macerals - a welcome news for the environmentalist.

Sulfides in the residuum were further separated in heavy liquids by the sink-float technique. The mean content of As in the sulfide concentrate is 4200 ppm, the As content in individual sulfide grains varies between zero and 7.9 atomic per cent. To examine the nature of bonding of arsenic in the sulfides, powder diffraction patterns for samples Nos. 91 and 267 (relatively large grain fragments picked by hand from the same concentrate) were recorded on a conventional X-ray powder diffractometer and their structures were refined by the Rietveld technique. An additional refinement for No. 267 used synchrotron radiation. Sample No. 267 is marcasite (138 ppm As), whereas No. 91 is a mixture of 78% pyrite and 22% marcasite (7300 ppm As); it is not clear whether the As in No. 91 is distributed evenly in both phases or not.

Structure refinements were performed to elucidate the mechanism of incorporation of arsenic into the structure of the sulfides, but the concentrations involved and the techniques employed only produced a feeble hint that As in both pyrite and marcasite may substitute for sulfur. In relation to iron whose occupancy refined as very close to its theoretical value, sulfur refined with an excess occupancy that signalizes a possible presence of a heavier atom (As). Conversely, a refinement of synchrotron data for a synthetic As-free marcasite has indeed shown a mild deficiency of sulfur.

Currently, experiments are underway to synthesize iron disulfides with elevated concentrations of arsenic that would be detectable by structure refinement. Understanding of the nature and quantity of As bonding may have further consequences for the techniques of coal burning and, ultimately, may lead to a reduction of the quantities of arsenic freed into man's environment.

PCM6 : WEpo16 : PO
Behavior of Zircon from Granodiorites and Gabbro-Anorthosites in the Shear-Zones and their U-Pb Ages (Belomorian Belt, Baltic Shield, Russia).

Tatiana F. Zinger (tatiana@am4160.spb.edu),
Boris V. Belyatsky (boris@bb1401.spb.edu) &
Nikolay L. Alexejev (alexjev@bb1401.spb.edu)
 199034 Institute of Precambrian Geology and
 Geochronology RAS, Makarova emb. 2, St.Petersburg,
 Russia

The shear zones play important role for establishing stages of the structural-metamorphic transformation of rocks. However, interpretation of U-Pb data is problematic due to different forms of zircons existing in them. Could these ages correspond to the real geological process or that is the age of the different stages of zircon transformation?

We studied the problem on examples of zircons from shear-zones in Paleoproterozoic (ca. 2.45 Ga) Pongoma granodiorite and Pezhostrovsky gabbro-anorthosite massifs. These rocks have been strongly sheared under T=600-640°C and P=7-8 kbar in the isochemical conditions. Morphology and the inner structure of zircons were studied using cathodoluminescence. Four morphological types of zircons were revealed in the granodiorite. The types 1-3 are represented by fragments of magmatic zircons, in different degree underwent by dissolution and recrystallisation (disappearing of oscillatory zoning). The type 4 is a new generation represented by fine transparent grains, which sometimes contain inherited cores of types 1-3 zircons. The U-Pb ages range from 2351±45 Ma to 2083±32 Ma for the type 4. The latter corresponds to the age of shear zone formation; the older ages have no geological significance and may reflect a gradual Pb loss during recrystallisation of zircon grains under deformation.

Zircons in the Pezhostrov leucogabbro also underwent to recrystallisation, but that did not result in appearance of new generation. Type 1 is represented by large fragments of prismatic microfractured crystals with oscillatory zoning; in the fractures sometimes are observed idiomorphic grains of apatite. These zircons were recrystallised to fine subidiomorphic crystals (type 2) which preserve oscillatory zoning. The U-Pb ages for both zircon types are close: 2441.7±3.3 Ma and 2436±36 Ma, accordingly. The apatite grains, which fill the fractures in the zircons, have ⁸⁷Sr/⁸⁶Sr ratio of 0.7044 suggesting their metamorphic origin. ²⁰⁷Pb/²⁰⁶Pb age of apatite is ca. 1789 Ma that is interpreted to correspond to the time of apatite crystallisation and, hence, as the minimum age of shear deformation and metamorphism. We suggest that recrystallisation of zircons in leucogabbro appears to have occurred very close to completion of primary crystallisation. Recrystallised zircons were extremely stable with respect to latter Pb loss during the amphibolite facies metamorphism and deformations.

Different behavior of zircons and their U-Pb systems is probably related to different contents of alkalis in rocks in the shear zones.

Thursday am Session

PCM6 : THam01 : G6
Chemical Variation and Alteration of Some Actinide and Rare Earth-Bearing Accessory Minerals: Implications for the Long-Term Storage of High-Level Radioactive Waste

C. Terry Williams (ctw@nhm.ac.uk)¹,
Greg Lumpkin (gri@ansto.gov.au)²,
Reto Gieré (giere@purdue.edu)³ &
Frances Wall (fw@nhm.ac.uk)¹

¹ Dept. of Mineralogy, The Natural History Museum,
 London SW7 5BD, U.K.

² ANSTO, Menai, NSW 2234, Australia

³ Dept. of Earth and Atmospheric Sciences, Purdue
 University, West Lafayette, IN 47907-1397, U.S.A.

