Electron Microscopy and Microanalysis Conference

to celebrate the 30th Anniversary of Scanning Electron Microscopy Laboratory of Biological and Geological Sciences and the 40th Anniversary of JEOL in Poland Kraków, 17-18th September 2007

Accessory minerals *in-situ*: microanalytical methods and petrological applications

Workshop, 15-16.09.2007, Kraków

Kraków, 15-18 September 2007

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organised by

Department of Cytology and Histology, Institute of Zoology Jagiellonian University

Department of Mineralogy; Petrology and Geochemistry, Institute of Geological Sciences, Jagiellonian University

Mineralogical Society of Poland

Polish Academy of Arts and Sciences

Kraków, 17-18 September 2007

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Faculty of Geology, Geophysics and Environmental Protection of the AGH – University of Science and Technology

Department of Geosciences of the University of Massachusetts, Amherst

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Dear Conference Participant:

The Electron Microscopy and Microanalysis Conference in Krakow has been organized to celebrate the 30th Anniversary of the Scanning Electron Microscopy Laboratory of the Biological and Geological Sciences, belonging to the Faculty of Biology and Earth Sciences of the Jagiellonian University. In addition, we are aiming to present and discuss scientific results obtained with the use of electron microscopy techniques as well as recent advances in these techniques in biological and geological applications.

The history of electron microscopy at Jagiellonian University is now longer than thirty years starting when, in 1972, Professor Wincenty Kilarski of Jagiellonian University had the idea to install a scanning electron microscope in the University. He had used electron microscopy techniques during his fellowship, funded by the World Health Organization and held in Philadelphia, to study the cancerous transformation of cells, and in 1972 decided to bring these techniques, which were modern at that time to the Jagiellonian University. After returning to Kraków, Wincenty Kilarski discussed his idea with the Rector of the Jagiellonian University, Mieczysław Karaś, to buy a scanning electron microscope for the University. The Rector supported this idea and indicated to a potential sponsor of this initiative, the enterprise Nafto-Budowa, that a main administrative centre was built within the Second University Campus. Since scanning electron microscopes are used not only to examine the ultrastructure of cell surfaces but also the surfaces of geological specimens, in 1974 Wincenty Kilarski also asked Rafal Unrug, at that time the Director of the Institute of Geological Sciences, to join him and thereby increase the chance to install a microscope at the University. During a meeting held on July 1, 1975, in the presence of Directors from three University Institutes: Professors Andrzej Jasiński (Institute of Zoology), Władysław Grodziński (Institute of Environmental Biology) and Rafał Unrug (Institute of Geological Sciences), Professor Wincenty Kilarski then proposed to organize a Scanning Electron Microscopy Laboratory for biologists and geologists at the Faculty of Biology and Earth Sciences. The efforts of these three Institutes, the Rector and Nafto-Budowa were fruitful and the first microscope for the Laboratory was purchased on January 21, 1976. Two additional microscopes were installed, first in 1995 (a Jeol JSM-5410) and then in 2001 (an Hitachi S-4700). In addition to the scanning electron microscopes, in 1985 a Noran X-ray dispersion spectrometer was purchased to analyze elements on the surfaces of biological and geological samples.

From the beginning, the Laboratory was open to all biologists and geologists not only of the Jagiellonian University but also from other Universities, and to other users from scientific and industrial institutions in Krakow and elsewhere in Poland. Today the Laboratory has divisions located in two Institutes, Zoology and Geological Sciences. The present conference is a chance to talk not only about the history of electron microscopy at the Jagiellonian University but also about recent results achieved using scanning and transmission electron microscope techniques, microanalysis as well as other more recent techniques, such as electron tomography.

On behalf of the Scientific and Organizing Committees

Elżbieta Pyza

Chairperson of the Scientific Committee

Head of the Scanning Electron Microscopy Laboratory of Biological and Geological Sciences, Faculty of Biology and Earth Sciences, the Jagiellonian

ACCESSORY MINERALS *IN-SITU*: MICROANALYTICAL METHODS AND PETROLOGICAL APPLICATIONS

With a few notable exceptions, accessory minerals have been regarded historically as exotic components within assemblages of much more abundant minerals, their presence having often been noted but not fully exploited. An example of this is the study of accessory phases that concentrate actinides. Although well established as geologic chronometers, there has been much less emphasis on the interpretation of their composition.

The remarkable potential of accessory phases to shed light on critical aspects of petrologic systems is now being harnessed. This has led to a better understanding of the conditions under which the more common accessory minerals crystallize and re-crystallize and the identification of the geological and petrological links between accessory phases and major rock forming assemblages.

As the composition of accessory phases has shown, they are likely not only to contain significant concentrations of geochemically important elements and but also to determine the bulk chemical budget of such elements. As a result accessory minerals are inherently sensitive indicators of processes that influence these elements, and consequently reflect changing geologic conditions. Advances in imaging techniques have been used to demonstrate the complex internal structures of accessory minerals which may reflect periods of mineral growth, deformation and alteration. Slow diffusion rates in some minerals coupled with the incorporation of radiogenic elements (U and Th) also provide a detailed chronological record for some polygenetic phases. Essentially, accessory minerals can now be studied routinely to provide a wealth of information on the P-T-X-t-d evolution of rocks.

The exploitation of the information held by accessory minerals has been critically dependent on developments in the field of analytical methodology and instrumentation. Improvements have included more efficient methods for locating, imaging and quantitatively analysing accessory minerals. The emergence of more sensitive methods of analysis has resulted in more sensitive instruments, lower detection limits for many elements and isotopes and a reduction in the size of the required aliquot to a single grain or domains within a grain. The analysis of individual domains is perhaps the most powerful application of *in situ* analysis. Such techniques are being used to establish the composition of individual domains, to study growth and dissolution textures and microstructures and to link them to co-existing major phases. This challenge has led in turn to further improvements in spatial resolution and sensitivity as new levels of understanding have developed in response to the demands for more detailed analyses of complex phases.

The workshop provides a timely opportunity to present and discuss the current status of mass ablation (isotopic) and ionizing radiation (non-isotopic) analytical

techniques, as well as high-resolution imaging methods, and their application to accessory minerals research. The present contribution aims to explore current advances in technique development and applications to petrologic problems. It also emphasises the value of a multi-disciplinary approach, and the recognition that the interpretation of data derived from the study of accessory phase minerals depends on understanding their internal structure and composition, as well as the external textural environment.

C.J. Hetherington

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Jasmi Hafiz Abdul AZIZ¹, Teh Guan HOE

ALICONA INFINITE FOCUS 3D PHYSICAL PROPERTIES CHARACTERIZATION OF PRIMARY GOLD PARTICLES FROM SELINSING GOLD MINE, PAHANG, MALAYSIA.

Gold is precious and usually occurs in very small quantities as primary gold in mineralized quartz veins and as secondary gold in alluvial deposits. The Alicona Infinite Focus 3D has played an important role in the investigation of the physical properties of gold particles from the Selinsing Gold Mine. The Alicona Infinite Focus 3D is an optical device for 3D surface measurement. Its operating principle combines the small depth of focus of an optical system with vertical scanning to provide topographical and color information from the variation of focus. Selinsing Gold Mine is one of the most active gold mining areas in Peninsular Malaysia. Based on the distribution and the style of mineralization, this area is in the Second Gold Belt of Peninsular Malaysia. Gold mineralization of the Selinsing deposit is in the form of a lode, sheeted stock work and dissemination in carbonaceous slates and metamorphosed volcanics. In this study the physical properties of the gold particles investigated are morphology, length, width, height, area and volume. Gold from this area is morphologically angular to sub-angular and discoidal to subdiscoidal with an average length of 1.373 mm and an average width of 0.981 mm. Based on the profile analysis, the heights of gold particles range from 261.4 µm to 408.8 μ m. The average particle area is 304.557 mm² and volumes range from 111501435 μm³ to 213410605 μm³.

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Bogusław BAGIŃSKI¹

P-T-T DATA ON THE CONTACT METAMORPHISM OF METAPELITIC ROCKS INDUCED BY THE KŁODZKO-ZŁOTY STOK INTRUSION (CENTRAL SUDETES, POLAND)

The Kłodzko-Złoty Stok intrusion (KZI) thermally influenced various types of rocks that it intruded (Bagiński 1989, 1998, 2002), including pelitic rocks of the Bardo unit. Various types of hornfelses were developed. The most interesting, as a potential source of information on its pressure, temperature and time of processes are sillimatite-corumdum-hercynite hornfelses with garnet. Additionally they contain minute grains of monazite as an accessory. Note that monazite crystals have been found, so far, only in this kind of rock, within the whole contact aureole of the KZI. This kind of rock, first described by Wierzchołowski (1976), occurs in the vicinity of Żelazno.

Determination of garnet, biotite and monazite compositions hasbeen carried out on a Cameca SX-100 microprobe in Warsaw. Garnet-biotite thermometry (Ferry and Spear 1978) revealed peak equilibrium temperatures at the range 700 to 730°C. Pressure conditions have been determined as 2 kbar using the Al inhornblende barometer (Hammarstrom et al. 1986) in amphibolite hornfelses from the thermal aureole, close to the sillimatite-corundum-hercynite hornfelses. Chemical EPMA dating (according to its principles given by Suzuki and Adachi (1991)) of fairly homogeneous monazites, growing as a minute crystals (up to 30 micrometers) within different mineral phases, displayed the time of crystal formation at approx. 330 Ma.