Currently under investigation by many laboratories worldwide, is a range of synthetic formulations aimed at the long-term storage of high-level radioactive waste. Many of these proposed formulations contain crystalline phases which have natural analogues in actinide and rare earth-bearing accessory minerals. Although laboratory-based studies on the stability of the natural analogues of these synthetic components have been underway for several years, until recently the majority of these studies have focused mainly on large single crystals, separated from their host rock, and so information including paragenesis, fluid composition and alteration often has been lacking. There are however, in the geological literature, descriptions of the natural analogues of these minerals which include this relevant information. In this presentation we will review and illustrate examples of corrosion, alteration and replacement of several of these accessory minerals, including zirconolite, pyrochlore, monazite, loparite and baddeleyite.

Zirconolite [ideally CaZrTi₂O₇], shows some degree of alteration in both metasomatic and igneous environments at hydrothermal conditions, with temperatures ranging from approximately 150 - 500/4C. However, under lower-T lateritic weathering of carbonate complexes, zirconolite shows no significant alteration. In contrast, *pyrochlore* [ideally (Ca,Nb)₂Nb₂O₇(OH,F)] can undergo extensive alteration within a wide range of geological environments, including weathering of carbonates. Such alteration can lead to a complete breakdown of the pyrochlore structure. However, these examples are from occurrences which geologically are relatively old, suggesting that metamictization of these minerals may be a key factor in the degree and extent of the alteration. Younger (i.e. less than ~10 million year) samples show little, or no, evidence of alteration indicating that, from a waste-disposal viewpoint, they are likely to be durable over several millions of years.

Examples of alteration of *monazite* [ideally (Ce,La,Nd,Th)PO₄] have been reported resulting from chloritisation of alkali granites. Lower-T "weathering" of monazite can also promote mobilisation of heavy-REE (relative to the light-REE). These elements are then locally reprecipitated, and possibly stabilised, as secondary Y- and Th-rich phases. *Loparite* [ideally (Ce,Nb,Ca)₂(Ti,Nb)₂O₆] occurs in the Lovozero alkaline complex, Russia, and during late-stage alkaline metasomatism, it can be replaced by a range of rare K,Na,Sr,Ba phospho-silicate minerals. *Baddeleyite* [ideally ZrO₂], often associated with pyrochlore and zirconolite from carbonate rocks, has been observed from Sokli, Finland to have early corrosion features, and overgrowths of later-crystallising baddeleyite with a significantly different composition.

PCM6 : THam02 : G6
Monazite, Rhabdophane and Florencite in the Metamorphic Complex of Sopron Hills, Eastern Alps

Géza Nagy (gnagy@sparc.core.hu)
 Hungarian Academy of Sciences, Laboratory for
 Geochemical Research, H-1112 Budapest, Budaorsi ut
 45., Hungary

Sopron Hills consists mainly of mica schists and orthogneisses, while kyanite quartzites and leucophyllites are also present in small amounts. The mica schists formed from Precambrian sediments by pre-Alpine metamorphic events, gneisses originate from Palaeozoic acidic igneous material, and they have been subjected to Alpine metamorphism together. Quartzites and leucophyllites have been formed from them by Mg-metasomatism (Demény et al., 1997).

PCM6

Physicochemical Behaviour of Accessory Minerals

Accessory REE minerals have been investigated by electron microprobe analysis. Monazite and rhabdophane were distinguished by oxide totals. Monazite Pb-Th-U dating was also applied on certain rock samples.

RESULTS

Monazite, xenotime and rhabdophane are common, florencite occurs in certain rocks. *Monazite* is present in all types of rocks, in variable amounts. In mica schists it has been formed during Hercynian metamorphism evidenced by textural positions and supported by Pb-Th-U ages of approx 300 Ma. In gneisses it is rare, igneous by origin with similar but highly uncertain age. Quartzites and leucophyllites partly inherited monazite from their source rocks, however new generation of monazite also has formed, giving ages around 80 Ma for the Mg-metamorphism.

Chemistry: Differences were found

- in Eu-anomalies: igneous monazites have high negative (Eu/Eu* < 0.35), metamorphic grains have moderately negative Eu-anomalies (Eu/Eu* = 0.4 to 1);
- in Y (and other HREE) contents;
- in Th contents, which can vary even within one grain. It increases parallel with Ca, to the expense of REE, nearly according to the replacement $2\text{REE}^{3+} = \text{Th}^{4+} + \text{Ca}^{2+}$.

Rhabdophane has often been found in many mica schists and gneisses. Two types were identified: *Type 1* is widespread. It forms aggregates of small-size grains, may be attached to apatite (Banfield et Eggleton, 1989) or form reaction rim on monazite grains. It usually has higher Y and Ca contents and less negative Eu-anomaly than the coexisting monazite. *Type 2* appeared only in few mica schists. It is very similar with monazite both by appearance, grain size and composition (Nagy and Draganits, 1999).

The two types of rhabdophane never occurred together, or with florencite or secondary monazite.

Florencite appeared only in some leuchtenbergite-bearing quartzites and leucophyllites. Often idioblastic, sometimes grown on monazite. Chemically it is rather pure, however, ThO₂ may sometimes reach 10 wt-%.

INTERPRETATION

Monazite was formed in Hercynian metamorphic processes in mica schists, and are (partly) of igneous origin in gneisses. Depending on the circumstances, it has survived Alpine metamorphic processes with original compositions and has been inherited by quartzites and leucophyllites, or partly or totally disintegrated (Poitrasson et al., 1996).

Rhabdophane may have been formed a) by simple hydration of monazite: *Type 2*; b) either by crystallisation from REE-containing hydrous solutions or from monazite reacting with Y-Ca-containing solutions: *Type 1*. During formation of quartzite and leucophyllite the formerly presumably existing rhabdophane has been transformed to secondary monazite or florencite.

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PCM6 : THam03 : G6 Uranium-Rich Microlite: Growth and Alteration in a Lithium Pegmatite in Mozambique

Reto Giere (giere@purdue.edu)¹,
Edgar Buck (edgar.buck@pnl.gov)²,
Terry Williams (t.williams@nhm.ac.uk)³,
Eric Reusser (eric.reusser@erdw.ethz.ch)⁴,
Joao Marques (jn_reynolds@hotmail.com)⁵,
Richard Guggenheim (richard.guggenheim@unibas.ch)⁶ &
Daniel Mathys (daniel.mathys@unibas.ch)⁶

¹ Earth&Atmospheric Sciences, Purdue University, West Lafayette, IN 47907-1397, USA

² Radiochemical Processing Laboratory, Battelle Pacific Northwest Laboratory, Richland, WA 99352, USA

³ Department of Mineralogy, The Natural History Museum, London, SW7 5BD, England

⁴ Mineralogy & Petrography, ETH-Zentrum, CH-8092 Zurich, Switzerland

⁵ P.O. Box 2072, Maputo, Mozambique

⁶ SEM Laboratory, University of Basel, CH-4056 Basel, Switzerland

Microlite, a Ta-rich member of the pyrochlore group, is a typical mineral in the early Paleozoic lithium pegmatites of the Mozambique Belt, where it occurs in association with albite, spodumene, lithian mica, potassium feldspar and quartz. These pegmatites are strongly altered as a result of tropical weathering, but microlite is preserved as euhedral crystals in a clay matrix, which consists mainly of kaolinite.

We have studied microlite from a pegmatite in the Mutala area, Alto Molocue, Mozambique. The crystals exhibit distinct growth zoning, characterized by a U-free core and a U-rich rim (*17 wt% UO₂). The core exhibits conjugate sets of straight cracks, representing the octahedral cleavage of microlite. These cleavage planes provided pathways for a late-stage U-enriched pegmatitic fluid, which interacted with the U-free microlite to produce a distinct U enrichment along these planes (*5 wt% UO₂) and led to formation of the U-rich rim. Following the incorporation of U, late-stage hydrothermal fluids deposited mica along the cleavage cracks. Subsequently, the crystals were further fractured, probably as a result of decompression during uplift. Later, groundwater penetrated these fractured crystals and deposited clay minerals along both fractures and cleavage planes. This low-temperature process also led to chemical alteration of microlite, during which Na, Ca and F were leached. This alteration under tropical conditions further led to localized redistribution of radiogenic Pb (formation of plumbomicrolite) and to hydration of microlite, but U remained immobile. Alteration effects are only observed in the U-rich rim, which displays abundant microfractures. As demonstrated by electron diffraction images, powder X-ray patterns and RAMAN spectroscopy, the U-rich rim is largely metamict.

This study shows that microlite is able to retain U during low-temperature alteration under tropical conditions. These conditions produce deep weathering profiles, which often extend below the water table where the groundwater is out of contact with the atmosphere. The observed immobility of U, thus, may indicate that microlite was not altered by surficial water but rather by groundwater with an Eh that was not high enough to oxidize U⁴⁺ to the mobile U⁶⁺. The chemical data demonstrate that the rate of Na, Ca and F ion exchange of metamict microlite greatly exceeds the rate of total dissolution. These alteration effects were not observed along the pervasive fractures in the U-free crystalline core, suggesting that the susceptibility of microlite to low-temperature alteration is enhanced by the microstructural damage caused by alpha decay of U.

Our investigation illustrates the importance of natural analogue minerals in evaluating the durability of pyrochlore-based nuclear waste form materials. Such waste forms are currently under development for the disposition of excess weapons plutonium.

PCM6 : THam04 : G6 Apatite-Monazite Relations in the Kiirunavaara Apatite Iron Ore, Northern Sweden

Daniel Harlov (dharlov@gfz-potsdam.de)¹,
Ulf Andersson (andersson@gfz-potsdam.de)¹ &
Jan Olav Nyström²

¹ GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, F.R. Germany

² Naturhistoriska riksmuseet, Box 50007, SE-10405 Stockholm, Sweden

Magnetite-apatite ores of the Kiruna type show strong evidence of being magmatic iron deposits formed in subvolcanic and volcanic environments from the Palaeoproterozoic to the Pliocene. They seem to represent immiscible Fe-rich melts separated from calc-alkaline to slightly alkaline parental magmas. The mineralogy of a series of morphological types of fluor-apatite-magnetite rocks from the largest deposit, Kiirunavaara, have been examined using BSE and EMPA. Many of the apatites contain numerous small (<1 - 5 μm) inclusions of Th-depleted monazite (ThO₂ < 0.4; UO₂ < 0.01 wt.%) clustered principally in the apatite core. These monazite inclusions are typically elongated along the c-axis of the apatite host. Monazites are also found along apatite-apatite grain boundaries.