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Bartosz BUDZYŃ^{1,2}, *Callum J. HETHERINGTON*², *Michael L. WILLIAMS*², *Michael J. JERCINOVIC*², *Gregory DUMOND*², *Marek MICHALIK*¹

APPLICATION OF ELECTRON BEAM TECHNIQUES TO PROVENANCE STUDIES: TEXTURAL STUDIES OF METAMORPHIC PEBBLES FROM THE SILESIAN UNIT, POLAND

Gneiss pebbles collected in Gródek and Krzesławice from the Upper Istebna Beds (Silesian Unit, Western Outer Carpathians) were studied using the Scanning Electron Microscope and Electron Microprobe. Those pebbles were derived from the Silesian Ridge, one of the possible internal source areas that supplied Carpathian basins with clastic material (cf. Oszczypko 2006, and refs. therein). Because the Ridge was eroded in Tertiary and subsequently covered by an overthrusted nappes, clastic material provides the only data about its geological structure and evolution. Microtextural observations and high resolution compositional mapping of minerals combined with quantitative in-situ analyses were used to constrain provenance and petrographic history of the analyzed pebbles. Comparison of pebbles from different localities indicates a common igneous protolith and a similar metamorphic history. Gneisses contain K-feldspar porphyroclasts that display oscillatory Ba zonation, interpreted to have formed during K-feldspar crystallization in granitic protolith. Monazite total U-Th-Pb chronology constrain the igneous age to ca. 590 Ma. Metamorphism resulted in complex reaction microtextures involving monazite, apatite, thorianite, allanite and bastnäsite-synchysite solid solution in a series of reactions that were dependent on the presence of a F-bearing fluid of various composition related to local mineral reactions. Unfortunately secondary monazite grains are too small for geochronological analysis Correlation of microtextural information with literature Ar-Ar geochronology suggests that metamorphic reactions occurred during the retrograde stage of Variscan metamorphism. Application of electron-beam techniques to study micro- and mineral textures was an important technique in deciphering the complex history of the studied pebbles, and provided information at a resolution beyond that of conventional optical microscopy.

Acknowledgments: Paweł Poprawa and Tomasz Malata are greatly acknowledged for providing sample of gneiss from Krzesławice. This work was partially supported by the Junior Fulbright Advanced Research Grant (to B.B.), the MNiSW research grant 2P04D04129 (to B.B.), and the Jagiellonian University research funds DS811 and BW.

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Ignacio GONZÁLEZ-ÁLVAREZ¹, Monika A. KUSIAK²

EPISODIC BASINAL BRINES IN THE BELT-PURCELL SUPERGROUP? A MONAZITE APPROACH

The Belt-Purcell Supergroup constitutes a remnant of an extensive, ~ 17 km thick, dominantly siliciclastic sequence. Sedimentation spanned from ~ 1.47 to 1.40 Ga. This study aims to present a comprehensive monazite (REE(PO₄)) study focused on two key coarse-grained facies of the lower Belt-Purcell Sequence. Monazite chemical analyses and age calculations comprise the core of this ongoing study to further evaluate the characteristics, scale and chronology of rare earth element mobility during diagenesis in the Belt-Purcell Supergroup.

Previous studies addressed whole rock geochemical compositions, and primary and multiple diagenetic monazite chemical ages. Primary and diagenetic monazite differs systematically in REE and Th contents, REE fractionations, and REE/Th ratio; and different facies display systematically HREE enrichment when normalized to post-Archean continental crust. These geochemical features have been linked to basinal brine activity.

Monazite data suggest that coarse-grained facies from the lower Belt-Purcell Sequence have potentially recorded, possibly due to their high permeability, three diagenetic cluster ages at ~1.4, ~0.9 and ~0.4-0.6 Ga. The exceptionally rare monazite-(Nd) has been described in the same stratigraphic interval in a recent study. Its textural and chemical composition supports a diagenetic origin that implies rare earth element mobility.

Protracted episodic migration of basinal brines over hundreds of million years through Paleoproterozoic sedimentary sequences has been described at other basins as the Paleoproterozoic Athabasca and McArthur River basins.

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CHARACTERIZATION, ANALYSIS AND INTERPRETATION OF ORTHOPHOSPHATE, SILICATE, AND OXIDE MINERAL TEXTURES USING EMP ON BOTH THE MICRO- AND NANO-SCALE, BSE AND SEM ON THE MICRO-SCALE, AND TEM ON THE NANO-SCALE

Recent and ongoing characterization of a variety of textures in orthophosphate, silicate, and oxide minerals will be described which utilize electron microprobe (EMP) analysis on both the micro- and nanoscale, back scattered electron (BSE) microscopy and scattered electron (SEM) microscopy on the micro-scale, and transmission electron microscopy (TEM) on the nano-scale. These examples will range from grain boundary reaction textures to dissolution-reprecipitation induced partial or total replacement of a mineral to localised diffusion to fluid-induced unmixing in mineral solid solutions contrasted with solid state unmixing.

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APPLICATION OF SCANNING ELECTRON-BEAM CATHODOLUMINESCENCE IMAGING AND SPECTROSCOPY TO THE ACCESSORY MINERALS

Luminescence, the ability of non-conducting crystalline materials to emit light in response to excitation by various forms of energy, has long been recognised and studied in the fields of physics and the materials science. The harnessing of luminescence to the study of geological materials gained prominence in the mid-1960's when cathodoluminescence (CL) was used to study the internal structure of minerals. Cathodoluminescence (CL) is the result of interaction between the studied mineral and a beam of electrons and is an increasingly important technique for the characterisation and interpretation of complex textural features in some minerals. Traditionally, CL was studied using a vacuum sealed electron flood-gun mounted on an optical microscope. The development of CL detectors that can be mounted on scanning electron-beam instruments (microscopes or electron microprobes) has opened new dimensions for the application of CL, providing the scope for improved spatial resolution as well as allowing simultaneous collection of compositional information. These advances have been augmented by detectors capable of operating as spectrometers, providing information about the wavelength, intensity, and subsequently the identity of luminescence emitters.

CL is an extremely sensitive parameter and varies as a function of very small changes in composition or structure of a mineral. Subsequently, it may be used to resolve very fine scale structures that may not be immediately recognised using conventional imaging techniques. The most common application of CL is to the study of sedimentary rocks, where a difference between the luminescence of detrital grains versus diagenetic cements in both silicate and carbonate environments is well known. Other applications to common rock-forming minerals include tracking the development of fluid alteration, fluid assisted mineral growth, and fluid assisted trace element migration in complex hydrothermal environments, including ore-bodies.

CL is also a well known property of many accessory phase minerals, including apatite, zircon, and xenotime. CL investigation of these important trace element repository and geochronometer minerals has highlighted the often complex growth and alteration textures of such minerals, and can aid with the application of high-resolution trace element and isotope *in situ* analysis. The diversity of applications will be demonstrated using natural examples from a range of igneous and

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metamorphic environments. These will include zircon from the Acasta gneiss and an alkaline complex in the Seiland Igneous Province, and zircon from the deep lithosphere. A second example, collected from a carbonatite in southwest Finaland, will be used to demonstrate the rich luminescence of apatite, as well as the influence of dissolution-reprecipitation, fluid-interaction, and associated complex textures.

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EPMA CHARACTERISATION OF MONAZITE AND XENOTIME FROM PENINSULAR MALAYSIA

The rare earth element (REE) bearing minerals monazite and xenotime are found in placer or alluvial deposits and recovered as by-products by the Malaysian tin industry. These phosphates occur in acidic and alkaline igneous rocks, pegmatites or quartz-mica gneisses. Monazite is radioactive because of the presence of thorium (Th) whereas some xenotime is radioactive because of thorium and uranium impurities.

Full elemental compositions of monazite and xenotime collected from different areas in Peninsular Malaysia were determined by EPMA. In addition, X-ray mapping was also performed to give a better picture of the distribution of the main elements, namely, Ce and Y, and of inclusions of U and Th.

EPMA analysis was carried out on 41 monazite samples, 22 from Klang Valley, 16 from Kinta Valley and 3 from Klian Intan. Ce contents range from 27.38-41.82 wt% for the Klang Valley, 28.09-42.37 wt% for the Kinta Valley and 34.26-42.51 wt% for Klian Intan. Monazite uranium contents range from 0.02-10.87 wt% and Th contents from 4.6044-13.0619 wt%. Xenotime Y contents range from 39.5876-43.3345 wt% and Th contents from 0.1356-13.0619 wt%.

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MONAZITE FROM THE HIGH TATRA GRANITOIDS: CHEMISTRY AND NEW U-Th-Pb DATING USING ELECTRON MICROPROBE CAMECA

The electron microprobe Cameca SX 100 (Masaryk University, Brno) was used for the chemical investigation and dating of monazite from the Granaty tonalite (High Tatra Mts.). In the rock, monazite typically occurs in specific association with large aggregates composed of biotite, apatite, Fe-Ti oxides (ilmeno-hematite) and muscovite. It may also occur as discrete crystals in quartz or in plagioclase. Grains measure from 5µm up to more than 50 µm. Chemically, the monazite is a typical Ce-monazite. The concentrations of some important elements show the following values: ThO₂ = 1.95-5.02 wt. %; UO₂ = 0.01-0.97 wt. %; PbO = 0.02-0.08 wt. %; $Y_2O_3 = 0.31-0.64$ wt. %; $La_2O_3 = 12.64-16.3$ wt. %; $Ce_2O_3 = 27.8-1000$ 2.56 wt. %; $Gd_2O_3 = 0.77$ -1.88 wt. %; $Dy_2O_3 = 0.19$ -0.69 wt. %. Only ThO₂ and UO2 contents show marked variations between monazite crystals. The mean Sm/Nd ratio of 0.18 is exactly the same as that of the bulk rock. The ages calculated using the procedure of Montel (Montel et.al 1996) for individual homogeneous monazite grains vary significantly (248 to 347 Ma). The isochron method gives a calculated total age of 297±15 Ma. This result qualitatively agrees with the late Variscan age of granitoid magma intrusion in the High Tatra Mts. The scatter of the monazite isochron ages, when compared to previously published zircon dates, points to a relatively long (ca 30 Ma) final magmatic stage in the entire Western Carpathians which would have involved several discrete magma batches.

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EXTRAORDINARY GOLD OF SELECTED DEPOSITS AND OCCURRENCES IN THE WESTERN CARPATHIANS

Almost two hundred occurrences and geological indications of gold mineralization have been hitherto known in the Western Carpathians. The majority of the occurrences/deposits are concentrated in two different lithological settings, i.e., in crystalline complexes (e.g. Dúbrava, Magurka, Pezinok) and in neovolcanite regions (Kremnica, Banská Štiavnica, Zlatá Baňa). At present, gold is exploited only at Banská Hodruša. "Invisible gold", predominantly in pyrite and arzenopyrite, is typical of crystalline complexes. "Metallic gold" occurs in timeand spatially different precious-metal mineral assemblages in vein systems. The gold occurs dominantly as sub-microscopic and microscopic admixtures mainly in sulphides and quartz. Gold discernible to the naked eye has been found in the mining area of the Kremnica deposit. Microprobe studies proved the existence of a continuous range of Au-Ag intermetallic alloys with finenesses from 410-960. Some gold grains show significant inhomogenity. The forms of the gold (both in primary occurrences and in waste products) are very variable (grains, leafs, wires, wire-shaped aggregates, sticks). The oldest, fine-grained generations of gold showing the highest Au contents are predominantly situated in the deeper levels of the vein systems. Younger generations of gold and electrum/ küstelite are, in comparison, typically more coarse-grained and are usually of relatively lower fineness. These latter formed during the final stages of the polyphase epithermal mineralization, especially in neovolcanics. They are typical of subsurface parts of the vein systems. The accompanying minerals are various Ag- sulphides, tellurides, selenides and sulphoantimonides. At deeper levels, gold occurs together with Bi sulphosalts.

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BIOSIGNATURES IN Mn-Fe-MINERAL FORMING PROCESSES IN THE OXIDISED ZONE OF THE BANSKÁ ŠTIAVNICA DEPOSIT (WESTERN CARPATHIANS)

The interesting and varied Mn- and Fe- mineral association within the southern subsurfacial parts of the Terézia vein, which represents the oxidation zone of the Banská Štiavnica deposit, is described. Associated with todorokite, cryptomelane, pyrolusite, coronadite as well as minerals of the Mn-ferroxigite-vernadite and/or ferroxigite-achtenskite ranges are also identified. The presence of insoluble Mnoxides and hydroxides is a good indicator of microbial activity. Microbial Mnmetabolism is particularly significant as a potential mechanism for biosignature production because of the acceleration of Mn oxidation (Mn II \rightarrow Mn IV). Scanning electron microscopy was used to study the typical stratification of the Mn-Fe mineral aggregates which reflects the progressive natural formation of layers within the aggregates. Some layers are characterised by vertically curved basalt-shaped products among which very thin fibres (mineralised basidias) constitute a cohesion-less weaving texture. Vertical structures with variably positioned clusters of bacteria-like structures and/or fungus-like structures, strongly cellular and porous fungus-like thalluses with marginal feathered and globular terminations probably corresponding to basidias, are commonly present. Here, the bacterial mucilage (glycokalyx, i.e., recrystalized microbial liquid), metasomed by todorokite, is probably partially preserved. Within the oxidised zone of the upper part of Terézia vein, the stromatolitic texture formed by the gradual growth of soil-contaminated spongy tissues. As with normal stromatolites, after gradually exiting, each stratulum was mineralised by Mn hydroxides mainly. Similar forms of todorokite from New Mexico, USA, have been studied by Boston et al. (2001).

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CHARACTERISTICS AND SOURCES OF INSOLUBLE CARBONACEOUS PARTICULATE MATTER (BLACK CARBON AND CHARCOAL) DEPOSITED ON SNOW COVER IN THE AREA OF SZRENICA, POLAND

Airborne carbonaceous aerosols and those deposited on snow cover cause climate forcing. The level of that forcing is significant but its scientific understanding is very low. It strongly depends on the size, chemical composition and structure of individual particles. This research concentrates mainly on two types of carbonaceous aerosols: soot that strongly absorbs solar radiation and the remains of fossil fuel combustion - charcoal particles. Both are easily recognized under the microscope. The aim of the project is to conduct individual particle analysis using TEM (Transmission Electron Microscopy) and OM (Optical Microscopy) on snow and airborne aerosol samples collected in the area of Szrenica. We plan to describe. Their optical properties, and the size and structure of the soot and charcoal particles, will help to define the process which led to their formation.

There is an increasing interest in carbonaceous particulate matter and its influence on climate. Nevertheless, there are very few publications concerning individual particle analysis, which allows description of particle optical properties and may be fundamental to modelling how anthropogenic activities affect climate. It is also a very useful method in assessing sources of pollutants.

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ACCESSORY MINERALS IN PODZOLIC SOILS IN THE TATRA MTS: WEATHERING MICROTEXTURES AND STABILITY ORDER

Accessory minerals derived from granitoids were studied in two podzolic soil profiles: [Foli]-Dystric Leptosol (WRB 1998) in the Dolina Pięciu Stawów valley formed on "Goryczkowa type" (Kohut, Janak, 1994) granitoid and Skeletic Podzol (WRB 1998) on Mt Beskid formed on "common Tatra type" granitoid (Kohut, Janak, 1994). Both soils are acidic over the entire profiles and their pH_{water} is not >4.5. The aim of the study was to determine weathering microtextures on selected minerals surfaces and to define their stability order. The size of etching features and their extension on mineral grain surfaces is one of two main indices of the stability of minerals in soil (e.g., Lång, 2000 and literature therein).

Samples were examined using a cold field emission scanning electron microscope (FESEM) Hitachi S-4700 coupled with an energy dispersive spectrometer (EDS) NORAN Vantage at the Institute of Geological Sciences of the Jagiellonian University.

Six accessory minerals were examined in the soils: apatite, Ti and Fe oxides, monazite, epidote group minerals, rutile and zircon. Zircon is very resistant to weathering; its surface is devoid of dissolution microtextures. Rutile is also quite resistant in hypergenic environments.

Four groups of dissolution microtextures were noted on apatite surfaces: eyeshaped holes; thin fissures; hacksaw terminations and irregular channels. Monazite is commonly covered with tiny and soft irregular etch pits. Fracture-like textures also occur on its surface. There are many different dissolution features on Fe and Ti oxides, e.g., parallel, elongated etch pits; deep and wide channels; ragged edges; rounded hollows. Triangular holes or skeletal structures are characteristic of epidote minerals.

Differences in weathering microtextures developed on different minerals are related mainly to chemical composition. The number of dissolution microtextures and their depth is governed by the chemical composition of the mineral grain, the chemical composition of the solution and the duration of the dissolution process (soil age) (Morton, Hallsworth, 1999). The distribution of weathering microtextures on mineral surfaces is related to crystallographic structure. The deepest dissolution features are observed along cleavage-plane directions.

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On the basis of surface microtextures, the order of mineral stability can be defined (from the most resistant minerals): zircon > rutile > epidote > monazite > Fe&Ti-oxides > apatite. Similar accessory mineral stability orders have been proposed by other authors (e.g., (Lång L. O. 2000 or Morton, Hallsworth, 1999).

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TI-BEARING MINERALS IN THE KARKONOSZE GRANITE FROM STRACONKA HILL NEAR JELENIA GÓRA

Straconka hill is situated in Miłków about 10 km S of Jelenia Góra. It is one of the largest known outcrops of grusified granite in the Karkonosze Mountains (Jahn et al., 2000). After mineralogical and petrological examination, the granites from Straconka mountain were divided into three groups, i.e., group I rocks with white feldspar, black biotite titanite, ilmenite and epidote, group II rocks with pink K-feldspar, green plagioclase, greenish biotite (chloritized) and rutile and group III rocks with pure white albite, completly sericitized K-feldspare, greenish biotite (chlorite) and rutile.

The rocks were examined using transmitted light microscopy and a cold field emission scanning electron microscope (FESEM) Hitachi S-4700 coupled with an energy dispersive spectrometer (EDS) NORAN Vantage at the Institute of Geological Sciences of the Jagiellonian University. Carbon coated polished sections were analysed using back-scattered electrons (BSE).

The group I rocks contain titanite (CaTi[SiO₅]) and ilmenite (FeTiO₃). In rocks of groups II and III, the only Ti-bearing mineral is rutile (TiO₂). All of these minerals usually occur in the vicinity of altered biotite or of chlorite that resulted from the hydrothermal alteration of biotite. Titanite crystals are usually xenomorfic and wedged between phyllosilicate cleavage planes. Ilmenite occurs usually as needles (several tens of μ m long). Rutile crystals are usually xenomorfic (occasionally forming sagenite within altered biotite).

The occurrence of Ti-bearing minerals adjacent to biotite, and within altered biotite or biotite alteration products, indicates that these minerals largely formed during the hydrothermal alteration of the granite. The different Ti-minerals in group I rocks compared to those in group II and III rocks suggest differing hydrothemal fluid compositions (e.g., higher content of Ca ions in the case of the group I rocks). The absence of Ti-minerals typical of chemical weathering is related to the very limited role of this process in grus formation.

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KAOLINIZATION PROCESSES IN SANDSTONES OF THE CRACOW SANDSTONES SERIES (UPPER SILESIA COAL BASIN)

Diagenetic processes noted in the Cracow Sandstones Series sandstones (Upper Silesia Coal Basin) are numerous and cause significant changes in primary rock compositions. The degree of change depends on the rock diagenetic potential (Bjorlykke, 1983). The most advanced diagenetic processes are: crystallization of kaolinite in pore spaces, kaolinization of feldspar, matrix and biotite and the crystallization of iron oxides.