In samples of primary magmatic ore, dendritic plates of magnetite are intergrown with apatite (REE₂O₃+Y₂O₃ = 0.7-1.2 wt.%; Na₂O+SiO₂ = 0.3-0.4 wt.%). Zones depleted in REE (REE₂O₃+Y₂O₃ = 0.05-0.2 wt.%) are developed along grain boundaries and cracks within the apatites. This depletion is correlated with a decrease in Si and Na (Na₂O+SiO₂ = 0.01-0.2 wt.%). It implies the operation of the exchange vectors (Y + REE)³⁺ + Na⁺ = 2Ca²⁺ and (Y + REE)³⁺ + Si⁴⁺ = Ca²⁺ + P⁵⁺. These characteristics suggest nucleation of the monazites from the primary REE-rich apatite due to depletion in Na and Si, induced by percolating fluids.

Deformed and banded ore types contain recrystallized apatite (REE₂O₃+Y₂O₃ = 0.3-1.1 wt.%; Na₂O+SiO₂ = 0.2-0.4 wt.%) and magnetite. Large (10-200 μm) Th-depleted monazite grains (ThO₂ < 0.5 wt.%; UO₂ < 0.01 wt.%) occur principally intergrown with the magnetite, and sometimes as inclusions in the magnetite. In a relatively low-temperature ore type, apatite brecciates the magnetite. This type also contains elongated bodies (100-1000 μm) of dolomite intergrown with numerous small monazite grains (10-20% of the dolomite volume). The apatites in either ore type also show marginal depletion in REE+Na+Si and abundant monazite inclusions.

Interstitial hydrous secondary minerals are characteristically found along the grain boundaries of the apatites: talc in the primary ore samples, and actinolite, muscovite and quartz in the deformed ore/rock. Chlorite occurs abundantly in both types. In samples where the apatite brecciates the magnetite, serpentine is characteristic. Only the actinolite contains appreciable amounts of F (0.3-1.6 wt.%). The presence of these silicate phases is indicative of low-grade, greenschist facies, post-magmatic H₂O-rich fluid infiltration along the grain boundaries of the apatite-magnetite rocks, supplying mainly Mg, Si, Al and K from the surrounding silicate rocks. The depletion of the apatites and accompanying monazite nucleation could be related to this fluid event.

PCM6 : THam05 : G6 Does Metamictization Control the Weathering of Zircon?

Etienne Balan (balan@lmcp.jussieu.fr)¹,
Patrick Trocellier², Daniel Neuville³,
Emmanuel Fritsch¹, Jean-Pierre Muller⁴ &
Georges Calas¹

¹ Laboratoire de Minéralogie-Cristallographie, CNRS UMR 7590, Universités Paris 6 et 7 and IPGP, Case 115, 4 Place Jussieu, 75252 Paris Cedex 05, France

² Laboratoire Pierre Süe, CEA - CNRS, Centre d'Etudes de Saclay, 91191 Gif sur Yvette Cedex, France

³ Laboratoire des Géomatériaux IPGP, 4 Place Jussieu, 75252 Paris Cedex 05, France

⁴ IRD, 213 rue Lafayette, 75480 Paris cedex 10, France

Zircon (tetragonal ZrSiO₄) is the oldest mineral found at the Earth's surface. Its resistance to dissolution is exceptional compared to that of other silicate minerals. Because of this important property, zircon is widely used in tracing and dating geological processes and it is considered as potential waste matrix for the plutonium. However, zircon may loose

its resistance in some environments (hydrothermal fluids, tropical soils) and the use of zirconium as an immobile element in weathering processes has been questioned. In addition, metamictization, i.e. the loss of crystal periodicity due to the accumulation of radiation induced defects, strongly modifies the properties of zircon. Little attention has been paid on the role of metamictization on the weatherability of zircon in natural environments. Here, we report new results obtained on zircons sampled in sediments and soils of the Amazon basin (Brazil). The zircons originate from the precambrian Guyana shield (0.5-3 Ga). Their actinide (U, Th) concentrations were measured by proton induced X-ray emission (PIXE) micro-analysis. Their metamictization degree, expressed as a radiation dose, was determined by Raman micro-probe. These zircons present a maximum degree of metamictization which coincides with the first percolation threshold of the metamictization process. Above this threshold, the amorphous phase is predominant. According to the measured range of actinide concentrations, it can be inferred that more damaged zircon disappeared during weathering processes. Otherwise, for the observed metamictization range, the soil formation does not appear to affect the zircon population. Since no protective Zr-enriched layer was detected by Rutherford backscattering spectroscopy (RBS) at the surface of the zircons, their resistance to weathering can be attributed to their low amount of radiation damage. Consequently, our results suggest that metamictization exerts a major control on zircon weathering at the Earth's surface.