Sandstone samples, from the cores of two boreholes G3 and G4 drilled near Byczyna, were studied using field emission scanning electron microscopy (FE-SEM; Hitachi S-4700) with energy dispersive spectrometry (EDS; Noran Vantage). Analyses were made on rough sample surfaces using secondary electrons images (SE) and on polished thin sections using back-scattered electrons (BSE). In both cases, samples were carbon coated. Supplementary data were obtained using optical microscopy, X-ray diffraction, infrared spectrometry and chemical analyses (ICP-ES for main elements and ICP-MS for rare elements).

Kaolinite in pore space forms crystals from 10-20 μ m in diameter. Several morphological types of kaolinite are present: a) large platy crystals, with irregular edges, which form vermicules, b) thin plates (>0.2 μ m thick and tens of μ m in diameter) forming elongate booklets. Biotite is commonly subject to kaolinization. Kaolinized biotite flakes are characterized by split margins and crystallization of Fe-oxides between plates. Replacement of feldspar by kaolinite involves crystallization of authigenic kaolinite within dissolution voids. Kaolinized matrix is characterized by higher Al contents than is matrix that has not been kaolinizated. The Al³⁺ and Si⁴⁺ ions needed to form kaolinite came mostly from the dissolution of feldspar and the kaolinization of micas or other framework components present.

Biotite kaolinization is related to gradual increase in Al/Si ratio and decreases in K, Fe and Mg contents. As a result of the kaolinization of biotite, crystallization of Fe and Fe-Ti oxides occurred and, in addition, crystallization of pyrite. The absence of blocky kaolinite suggests that the temperature of formation of this mineral $<120^{\circ}$ C.

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SCANNING ELECTRON MICROSCOPY STUDIES OF CARBONATE CEMENTS IN SANDSTONES

The identification of carbonate cements is most often based on the following investigation methods: observation under a polarizing microscope combined with staining analysis, cathodoluminescence studies (CL), scanning electron microscopy (SEM) and investigations by means of energy dispersive spectroscopy (EDS).

In studies of calcite and dolomite, the best results are reached by combining scanning electron microscopy and CL analysis. CL studies of calcite in thin sections, e.g., in the cements of the Rotliegend and Miocene sandstones, revealed the common presence of manganese and its homogenous distribution in the crystal lattice (Kuberska, 2004). Studies and maps of element distribution made using a microprobe revealed an inter-dependence between Mn-calcite (yellow or orange luminescence in CL) and non-luminescent calcite whose chemical analysis revealed only calcium, oxygen and carbon. The chemical analyses of dolomites using an electron microprobe commonly proved the presence of manganese and iron. These elements commonly define crystal zoning whose causes can be specified.

Scanning electron microscopy is widely used in studies of ankerite and siderite e.g., in the Carboniferous and Jurassic sandstones (Kozłowska, 2004). The polarizing microscope makes it possible to identify these minerals by staining with Evamy solution. Ankerite stains dark blue whereas siderite does not stain. CL analysis is of no use as, due to the high Fe⁺²contents, both minerals are non-luminescent. Quantitative chemical analysis performed on dolomite enables identification of nonferrous dolomite, Fe-dolomite or ankerite. Point analyses on siderite allow recognition of which parts of the crystal belong to the siderite-magnesite solid solution series and which to the siderite-rhodochrosite series. Changes in the chemical composition of siderite and ankerite are revealed in BEI images by different shades of grey. Where both ankerite and siderite occur, major element distribution maps are used to separate the two minerals.

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ZIRCON INHERITANCE MASKING THE MAGMATIC AGE OF VOLCANIC ROCK: EXAMPLE FROM LATE VARISCAN RHYOLITE IN THE GÓRY SOWIE, POLISH SUDETES

Our project aimed to determine the age of subvolcanic dykes cutting the middleupper Visèan conglomerates filling one of the mollase half-grabens in the Góry Sowie Block (the so called Culm of Walim, Central Sudetes, SW Poland). The sample was collected from rhyolite exposed in an old quarry west of the town of Walim. It was crushed, sieved, and the heavy fraction 0.06–0.25 mm was separated using the conventional heavy liquid procedure. Hand-picked zircons were mounted in epoxy resin, and studied using optical microscopy, CL imaging, and SHRIMP analysis in VSEGEI, St. Petersburg.

Most of the zircon grains in the fraction studied are short- to normal-prismatic, c. $100 \times 60 \mu$ in size. They are euhedral, subhedral to subrounded, transparent or cloudy. Some contain distinct cores and inclusions. The internal structure of the crystals is diversified: from CL dark and rather homogeneous, to more common, recurrently zoned.

Nineteen points in eighteen grains were analysed. Most of the dates are Precambrian, up to the oldest, concordant age of 2.02 Ga. Four grains yielded 207 Pb- 206 Pb ages ranging between c. 550-720 Ma, but these are positively discordant and thus indicate only minimum ages. A group of three fairly concordant points, all from euhedral and rather weakly zoned crystals, yield 206 Pb- 238 U ages ranging between 475±5 Ma and 514±5 Ma and roughly corresponding to the well established age of the Sudetan orthogneisses.

The routine preparation and SHRIMP analytical procedure have not allowed the true magmatic age of the rhyolite to be determined. All the measured points appear to represent inherited materials. A second check of the crushed sample, made after the analytical session, revealed that the grain fraction <0.06 mm contains euhedral prismatic zircons, c. $80x30 \mu$ in size and smaller, that may represent the rhyolite magmatic stage. However, such small grains are difficult to analyse using the standard SHRIMP procedure.

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CHIME DATING OF MONAZITE FROM BENEŠOV-TYPE GRANITOID, CENTRAL BOHEMIAN PLUTONIC COMPLEX

The Bohemian Massif (BM) represents a collage of terranes in the easternmost part of the Variscan orogenic belt in Europe. It includes the Central Bohemian Plutonic Complex (CBPC), a ~3200 km² elongated body between Klatovy (SW) and Říčany, near Prague. The CBPC was emplaced between two contrasting terranes: the unmetamorphosed to weakly-metamorphosed Teplá-Barrandian Unit (TBU) to the NW, and the Moldanubian complex to the SE, which underwent highgrade metamorphosed Cambrian to Middle Devonian overlap sequence over a folded, unmetamorphosed Cambrian to Middle Devonian overlap sequence over a Neoproterozoic Cadomian basement. The oldest members of the CBPC, the Sázava suite tonalites and associated gabbros, were emplaced syntectonically into the TBU, in a transpressional regime at c. 354 Ma. Subsequently, between 350 and 337 Ma, high-K calc-alkaline granitoids and high-Mg melanocratic granites and syenites (durbachites) were intruded along the Moldanubian-TBU boundary, during normal faulting which exhumed the Moldanubian metamorphic complex.

The Benešov suite of the CBPC is exposed in the NE part of the complex, at the contact with the underlying Moldanubian complex. The suite is mostly amphibolebiotite quartz diorite, with associated gabbros, biotite granodiorites and leucocratic two-mica granites and granodiorites. The Benešov granitoids resemble those of the Sázava suite, except for the development of a strong subsolidus foliation and an associated metamorphic overprint. Previous authors have suggested that the Benešov suite is pre-Variscan, due to the intensity of deformation and metamorphism. To date the emplacement of granitoid body, 172 spots on 15 monazite grains were analyzed with a JEOL JCXA-733 electron microprobe. Compositions vary widely, with 0.03-12.03 wt% ThO₂, 0.009-1.933 wt% UO₂, 0.015-0.554 wt% PbO and 0.39-3.64 wt% Y₂O₃. Most data define an isochron age of c. 329 Ma, with minor age modes at c. 552 Ma and c. 1550 Ma. Additional U-Pb zircon dating is needed to distinguish age of components derived from source rocks, magmatic crystallization and metamorphism in the Benešov suite.

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ADVANCED TRANSMISSION ELECTRON MICROSCOPY FOR CHARACTERISATION OF COATED MATERIALS FOR AEROSPACE

The micro/nanostructure characterization of coatings is very complex and best performed by advanced transmission electron microscopy (TEM). Advanced TEM provides detailed structural-, phase- and crystallographic data which allow explanation, quantification and tailoring of the coating micro/nanostructure. Such analytical TEM investigations were performed for coated TIMETAL 834 microstructure characterisation in the present study.

TIMETAL 834 (Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si-0.06C-0.09O, wt%), a near- α titanium-base alloy, is used for compressor parts in modern gas turbine engines. To improve high-temperature oxidation resistance of the material so as to increase the combustion temperature of the engine, an intermetallic (Ti-Al-Ag) coating was produced on the TIMETAL 834 by magnetron sputtering.

Specimen preparation is an important part of TEM investigations of thin coatings. Thus, TEM investigations were carried out on cross-section thin foils prepared using a Focused Ion Beam (FIB) miller which enables the cutting of samples of uniform thickness from desired areas. Phase identifications were performed using combined crystallographic techniques (selected area electron diffraction, SAED) and electron spectrometry methods (energy dispersive X-ray, EDS and electron energy loss, EELS, EFTEM).

The investigations revealed that a 7 μ m thick coating is composed of two different sub-layers. The outer columnar sub-layer contains mainly γ -TiAl (tetragonal primitive) and some TiAl₂ (orthorhombic) whereas the inner amorphous sub-layer contained mainly Ti₅Al₃O₂ (cubic). EELS measurements and EFTEM elemental maps confirmed the presence of oxygen in the latter sub-layer.

A relationship between coating microstructure, its chemical composition and improved oxidation resistance of coated TIMETAL 834 has been established.

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CARBONACEOUS AEROSOL PARTICLES PROBED BY TRANSMISSION ELECTRON MICROSCOPY COMBINED WITH X-RAY MICROANALITICAL TECHNIQUES

Carbonaceous particles are an important component (150 Tg/vr) of atmospheric aerosols because of their considerable influence on climate by their altering of the radiation balance (IPCC. Climate Change 2001) and their possible health effects. The carbonaceous component of atmospheric aerosols is composed of two main fractions each characterised by slightly different thermal, optical and chemical behaviours. A light-scattering organic fraction (OC) is easily oxidized. Lightabsorbing black carbon (BC) particles are resistant to oxidation at temperatures below 400°C (Penner and Novakov 1996, Pöschl 2005). Both OC and BC are derived mainly from fossil fuels, biofuels and biomass burning. Part of the OC fraction originates from vegetation. The macroscopic properties (optical, thermal) of the carbonaceous aerosols result from the morphology and nanostructure of the individual atmospheric particles. It is therefore important to accurately detect and identify characteristics such as size, surface area and chemistry to properly assess radiation and health effects (Pawlyta 2006). We have characterized the morphology, nanostructure and elemental composition of carbonaceous particles by transmission electron microscopy combined with x-ray microanalytical techniques. Samples were collected in locations dominated by vehicle exhaust or residential wood smoke. The source contributions were verified by measurements performed on samples collected directly from specific sources (wood and coal burning, vehicle exhaust).

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APPLICATION OF TRANSMISSION ELECTRON MICROSCOPY (TEM) TO THE CHARACTERIZATION OF COAL AND COKE MICROTEXTURES

The results of studies on the microtexture characterization of coals and cokes are presented. Three samples of coal and their cokes were examined using optical microscopy (OM) (Taylor et al., 1998) and transmission electron microscopy (TEM) (Rouzaud and Oberlin, 1990). Maceral compositions (ICCP SYSTEM, 1998 and 2001) were established and reflectance measurements performed to determine the optical properties of the coals. Anisotropy measurements (Duber et al., 2000) were made on the cokes and concentrations of various structural forms estimated. TEM analysis relied on 002 DF observations of BSU domains. The application of digital image processing enabled automatic and quantitative characterization of their dimensions. The TEM results are correlated with the optical parameters of the coals and cokes.

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THE APPLICATION OF IMAGE PROCESSING IN STUDIES OF COAL AND COKE MICROTEXTURE

Cokes obtained by pyrolysis of bituminous coals have various physical (hardness, mechanical strength) and chemical (reactivity) features related to their structure and texture (Rouzaud and Oberlin, 1990). Application of 002 dark field (002 DF) enabled observation of basic structural units (BSU). These units have a tendency to mutual orientation in space and to merge into domains forming the microtexture of coal and coke (Rouzaud and Oberlin, 1990). These domains have varying shapes and dimensions. Application of digital image processing (Russ, 2002; Wróbel and Koprowski, 2001) allowed the quantitative characterization of the coal and coke microtexture. An algorithm of the processes used to distinguish and measure the domains obtained on the microscope images is presented in this paper.

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CALCIUM CARBONATE PRECIPITATION IN DIFFERENT WATER-SPRING ENVIRONMENTS

The crystallization of calcium carbonate in aqueous solutions is a topic of interest to many investigators in a variety of fields, e.g., geology, geochemistry, biomineralization, chemical engineering, as calcium carbonate is encountered in countless situations both in the natural environment and in industry. The morphologies of calcium carbonate precipitates are highly sensitive to local conditions, i.e., temperature, supersaturation, pH and the presence of inorganic or organic impurities.

Calcium carbonate occurrences from three sites involving different conditions of precipitation are presented here:

1. Active precipitation of $CaCO_3$ occurs in some water-springs in the carbonate rocks of the Polish Tatra Mountains where water temperatures do not exceed 6°C during the summer months. A dense moss cover of *Palustriella commutata* inhabiting the spring areas promotes calcite precipitation by inducing supersaturation due to photosynthetic uptake of CO_2 . As a result, intensive calcification of the water-drained, lower parts of the moss covers occurs.

2. In a cold, pH neutral, sulfurous spring in Wrząsowice village (near Kraków), calcite aggregates precipitate on an air-water surface beside elemental sulfur accumulated by sulfur-fixing colonies of microorganisms.

3. The third site is an anthropogenic shallow pool of highly alkaline waters (~12.5 pH) sourced from a metallurgical waste dump in Nowa Huta. The calcite crystals precipitating on the air-water surface due to evaporation have a characteristic, elongated, burgeon-like morphology.

The temperature, pH and water chemistry was determined and the saturation index SI with respect to calcium carbonate polymorphs (calcite, aragonite) calculated. The effect of precipitation conditions on calcite-crystal morphology at each site is discussed.

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SEM-EDS IN A PRELIMINARY PETROGRAPHIC STUDY FOR U-Pb DATING OF DIAGENETIC XENOTIME OVERGROWTHS ON ZIRCON GRAINS IN SANDSTONES

U-Pb dating of diagenetic xenotime overgrowths on detrital zircon grains in sandstones utilising ion microprobe (SHRIMP) has proved a successful technique for dating non-fossiliferous sequences (Rasmussen 2005). This study forms part of a larger project testing the applicability of diagenetic xenotime geochronology to dating sandstones from the stratigraphically well constrained Carboniferous Clare Basin of Western Ireland and the Pennine Basin in Northern England (Waters and Davies 2006). FE-SEM HITACHI S-4700 coupled with back-scattered electron detector YAG and Energy Dispersive X-Ray Spectrometer (NORAN Vantage) was a versatile and inexpensive choice for the preliminary stage of in-situ petrographical analysis. This approach greatly enhanced our previous conventional optical microscopy observations of xenotime overgrowths in the samples. High average atomic numbers of zircon and xenotime relative to the rest of the constituent minerals in the SEM images allowed for fast visual recognition of the co-joined minerals. The crystals were marked on a standard grid for future reference and simple statistical estimates. Chemical analyses (EDS, no standard) were performed to measure elemental abundances in xenotime and zircon (especially: Y, REE, U and Pb) with precision up to 1 wt.%. Xenotime overgrowths which were either of uncertain genesis, chemically inhomogeneous or < 9 mm in diameter (~90%) were rejected. Our diagenetic textural study combined with the planned U-Pb dating of separated xenotime overgrowths (to be undertaken using SIMS) should yield a precise isotopic timeframe for sedimentation that will be compared with available biostratigraphical data (Waters and Davies 2006).

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PARTICLES ON PINE NEEDLES AS INDICATORS OF SUSPENDED DUST MIGRATION AROUND FLOTATION TAILING PONDS – A PRELIMINARY STUDY

Since 1974, a large amount of waste (about 50 million tons) has been stored in the Olkusz-Pomorzany tailing ponds in the Silesian-Krakowian ore district. The fine-grained waste material is composed of particles less than 40 micrometers in diameter (Górecka et al. 1994). The small waste particles, containing metals, are easily blown around in the wind. The finest particles remain in the air as components of atmospheric dust. The area studied is covered with young, pine forest. Coniferous needles are often used to evaluate environmental risk (Wytteenbach et al. 1987, Dmuchowski, Bytnerowicz, 1995).

In the present study, the suitability of Scots pine needles as passive samplers for the estimation of dust particles migration around flotation tailing ponds was tested. Particles trapped on pine needles were studied using a scanning electron microscope and energy dispersive X-ray microanalysis. Particle sizes and morphologies, and the nature of the compounds hosting metals ions, were examined. A large majority of the examined particles are $<10 \ \mu m$ in size. Almost 80% of them represent respirable dust. All the components in the flotation wastes appear among the chemical compounds identified in particles on the pine needles. The quantity of waste particles decreases with distance from the flotation tailing ponds. The analysis of dust particles on pine needles could be a useful method for estimating the travel directions and distances of suspended dust migration around open flotation tailing ponds and around other point sources of dust particles with chemical compositions differing from the environmental background.

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INDIRECT ESTIMATION OF LITHIUM CONTENTS IN MICAS BY ELECTRON MICROPROBE ANALYSIS

Li-micas are typical for most rare-metal granites and, especially, for pegmatites. Lithium is not detected by electron microprobe analysis (EMPA) using the prevailing method of analysis of geological samples. Therefore, the development of a technique for the indirect estimation of lithium contents up to 8 wt% Li₂O by EMPA is the major problem in the analysis of Li-micas. Some empirical approaches based on major element correlations have been previously elaborated (Lapides et.al, 1977; Tindle, Webb, 1990; Tischendorf et.al, 1997; Tischendorf et.al, 1999; Yavuz, 2001; Zagorsky et.al, 1999)

Li-Al micas from the muscovite-polylithionite series were examined in the present study. Femic element contents in this type of Li-bearing mica are very low (Mg+Fe+Mn+Zn <5 wt%). Published data (Lapides et.al, 1977; Zagorsky et.al, 1999) show that a progression from muscovite to Li-rich mica involves increasing silica contents and decreasing Al contents. Therefore, the transition from muscovite to polylithionite is due to the replacement $Al^{VI}+Al^{IV}=2Li^{VI}+Si^{IV}$ and the levels of Al/Si should indicate the potential presence of Li₂O. Our studies provide a new experimental equation that enables the quantitative estimation of lithium contents in non ferrous (Mg+Fe+Mn+Zn <5 wt%) Li-Al micas:

 Li_2O (wt%) = -1.35-8.2*Ln(Al₂O₃/SiO₂). However, our equation is not valid for high-lithium micas with extremely low Al/Si such as the polylithionites.

Electron microprobe analyses were carried out using a Tescan Vega TS5130MM with INCA Energy 350 spectrometer (IEM RAS). The investigation of the functional relation of the integral intensities ratio of the AlK α and SiK α lines (S_{AlK α}/S_{SiK α}) vs lithium content in the same micas demonstrated the possibilities of using this ratio for indirect quantitation of lithium over a wide range.