**PCM6 : THam08 : G6
Alteration of Zircon Under Experimental
Hydrothermal Conditions**

Thorsten Geisler
(thorsten.geisler@mineralogie.uni-hamburg.de)¹,
Robert T. Pidgeon (tpidgeon@cc.curtin.edu.au)²
& **Wilhelm van Bronswijk**
(w.vanbronswijk@info.curtin.edu.au)²

¹ Mineralogisch-Petrographisches Institut, Universität
Hamburg, Grindelallee 48, 20146 Hamburg, Germany
² School of Applied Geology, Curtin University of
Technology, GPO Box U1987, Perth 6845, Australia

Hydrothermal experiments with metamict zircons were carried out at temperatures between 175 to 650°C with different reactive solutions (e.g., 2 M Al₂Cl₃, 2 M CaCl₂ solutions) for 72 to 2300h. In contrast to previous studies (e.g., Sinha et al. 1992, Rizvanova et al. 2000), we used homogeneous, unaltered (as indicated by low concentrations of Ca and Al) metamict zircon grains from alluvial, gem-type zircon gravels (Sri Lanka) as starting material. Structural and chemical alteration after hydrothermal treatment was recorded by micro-analytical tools and imaging techniques. Cathodoluminescence (CL), backscattered electron (BSE) and differential interference contrast imaging (DIC) revealed that sharp bounded reaction rims were developed around apparently unreacted zircon, similar to experiments at 450°C in a 2 M CaCl₂ solution (Geisler et al., in press). The kinetics of rim formation is very fast indicating fast diffusion pathways and is correlated with the ion size of solvent cations (e.g., Ca²⁺, Al³⁺, H⁺). The reaction rims suffered severe radiogenic Pb loss, as determined by sensitive high resolution ion microprobe. Furthermore, electron microprobe analysis revealed that fluid-zircon exchange reactions comprise loss of Zr and Si and gain of the solvent cations to preserve electroneutrality. Ion exchange is also reflected by a reduction of the Z contrast in BSE images. Interestingly, significant loss of U and Th from the reaction rims was seen only in low temperature runs (350°C). Micro-Raman spectroscopy, an increased CL intensity and an increased hardness (indicated by DIC images) of the reaction rims clearly prove that the amorphous domains of the reacted metamict zircon are recrystallized to a significant extent at temperatures of more than ~300°C. We conclude that leaching catalyzed recrystallization and that at higher temperatures recrystallization is the rate determining process. The activation energy to recrystallization, i.e., the self-diffusion of network forming species, is strongly reduced in a hydrothermal environment in comparison with recrystallization under dry conditions (Geisler et al., in preparation). At a temperature of 175°C, only pre-existing, distorted and strained crystalline domains - which are still located within an amorphous matrix in partially metamict zircon (e.g., Salje et al. 1999) - were recovered, resulting in a distinct leaching process. The ion-exchange process in general and particularly the U and Th loss behavior at low temperatures as well as the kinetics of rim formation can qualitatively be explained by the percolation-type model for radiation damage in zircon (Salje et al. 1999). Our results have

important implications for zircon geochronology and the application of zircon as a host phase for weapon-grade plutonium.

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**PCM6 : THam09 : G6
Experimental Resetting of the U-Th-Pb System
in Monazite**

Anne-Magali Seydoux-Guillaume
(seydoux@gfz-potsdam.de)¹,
Jean-Louis Paquette
(paquette@opgc.univ-bpclermont.fr)²,
Jean-Marc Montel (montel@cict.fr)³ &
Wilhelm Heinrich (whsati@gfz-potsdam.de)¹

¹ GFZ-Potsdam, Telegrafenberg-PB 4.1, 14473 Potsdam, Germany
² Laboratoire de mineralogie UMR 6524 Magmas et volcans, Université B.Pascal, 63038 Clermont-Ferrand cedex, France
³ LMTG-UMR 5563, Laboratoire de Minéralogie, Université Paul Sabatier, 39 Allées Jules Guesde, 31000 Toulouse, France

Monazite is used in geochronology to determine the timing of magmatic and metamorphic events. Generally, ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U ages in monazites are concordant; nevertheless, discordant U-Pb ages have also been reported. This may result from mixing of different populations of grains crystallised at different times or from presence of inherited cores, or else by diffusive Pb loss. In nature, the U-Th-Pb system of monazite crystals may be reset by diffusive loss of Pb or by growth of newly formed rims related to dissolution/precipitation process via coexisting fluid. Consequently, it could be sometimes difficult to properly interpret the obtained ages.

Abraded fragments (200 to 400µm) of a large and chemically homogeneous Brazilian monazite crystal characterised by a concordant U-Pb ages of 474 ± 1 Ma (²⁰⁸Pb/²⁰⁶Pb=19.5) were hydrothermally treated at varying temperatures with solutions of different compositions. Experiments with pure water at 800 to 1200°C, 700 MPa and duration of 5 to 60 days showed that even at 1200°C, dissolution and recrystallization of new monazite are confined to the outermost surface of the grain. Neither diffusion of Pb at the EMP scale, nor significant discordancy was observed. Experiments were performed at 800°C/30 days and 1000°C/14 days using different fluid compositions at quartz saturation: a 10 wt% CaCl₂ fluid, a 10 wt% SrCl₂ fluid, a 10 wt% NaCl fluid and a fluid containing NBS 982 Pb standard (²⁰⁸Pb/²⁰⁶Pb=1). Product monazites from each run were analysed with SEM, EMP, ID-TIMS and SIMS.