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ELECTRON MICROSCOPY AND ENERGY DISPERSIVE SPECTROMETRY IN THE STUDY OF ROCK WEATHERING ZONES IN POLLUTED URBAN ATMOSPHERE

Building stones exposed to an urban atmosphere are subject to significantly accelerated weathering caused by relatively high concentrations of atmospheric pollutants. The determination of weathering rates and mechanisms is interesting not only from a scientific point of view but also for practical reasons. The depth of the weathering reaction zone and its chemical and mineralogical composition are important factors in planning for monument conservation. Knowledge of the links between rock composition and texture and weathering rate is the basis for the proper selection of stone building materials.

The rich variety of stone materials used in the historical buildings of Cracow and the high levels of atmospheric pollution there provides an opportunity for systematic studies. Different types of weathering crusts are developed on various rocks depending on whether the weathered surface is vertical, horizontal or overhanging, and on rock properties, e.g., porosity.

Numerous minerals have been recorded in weathered reaction zones in Cracow. In addition to predominant gypsum, other sulphate minerals such as bassanite, hexahydrite, epsomite, melanterite, langbeinite, mirabilite, syngenite, burkeite, celestite, carbonates such as calcite and dolomite, chlorides such as halite and sylvite, and nitrates such as nitronatrite and nitrammite may be present. Salt weathering is an important process in the urban environment.

Numerous methods are applied in the investigation of weathering processes – optical microscopy, X-ray diffraction and chemical- and isotopic analyses. Electron microscopy with energy dispersive spectrometry is of special importance. The identification of small crystals, and the determination of their morphologies, is important for the evaluation of the conditions of formation of secondary minerals within weathering crusts. Concentrations of secondary minerals are commonly too low for identification using other methods (e.g., X-ray diffraction). Anthropogenic dust particles are easily identified in weathering zones because of their morphology and chemical composition. Increasing amounts of finely dispersed aerosols have become significant influences on weathering processes recently. Scanning electron microscopy enables detailed study of the microtexture of weathering zones.

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CRYSTALOCHEMICAL FEATURES OF ZIRCON CRYSTALS FROM IELOVA METAMORPHIC SEQUENCE (SOUTH CARPATHIANS, ROMANIA)

Ielova crystalline sequence is one of the most controversial units of the Romanian Carpathians. It is located in the south-eastern part of the country, in the so-called "Banat" region, between Mehadica Valley in north and Danube Valley in south. Geologically, it belongs to the Southern Carpathians, but a more detailed affiliation is difficult to give. Based on different criteria, it was considered as part of the Danubian domain (Codarcea, 1940), (Berza et al., 1983), (Berza and Iancu, 1994), (Krautner et al., 1988) or of the Getic one (Krautner and Krstic, 2002), (Medaris et al., 2003). Lithologically, Ielova crystalline sequence mainly consists of amphibolites and gneisses with garnet and biotite.

For establishing the affiliation of the Ielova unit to one of the two main domains of the South Carpathians, a complex geochronological and geochemical investigation was performed. As part of this research, zircon crystals were extracted from the gneissic rock and were investigated by means of a LA-ICP-MS device, for U, Th and Pb contents for age determination. Electron microprobe analyses were performed for defining the crystal chemical characteristics of zircons. The crystals'morphological features were emphasized by SEMcathodoluminescence (CL) and back-scattered electron imaging.

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THE SEM-EDS METHOD AND THE CHARACTERIZATION OF ALTERATED STRZEBLOW GRANITE (STRZEGOM-SOBÓTKA MASSIF)

The Strzegom-Sobótka Massif occurs in the central part of Sudetes Mountais and is composed of different types of granites representing individual intrusions (Puziewicz, 1990). Strongly altered biotite granodiorite from Strzeblów was investigated.

Sixteen samples was studied using SEM-ESD (Hitachi S-4700 with NORAN Vantage), optical microscopy and XRD (Philips X`Pert APD type diffractometer).

The Strzeblów biotite granodiorite is strongly altered. It is considered that the alterations are related to hydrothermal processes and probably to weathering. The mineral assemblage consists of albite (Ab 90-100%), K-feldspar, micas and kaolinite. Three main processes can be observed, namely, albitization related to reduction in amounts of Ca-Na plagioclase and K-feldspar, kaolinization of micas and feldspar and arenitization.

As albitization usually involves quartz dissolution (episyenitization) (Davisson, Criss, 1995), quartz is scarce or absent in the studied samples. Kaolinization of mica and K-feldspar is not complete. Although Al/Si is typical of kaolinite, the presence of K, Fe and Mg indicates that removal of these elements was not completed. Desintegration of the rock is a result of advanced arenitization. The chemical composition of the rock remains almost stable during this process. Using SEM-EDS, the sequence of alterations can be established as initial albitization and episyenitization followed by kaolinization and, lastly, arenitization.

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Accessory Minerals *In-Situ*: Microanalytical Methods and Petrological Applications

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REMARKS ON GENESIS AND STABILITY OF PHOSPHATES IN SILICIC MAGMATIC SYSTEMS

Distribution and compositional mineral data gained by combination of cathodoluminiscence and microprobe technique provide excellent opportunity for investigation of the details of phosphate behaviour, and namely apatite. The research of main phosphates in silicic rocks (apatite, monazite and xenotime) is an important tool for the discrimination of granitic rocks. In the West-Carpathian Variscan basement it was shown that concentrations and compositional peculiarities of accessory phosphates are characteristic for each of the granite suites: I-, S-, A- and specialized S-type.

Apatite in the early magmatic granite differentiates with I-type affinity is very abundant, locally in the quantity of rock-forming mineral. Fractionation of apatite effectively decreases P and REE concentrations, and as a consequence, also the amount of apatite originating from the residual melts. Apatite crystallizes in two maxima: as an early-magmatic and a late-magmatic mineral phase. The earlymagmatic apatite is usually included in biotite, late-magmatic forms paragenesis with titanite, and magnetite as a result of increase activity of Ca^{2+} released from anorthite component interacted with products of disintegrated titanomagnetite. biotite and earlier apatite (Broska et al. 2007). Such parageneses are typical in evolution of I-type granitic rocks. In the S-type granites where bulk of phospohorus is split into monazite and apatite, the latter is not so abundant. Compositionally, this apatite is typical by increased Mn. The low apatite concentration in S-type granite, which is typically peraluminous, is connected also with effect of berlinite substitution in feldspars which blocks part of P from the melt. It is significant effect especially in more evolved granites. In sufficient amount of P in feldspars and increased activity of fluorine, corrosive fluids can locally precipitate secondary apatite as disseminated fine grains inside of alkali feldspars, or in the form of tiny veins in/out of the rock. In contrast to primary early-magmatic fluorapatite, the late to post-magmatic apatite is closer to the stoichiometric fluorapatite, with significantly lower Mn contents and low concentrations of REEs.

Monazite-(Ce) is the typical mineral of S-type granitic rocks as early magmatic phase, commonly occurs in A-type granitoids, but it is absent in the I-type

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tonalites, with exception of their late magmatic differentiates. In the A-type and evolved S-type granites monazite has an increased cheralite component. Monazite-(Ce) during evolution of felsic melts shows variability in the abundance. It was shown that in the granites of the Western Carpathians Harker diagrams show irregular kinked distribution of LREE, although in generally negative trend. The irregularity in LREE is reflected also in the monazite concentrations. After the decrease of Ce vs SiO₂ with differentiation, monazite concentration decreases. But on the level of ca 70 wt. % SiO₂ there is an increase of Ce and also the increase of monazite concentration. This can be explained by the presence of berlinite molecule in feldspars because apatite and monazite concentrations should be controlled by this behavior. This effect has been firstly explained by experimental work of London (1992) who found that berlinite substitution starts to operate during the increase of a peraluminosity of melt. While P is trapped by feldspars, apatite becomes soluble and monazite-(Ce) is not stable. The sinking of P into feldspar decreases P in the melt and this element is inaccessible for the precipitation of common accessory phosphates, such as monazite and apatite.

Xenotime-(Y) occurrences are the most variable. No significant correlation between amount of Y and HREE and xenotime-(Y) concentration exists. Magmatic xenotime occurs with monazite and displays a minor compositional zonation involving Si, Th and U. The elements for the formation of secondary xenotime-(Y) in the granitic rocks results come from the leaching of P and (Y + REE), mainly from zircon and apatite.

In contrast to the main accessory phosphates characterized above, the F- and Lirich granites from the Gemeric unit (specialized S-type) show a different mineralogy: They contain other, rarer phosphates. In the albite- and topase-rich rock where kryophylite and phengite are only micas stable, the stability of apatite seems to be suppressed and abundant phosphorus in the strongly peraluminous melt, together with excess Na, Mn, Fe and Sr, forms other phosphates – lacroixite (Na), arrojadite (Fe, Na, Mn), goyazite (Sr, Al) and amblygonite (Li). The obvious reason for the excess of the above elements is the lack of biotite and Ca plagioclase. Although some apatite may be stable in early stages, monazite and xenotime lack totally.

The formation of REE phosphates during metamorphism occurs both during prograde and retrograde stages (e.g. Catlos et al., 2002, Finger and Krenn, 2007). The remobilization of primary magmatic phosphates during metamorphic overprinting is significant. Apatite is easily soluble in acid fluids, and both monazite-(Ce) and xenotime-(Y) are unstable during fluid-activated overprinting. The low temperature alteration of monazite in S-type granites leads to the formation of apatite enriched in the britholite component, but medium grades of metamorphism results in the formation of apatite and LREE enriched epidote (partly allanite) as a corona enclosing the monazite-(Ce) core. Xenotime-(Y) shows a similar alteration pattern, but with different REE distributions in the products. At greenschist / amphibolite facies, rims of secondary Y-rich apatite and Y-rich epidote form around xenotime-(Y). In low-Ca granites however, apatite lacks in this alteration assemblage since xenotime-(Y) breaks down directly to the Y-

enriched epidote. The fluid responsible for the breakdown of monazite and xenotime contains elements released from alteration of anorthite (Ca) and biotite (Si, Al and F). The EBSD technique indicates the low crystallinity of the REE-rich epidote phases.

In the HP and UHP conditions the solubility of REE's in apatite increases with the increase of pressure (Liou et al. 1998, Broska and Janák, 2007). In the decompression regime monazite exsolution in apatite may occur. Such tine lamellae monazite shows increase MREE's. The formation of monazite from fluorapatite due to fluid-induced metasomatism has been experimentally modelled at granulite facies P-T conditions (Harlov et al., 2005).

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INSIGHTS AND OBSERVATIONS FROM IN SITU ION MICROPROBE MONAZITE GEOCHRONOLOGY (MENDERES MASSIF, WESTERN TURKEY)

Monazite (REEPO₄) commonly occurs in a variety of high-grade metamorphic and igneous rocks. The mineral is ideal for understanding the tectonic history of rocks that have experienced extreme crustal temperatures and multiple metamorphic events as the mineral remains impervious to diffusive Pb loss at conditions >900°C (Cherniak et al., 2004). Monazite appears resilient to radiation damage (Meldrum et al., 1998), but ages can be affected by fluids as dissolutionreprecipitation reactions occur along a retrograde path (e.g., Seydoux-Guillaume et al., 2002). However, the mineral's ability to recrystallize during multiple geologic events provides a record of information about complexly metamorphosed regions and can be used as a complement to other geochronologic data.

Here we report some key observations regarding the ages of monazite from the Menderes Massif in western Turkey. The region is a metamorphic core complex that exposes amphibolite-facies rocks with ages of prograde metamorphism ranging from the Cambro-Ordovician to the Eocene-Oligocene (e.g., Cemen et al., 2006). The massif experienced a transition in the Cenozoic from blueschist-facies compressional metamorphism to large-scale extension and core complex formation. This type of tectonic and petrologic succession may be "normal" for orogens due to gravitational collapse of overthickened crust, or, alternatively, extension may be driven by other forcing factors, such as back-arc spreading or orogenic escape (e.g., Seyitoglu and Scott, 1996). Timing extension is crucial because it delineates among different mechanisms for the exposure of high-grade metamorphic and igneous rocks in this core complex.

This study focuses on the Alasehir detachment, located along the northern margin of central Menderes metamorphic core complex and exposes garnet-bearing schists and gneisses intruded by granites (e.g., Hetzel et al., 1995). The detachment dips approximately 10-20°N, extends ~150 km in length, and plays a key role in developing models for the evolution of the massif. Trace element geochemical data are consistent with the granites being generated under a compressional volcanic-arc regime, possibly due to the subduction of the Eastern Mediterranean floor along the Hellenic trench. Based on monazite geochronology, the magmas were then

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subjected to extension/exhumation from 21.7 ± 4.5 Ma to 9.6 ± 1.6 Ma ($\pm1\sigma$). The age range is difficult to interpret, but the ion microprobe technique allowed the chemistry and textural relationships of the monazite dated in the granites to be preserved and analyses of zones within larger grains were feasible (Figure 1).



Fig. 1. (A) Backscattered electron (BSE) image of a Menderes Massif monazite grain(circled) (B) cathodoluminescence (CL) image of the same area as (A). (C, Upper): high contrast BSE image of the dated monazite grain (C, Lower): secondary electron (SE) image. Circles outline the ion microprobe spot. Ages are $\pm 1\sigma$. (D, Upper): X-ray Th map of the dated monazite grain (D, Lower): X-ray Y map of the dated monazite grain.

All monazite grains were imaged using SE after dating to determine where the ion microprobe spot was located. SE images, X-ray element (Th, Y) maps, BSE, and CL images are useful in deciphering the significance of the ages. The oldest age is in a region of low Th and darker appearance in BSE. Although monazite does not show any color or contrast in the CL image, surrounding minerals are significantly zoned and have experienced multiple growth events. Fracture patterns clearly seen within the plagioclase in the CL image are consistent with the rock's extensional history. This rock and metamorphic assemblages collected nearby show significant fluid/rock interaction visible in the CL images that are not able to be observed by X-ray mapping or BSE imaging.

Monazite ages reported here have a higher uncertainty than is typical for ion microprobe geochronology, and appears to be the result of higher amounts of common Pb. Average radiogenic 208 Pb (208 Pb*) content for the Menderes Massif monazites is 71±4%, whereas our measured standard 208 Pb* content is 98±1%. The assumption that common Pb is negligible in monazite (e.g., Cocherie and Legendre, 2007) may be incorrect when applied to younger monazite exposed to fluid/rock interaction along a retrograde path.

We suggest that to understand the meaning of monazite ages from rocks that have experienced multiple tectonic events requires: (1) a method that is nondestructive, (2) multiple analyses of chemically distinct zones within the grains themselves, and (3) chemical information from both the rock and the monazite's surrounding assemblage. An ideal geochronologic approach includes: (1) ion microprobe geochronology, (2) high contrast BSE and X-ray mapping, (3) wholerock chemical data, and (4) CL imaging.

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LA-MC-ICPMS APPLIED TO *IN SITU* U-PB DATING OF 2 MA ZIRCONS USING A MULTI-ION COUNTING SYSTEM

Zircon is a remarkably robust mineral, generally forming a close reservoir for radiogenic Pb even when subject to intense and prolonged heating. However, it may suffer partial resetting due to intense α -recoil associated with high U content. alteration related to fluid interaction and inhered cores frequently remain in zircon grains from orthogneiss, migmatites and leucocratic granite. This means that whole grain analyses are not suitable for solving the complex history of many geological problems. Furthermore, cracks and inclusions contributing to enhance common-Pb contribution must be avoided. Consequently, many studies require in situ dating. Furthermore, U-Pb dating of very young zircons (about 1-2 Ma) needs to avoid any chemical stage leading to common Pb contamination when measuring isotopic ratios for material containing less than $0.1 \,\mu\text{g/g}$ of radiogenic Pb. In addition, a real need for U-Pb geochronology is evident since phases dated by K/Ar or ⁴⁰Ar/³⁹Ar generally are much less robust than zircon. Until now, the unique isotopic method providing sensitive in situ measurements involving no common Pb contamination associated with the analyses was the ion microprobe (SIMS, eg. SHRIMP). Recently, an alternative method has emerged: the MC-ICPMS coupled with a laser. A multi-ion counting system (MIC) allows high sensitivity and precision to be achieved for such transient signals.

The goal of the laser ablation ICP-MS method applied to U-Pb zircon geochronology is to approach SHRIMP performance levels and, if possible, to improve some of the weaknesses of this reference in situ method. Firstly, such high resolution sensitive ion microprobes are expensive. Secondly, more than fifteen minutes is necessary to record reliable isotope data for one spot analysis. Thirdly, high mass resolution (M/ M~5000) is required to eliminate all potential polyatomic interference produced in the source (Zr₂O, HfSi, etc.). Obviously, high mass resolution leads to a lowering in the sensitivity by a factor of about 10. On the contrary, these polyatomic ions are dissociated in the plasma of the ICP-MS. LA-MC-ICP-MS technology is superior in this respect. On the other hand, the main strength of ion microprobes is their high spatial resolution. In addition, despite the need for high resolution mode, the SIMS are especially designed to remain very sensitive, to such a point that ²⁰⁷Pb/²⁰⁶Pb and ²³⁸U/²⁰⁶Pb ratios are obtained with an accuracy and precision better than 1% and 3% respectively with a pit of only 20 μ m or less in diameter and 1 or 2 μ m in depth, which is far below the volume analyzed by laser ablation (crater 20 µm in diameter and in depth). In addition,

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only low electronic background (~0.1 cps) and no potential common-Pb contamination are involved.

The key points to achieve the best accuracy using laser ablation (UV 213 nm) and MIC are as follows: 1- A reference standard with relatively low Pb content is required. The energy of the laser is adjusted to avoid the ion counter collecting ²⁰⁶Pb to be saturated when unknown samples are analyzed. The zircon standard 91500 (CNRS-CRPG, Nancy) containing 14 ppm of Pb is a good candidate. According to the expected age of the unknown zircon, the ²⁰⁶Pb count can be adjusted in the range of 10000 to 60000 cps. 2- U/Pb fractionation, due to the greater volatility of Pb during laser ablation, is potentially a critical point of the laser method. By careful defocusing the laser, it is possible to obtain a constant ²⁰⁶Pb/²³⁸U ratio during the ablation time. 3- This ratio can be adjusted close to the real value by adjusting the sample gas. Whatever the case, the ratio can easily be corrected using the standard. ²⁰²Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb peaks were collected using five ion counters while ²³⁸U and ²³²Th were collected on two Faraday cups. All masses were simultaneously collected in static mode. After undertaking blank subtraction, the raw value of each sample was normalized with the average of the standard analyzed, before and after the sample, according to the following sequence: blank1, Sdr 91500(1), blank2, sample1, sample2, blank3, Sdr 91500(2), blank4, etc.

In a first stage we demonstrated (Cocherie et al., 2005; Cocherie et al., 2006), using already dated zircons (ID-TIMS and SHRIMP) in the range of 290 to 2400 Ma, that LA-MC-ICPMS has become a reliable and precise method.