For all runs, EMP profiles never show diffusion profiles. Significant overgrowths of newly formed monazite are documented by SEM analyses. They occurred only in the 1000°C experiments and if the CaCl₂ or Pb-bearing fluids were present. In the CaCl₂ experiment at 1000°C, two zones can be distinguished in the crystal: a core, corresponding to the initial monazite, and a rim, consisting of a newly formed monazite, which was enriched in Ca and free of Pb, produced by dissolution/precipitation. ID-TIMS dating of single grains treated with CaCl₂ and SrCl₂ solutions at 1000°C is characterised by a significant discordancy of analytical points. Pb loss is more important with the CaCl₂ fluid (67% discordancy), than with the SrCl₂ one (16% discordancy). Experiments with Pb-standard produced sub-concordant monazite, which ²⁰⁷Pb/²⁰⁶Pb apparent age is older than before the experiment (544 Ma at 800°C and 495 Ma at 1000°C). It is obvious that a newly grown monazite rim has incorporated Pb from the fluid.

For all these experiments no detectable diffusion occurred; the efficient resetting mechanism is always dissolution/precipitation. It is clear that the extent of this process is depending on fluid composition. According to these results, we believe that dissolution/precipitation rather than diffusion control resetting of monazites in natural rocks.

**PCM6 : THam10 : G6
Microgeochronology, Microgeochemistry and
Microstructure of Altered Zircon from the
Acasta Gneiss Complex, Slave Province,
Canada**

Nicole Sanborn (nsanborn@nrcan.gc.ca)¹,
Richard Stern (rstern@nrcan.gc.ca)¹,
Sharon Carr (scarr@ccs.carleton.ca)² &
Gianluigi Botton (gbotton@nrl.nrcan.gc.ca)³

¹ Geological Survey of Canada, 601 Booth St., Ottawa, ON K1A0E8, Canada
² Dept. of Earth Sciences, CNS, rm 2240 Herzberg Laboratories, Carleton University, 1125 Colonel By Dr., Ottawa, ON, K1S 5B6, Canada
³ Materials Technology Laboratory CANMET, Natural Resources Canada, 568 Booth St., Ottawa, ON, K1A 0G1, Canada

A 2.9 Ga granitic dyke from the Acasta Gneiss Complex (AGC) exhibits signs of fluid alteration from outcrop- to grain-scale. Thin-section observations consistent with alteration include extensively sericitized feldspars, and the presence of secondary minerals such as calcite and epidote. Zircons separated from the dyke are strongly paramagnetic, stubby to elongate prisms, with irregular or embayed margins. The zircons commonly contain inclusions of epidote, quartz and uranohthorite, and in some cases may be partially replaced by the latter. SEM back-scattered electron (BSE) images reveal primary igneous oscillatory zoning, however, these primary features are overprinted by irregular domains having weak BSE response, the boundaries of which may or may not transgress the igneous zoning. Similar features have been observed in most zircons from the AGC, including the oldest-known terrestrial rocks, and in numerous other Archean and Paleoproterozoic samples, and are interpreted to reflect fluid alteration. Despite its prevalence, the characteristics and processes of fluid alteration have seldom been studied *in situ*. The SHRIMP ion microprobe was used to characterize the trace element chemistry (Ca, Ba, P, Th, U, Hf, Y, REEs) and U-Pb isotopic systematics of altered zircon, and transmission electron microscopy (TEM) was used to characterize its crystal structure.

Trace element analyses indicate that LREE are preferentially enriched in the altered zircon domains. In one example, an unaltered zircon domain has (Sm/La)_{CH} = 39, while an adjacent altered domain has (Sm/La)_{CH} = 7; (Yb/Gd)_{CH} ratios from the same two domains are roughly comparable (53 and 63 respectively). In addition to enrichment in LREE, altered zircon also contains elevated concentrations of Ba, Ca (up to 2%wt) and common Pb (> 50 ppb). SHRIMP U-Pb analyses of unaltered zircon domains are near-concordant, whereas altered domains are variably normally discordant. Alteration by Ca-rich fluids was an important means of preferentially removing radiogenic Pb from the zircon. SHRIMP Pb-Pb ages from uranohthorite inclusions indicate that alteration occurred as early as 2.2 Ga.

A membrane suitable for TEM was milled, using a focused Ga ion beam, through a region of a zircon grain comprising unaltered and altered zircon to test for the presence of secondary minerals as hosts for Ca, and LREE. No secondary phases were detected at the nanometre scale, suggesting that Ca and LREE are somehow accommodated within the altered zircon lattice. Electron diffraction patterns indicate that altered zircon is heterogeneous, composed of a mixture of low-Ca distorted-crystalline domains and amorphous, high-Ca domains. In contrast, unaltered zircon has a moderately distorted crystalline lattice. We infer that metamictization is a required condition for alteration to occur, however cracks and other structural weaknesses likely control the grain-scale distribution.

PCM6 : THam11 : G6**Near Complete Erasure of the U-Th-Pb System in Zircon by Hydrous Metamorphism- Potential Fractionation of Radiogenic Pb Isotopes**

Werner Hansmann (hansmann@erdw.ethz.ch)¹,
Othmar Müntener (othmar@erdw.ethz.ch)¹,
Joerg Herrmann (joerg.herrmann@anu.edu.au)² &
Thomas Pettke (pettke@erdw.ethz.ch)¹

¹ Department for Earth Sciences, ETH Zurich, CH-8092 Zurich, Switzerland

² Research Scholl of Earth Sciences, ANU, Canberra 0200, Australia

Zircons from Permian metagabbros and an associated leucogranite from Val Malenco (N Italy) dated by the conventional U-Pb single grain method showed discordance patterns that could not be explained by simple Alpine metamorphic lead loss mechanisms. The unexpected presence of exotic grains in one gabbro and missing effects from air abrasion treatments on the degree of zircon discordance caused a reexamination by a combined cathodoluminescence (CL) and LA-ICP-MS study. CL imaging revealed that essentially all crystals of the three different zircon populations studied are composed of two distinct generations of zircon formation / recrystallisation. The inner parts consist of partly oscillatory zoned zircon with generally low to intermediate CL intensity. The outer domains characterised by high CL intensity show inward directed recrystallisation fronts. Corroded cores were observed in zircons from the leucogranite only. The ratio of recrystallised to primary zircon domains varies between the three rock types and is clearly correlated with the extent of hydrous metamorphic overprint. In the gabbro showing the largest proportion of recrystallised material the two different zircon generations can be distinguished by their Y, REE, Th and U characteristics obtained by LA-ICP-MS analyses. Depletion in these elements due to the hydrothermal alteration event amounted to about one order of magnitude for Y and REE and in part to more than two orders of magnitude for Th and U. Existing Eu/Eu* anomalies of < 0.15 in unaltered domains became reduced or even erased in altered zones. Th/U ratios were lower in the alteration zones in all sample pairs and generally reached values < 0.25. The low U content (6 - 33 ppm) of the exotic zircons indicates that they largely consist of altered zircon in which the U - Th - Pb had been erased to a very large degree. The almost completely recrystallised zircon with only 6 ppm U is characterised by an apparent ²⁰⁸Pb/²³⁸U age significantly older than the upper concordia intersection age of 278 MA suggesting inverse discordance caused by the drastic recrystallisation. It also has a radiogenic ²⁰⁸Pb/²⁰⁶Pb corresponding to a Th/U ratio of 2.8 which is about 10 times larger than observed in the altered zircon domains. These suggests that during the severe alteration leading to an almost complete Pb loss fractionation of these two Pb isotopes may have taken place due to differences in their distribution within the zircon. Minor preferred loss of ²⁰⁸Pb compared to ²⁰⁶Pb resulting from the same alteration processes is also indicated. Since inheritance shows the same effect on the ²⁰⁷Pb/²⁰⁶Pb ratio a strong prove for the absence of inherited components still needs to be provided.

PCM6 : THam12 : G6**Insights into the Nature and Behaviour of Metamorphic Monazite; A Chemical and Isotopic Study by EMP, SIMS and LA-PIMMS**

Gavin Foster (g1f3@le.ac.uk)¹, Randy Parrish²,
Martin Whitehouse³ & Matt Horstwood²

¹ Department of Geology, University of Leicester, Leicester, UK

² NIGL, Keyworth, Nottingham, UK

³ Swedish Museum of Natural History, Box 50007, S-10405 Stockholm, Sweden

-Of the U-Th- rich accessory phases commonly used in geochronology, monazite is fast becoming the mineral of choice in the dating of medium to high-grade metamorphism in orogenic belts. However, unlike common rock forming minerals such as garnet, the interpretation of age data from metamorphic monazite is highly problematic. These problems arise largely due to a poor understanding of the reactions responsible for the formation and breakdown of monazite during regional metamorphism. However, high precision TIMS analysis and spatially precise *in situ* age determinations (SIMS, LA-PIMMS, and CHIME) have also identified additional complexities. For instance, in young metamorphic monazites (<100 Ma) single crystal and *in situ* age determinations indicate that significant (10-20 Ma) inter- and intra-crystalline age variations commonly exist. What is more, the temperature at which Pb diffusion

occurs in monazite is a subject of some debate, paradoxically only a few studies document the existence of diffusive Pb loss yet polymetamorphic monazites are often significantly discordant. The factors that are controlling this behaviour of monazite are potentially manifold and include: continuous growth during a single metamorphic event, sporadic growth during a single or multiple events, and/or thermally induced Pb loss or U gain. In this contribution, using a multidisciplinary approach, we attempt to address some of these problems.

A number of monazites from samples of differing metamorphic grade and tectonic environment have been studied. In all cases single crystal TIMS analyses have revealed that significant inter-crystalline age variations exist within a given population. Through a combination of chemical mapping, quantitative EMP analysis, and SIMS and LA-PIMMS *in situ* age determinations, the nature of monazite growth and its susceptibility to diffusive Pb-loss is examined. We believe this study to be an important step towards the understanding of metamorphic monazite and a necessary pre-requisite to the determination of the reactions responsible for monazite growth and consumption during regional metamorphism

PCM6 : THam13 : G6**Micro-Dating of Monazite by New XRF-Microprobe Technology Applied to Polymetamorphic Rocks of the Monte Rosa Nappe**

Nadim C. Scherrer Scherrer

(scherrer@mpi.unibe.ch)¹,

Randall R. Parrish (rrp@nigl.nerc.ac.uk)²,

Alfons Berger (berger@mpi.unibe.ch)¹,

Andriy Cheburkin

(acheburkin@nickel.laurentian.ca)³ &

Martin Engi (engi@mpi.unibe.ch)¹

¹ MPI, Baltzerstr. 1, University of Bern, 3012 Bern, Switzerland

² Nerc Isotope Geoscience Lab., British Geological Survey, Keyworth, Nottingham, NG12 5gg, U.K.

³ Dept. of Earth Sciences, Laurentian University, Sudbury, Ontario, Canada

A newly developed XRF-microprobe at the Institute of Mineralogy and Petrology, University of Bern, Switzerland, has been applied for precise chemical Th-U-Pb dating of individual monazite grains separated from Pb-free polished petrographic thin sections.

The instrument performance was tested on a dataset of over 70 monazite grains individually drilled from 25 thin sections characterised by electron microprobe. 14 samples were selected so as to regionally represent the pre-granitic basement rocks (garnet-mica gneiss) of the Monte Rosa gneiss nappe (western Central Alps).

Summarising the geological results, there are two distinct phases of monazite growth in these polymetamorphic rocks apparent: one during Permian times (280 ±40 Ma), and a younger phase of Alpine age (35 ±10 Ma). The two age groups occur side by side at thin section scale but they are clearly separated by context: the younger ones are restricted to grains within the matrix, and the older ones to monazite inclusions in garnet, or, more rarely, inherited cores of large matrix grains. Of all sampled sites there are two exceptions to this rule, i.e. where all dated grains (matrix and inclusions) fall into the older category. Monazite in these two rocks must have largely escaped the effects of Alpine metamorphism, which included eclogite facies conditions (Eocene) followed by amphibolite facies conditions (Oligocene).

The non-destructive nature of the XRF-microprobe permitted a comparative study of dating methods by sequentially applying chemical dating by electron microprobe analysis (EMPA), chemical dating by XRF-microprobe analysis, and isotopic ²⁰⁸Pb/²³²Th dating by LA-PIMMS (Laser-Ablation Plasma Ionisation Multi Mass Spectrometry) analysis.

As an example, the precision achieved with the XRF-microprobe for a well characterised monazite age standard FC-1 (TIMS age 54.3 Ma; μ -XRF age 55.3 ±2.6 Ma), doubly polished to 30 μ m in thickness, is below 5% (2 sigma) after 90 minutes integration time (50 kV; 30 mA) at a spatial resolution of 90 μ m. The sample characteristics are: 200-300 ppm of Pb (μ -XRF), 3.8-5.1 wt% of Th (EMPA) and 0.4-1.4 wt% U (EMPA).

Combined with an electron microprobe and conventional optical microscopy, the XRF-microprobe is thus a competitive low-cost and non-destructive alternative to more costly isotopic methods. The XRF-microprobe is easy to use and maintain.

PCM6 : THam14 : G6**U and Pb Isotopes of Uraninite and Galena Measured on Ion Microprobe**

Lena Zetterström (lena.zetterstrom@nrm.se)¹,
Torbjörn Sunde¹, Hans Schöberg¹ &
Mostafa Fayek (mfayek@utk.edu)²

¹ Swedish Museum of natural History, Box 50007, SE-104 05 Stockholm, Sweden

² University of Tennessee, Dept of Geological Sciences, Knoxville, TN 37996-1410, USA

Uraninite may be regarded as a natural analogue for spent nuclear fuel. Thus, studies of the U-Pb system of uraninite can give insight into the effects of a geological environment on spent nuclear fuel. One major disadvantage of uraninite as a tool in conventional geochronology, is its tendency to be inhomogeneous and discordant. However, *in situ* ion microprobe analyses of uraninite may yield information about the history of the U-Pb system and the effects of geological events on the uraninite crystals. One unique natural analogue site is the Oklo uranium deposit (Gabon), where natural fission reactors formed ca 2 Ga ago. Establishing the detailed geochronology of Oklo has been the aim of a study, during which uraninite isotopic analysis on ion microprobe needed to be developed. The results of this method development are discussed in this presentation.

The main problem with U-Pb ion microprobe analysis of uraninite is that it requires a homogenous, concordant uraninite standard for calibration. In this presentation, we do not discuss the inter-element fractionation, but only the isotopic fractionation of Pb and U. Since U in the Oklo natural reactors is inhomogeneously depleted in ²³⁵U it is necessary to analyse its isotopic composition. Here, we present the results of uraninite Pb and U isotopic analyses of two different uraninite crystals, selected as potential standards. We also present Pb isotopic analyses of a galena standard, since the isotopic composition of radiogenic Pb in galena is of importance in the study of the U-Pb system of uraninite.

The results show that there is a large (0.5 - 2%/amu) fractionation of Pb isotopes during uraninite analysis in favour of the heavier isotope. The fractionation needs to be monitored during analyses of unknown uraninite crystals by parallel analyses of a standard in the same analytical session. The fractionation observed during this study is different from what was reported by Holliger (1988). Fractionation of U isotopes during uraninite analyses was observed to be between 1 and 2%/amu. Fractionation of Pb isotopes during ion microprobe analyses of galena was determined to be 0.46%/amu in favour of the lighter isotope. This is also a larger fractionation than what has been observed in other studies (Hart et al, 1981).

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