In a second stage we considered a 2 Ma phonolite from the Mont Dore region (French Massif Central) already dated by the K/Ar method applied to whole rock (Cantagrel and Baubron, 1983) and showing strong field geochronological constrains. Euhedral clear zircon grains were extracted from the rock and mounted for SHRIMP II analyses at ANU Canberra and a second mount for LA-MC-ICPMS. Knowing the ²³²Th/²³⁸U ratio measured in the zircon and the Th/U ratio of the magma in equilibrium it is possible to correct the measured ²³⁸U/²⁰⁶Pb* for Th disequilibrium. Then, using a Tera and Wasserburg (1972) uncorrected Concordia diagram, we obtained an age of 2.095 ± 0.038 Ma (MSWD = 0.96, 12 spots) and of 2.135 ± 0.029 Ma (MSWD = 2.3, 18 craters) with SHRIMP II and LA-MC-ICPMS. All uncertainties are given at 2σ level.

Finally, we decided to date a young zircon standard from CRPG Nancy: 61.308B (Wiedenbeck et al., 1995). Because the rock type from which this crystal was derived is unknown, no Th disequilibrium correction can be carried out. The LA-MC-ICPMS age is 2.510 ± 0.046 Ma (MSWD = 1.9; 12 craters) while the recommended 206 Pb/ 238 U age is 2.508 ± 0.002 Ma. Both are uncorrected (for Th disequilibrium) 238 U/ 206 Pb* ages.

Now, an alternative U-Pb dating method to SHRIMP is available to be applied to very young zircons (~ 2 Ma). A MC-ICPMS instrument coupled with a laser and using a multi-ion counting system allows highly precise and accurate dating.

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DATING SUPERCONTINENT CYCLES INVOLVING THE ARCHEAN WYOMING CRATON, USA: NEW CONSTRAINTS FROM THE MICROANALYSIS OF "ROSETTA GRAINS" OF ZIRCON, TITANITE, AND MONAZITE

Precambrian exposures in the Archean Wyoming craton, USA, are restricted to isolated, Laramide-age block uplifts, so studies of cratonic evolution are necessarily restricted to these uplifts. The easternmost of these uplifts is represented by the Black Hills (South Dakota), from which selected grains of Precambrian zircon, titanite, and monazite in crystalline rocks have been spot-dated by ion microprobe (SHRIMP) and/or electron microprobe (EPMA) techniques. Three key mineral grains (one of each U-bearing accessory) are referred to herein as "Rosetta grains" because they represent unusual yet important microtextures or occurrences in their respective rocks which, combined with their inferred crystallization ages, permit important details of 2900-1700 Ma PTDt evolution of the Black Hills terrain to be deciphered. This 1200 Myr timeframe is significant because it encompasses the ~2900-2550 Ma assembly of supercontinent Kenorland, its ~2500-2100 Ma fragmentation, and the ~1900-1700 Ma assembly of supercontinent Laurentia - tectonic events all of which involved the Wyoming craton as an integral participant. These "Rosetta grains" of zircon, titanite, and monazite are fully characterized below, from oldest to youngest, and their tectonic significance in terms of supercontinent assembly and break-up is also established.

Zircon: The Black Hills uplift exposes a Precambrian crystalline core of Neoarchean basement granitoids nonconformably overlain by two Paleoproterozoic intracratonic (back-arc?) rift successions. Magmatic zircon (Th/U = 0.6-0.9) in these granitoids yields ²⁰⁷Pb/²⁰⁶Pb ages (upper-intercept, U-Pb concordia) ranging from 2596 ± 11 to 2559 ± 6 Ma (all ages reported at $\pm 2\sigma$), indicating a timeframe of subduction-related magmatism believed to have been associated with the final assembly of Kenorland. Interestingly, among the ~ 200 zircon grains examined from 3 rocks with BSE imagery, only a single grain exhibits a xenocrystic core of yet-older magmatic zircon. Epitaxially overgrown by the 2560 Ma zircon, this older zircon fragment preserves a nearly-concordant, $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2894 \pm 6 Ma. Representing the oldest crustal material reported thus far in the Black Hills, this xenocryst is interpreted as an unmelted residue of ~2900 Ma mafic lower crust that is inferred to underlie the Black Hills, which also constitutes a likely source for the 2600-2560 Ma granitic magmas. This interpretation is supported by a ~2900 Ma model $T_{\rm DM}$ age for the 2560 Ma granitoid. It is further believed that older Black Hills schists intruded by the 2600-2560 Ma granitoids were originally deposited

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some time between ~ 2900 and ~ 2600 Ma – i.e., prior to the $\sim 2600-2550$ Ma collision of the eastern Wyoming and southern Superior cratons to form part of Kenorland.

Titanite: In the northern Black Hills, a 1-km-thick layered sill that intrudes only the older of the two rift successions provides a key constraint on the timing of mafic magmatism and of older rift-basin sedimentation. SHRIMP spot analyses of rare titanite megacrysts sampled from a horizon of dioritic pegmatite in the uppermost sill yield a 207 Pb/ 206 Pb upper-intercept age of 2480 ± 6 Ma, and EPMA determination of Ce/Nb and Al/Fe ratios of the titanite indicate a magmatic (versus metamorphic) origin. Locally, these data are interpreted as indicating that an episode of gabbroic magmatism occurred at 2480 Ma, probably in response to incipient rifting along the eastern margin of the Wyoming craton. These data further constrain a 2560-2480 Ma timeframe for deposition of the older sedimentary rift succession and a ~2480-2015 Ma hiatus across a prominent unconformity, which is overlain by the younger rift succession of $\sim 2015-1880$ Ma age. Regionally, layered mafic intrusions of similar thickness and identical age to the Black Hills gabbro occur along a rifted belt in the southern Superior craton (Sudbury region, Ontario), and they are spatially aligned with the Black Hills gabbro in a Kenorland restoration of the Wyoming and Superior cratons. Moreover, the ~2480-1880 Ma timeframe for rifting inferred in the Black Hills incorporates the ~2500-2100 Ma timeframe independently inferred for incipient to final fragmentation of Kenorland.

Monazite: A kyanite-zone metapelite from the southern Black Hills has been analyzed by microstructural methods in order to unravel its polyphase deformational history associated with the assembly of southern Laurentia. Three deformational fabrics are recognized in oriented thin sections of this rock: an ENEtrending S_1 fabric, preserved as oblique inclusion trails in garnet porphyroblasts; a NNW-trending S_2 fabric, preserved as microlithons in the rock matrix; and a flattening fabric, S₃, which transposed S₁-S₂ and dominates the matrix. A complex monazite porphyroblast has been analyzed in situ by EPMA (Ultrachron) in order to constrain the timing of S_1 - S_3 fabric formation associated with monazite growth. Among ~ 100 monazite grains examined in thin section, the core of this single grain uniquely preserves the S₁-S₂ fabrics as sigmoidal inclusion trails. The mean total-Pb date of this domain is 1750 ± 10 Ma (n = 39 spots), which is equivalent to a 207 Pb/ 206 Pb date of 1747 ± 10 Ma obtained for the same domain. Analytically, these results validate the total-Pb dating method generally, and the Ultrachron in particular, for reliable age determination in low-Th monazite. Tectonically, these results are interpreted as constraining 1750 Ma minimum ages for the S₁-S₂ fabrics and the sequential, D₁-D₂ collisional events that imposed them. These events correspond to ~N-directed accretion of the Yavapai arc terrane and ~E-W-directed collision of the Wyoming and Superior cratons, respectively, during ~1775-1690 Ma assembly of this part of southern Laurentia. A higher-Th,Y rim of this same grain truncates the S₁-S₂ sigmoid and is associated with resorption textures in garnet porphyroblasts, coupled release of Y, and an S₃ fabric that pervasively overprinted S₁-S₂ in the rock matrix. The mean Ultrachron age of this domain is

 1692 ± 5 Ma (n = 17 spots). These results support a ~1715-1690 Ma timeframe for localized doming (D₃) related to late-syn- to post-tectonic granite magmatism, the onset of which is independently dated isotopically at 1715 ± 3 Ma.

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PEPITA: DATA MANAGEMENT, OUTLIER REJECTION, CALCULATION OF ISOTOPE RATIOS AND TRACE ELEMENT CONCENTRATIONS FROM LA-ICP-MS RAW DATA

Raw output data of time-resolved laser ablation ICP-MS analyses contain of high number of analyte intensities, usually as cps values. Manual handling of such vast data matrices in common spreadsheet programs and the expression of trends, isotope ratios and finally the concentrations is a rather time consuming procedure.

We present a new data handling protocol by means of a Windows-based software, PEPITA, that conveniently and rapidly processes the LA-ICP-MS raw data. It can store all necessary information, settings, and user preferences. It uniformly performs robust outlier tests, correction for elemental fractionation, instrument mass-bias and common Pb, and it finally computes element concentrations or isotope ratios, together with their propagated errors.

Standard composition data, standard analyses and the used dwell-times are stored in separate files. Blank substraction is done by extracting the blank portion of the data files or by using blank measurement files. Data file import is designed to comply with output file formats of Perkin-Elmer, Thermo and VG.

Preferred time slices for the calculation are selected on a time-intensity plot. Both raw intensity data and isotope ratios can be tested for outliers.

Signal intensity often shows fluctuations and can contain large, individual outlier peaks. Calculated averages can thus be severely biased especially if the count rate is low. PEPITA offers several methods to visualize extreme values and reject them, in a single step or iteratively (e.g. 1-2-3 sigma rejection, Grubbs-test).

Results of data analysis can be exported (copied to clipboard, written into a new file or appended to an existing file) and U-Pb data can be directly processed further by Isoplot (Ludwig, 2003). For trace element analyses, the export includes: (a) list of files, time slices used, rejection algorithm and criterion, (b) average concentrations, limit of detection and other statistical parameters, (c) concentrations and errors in time slices (d) warning in case of incompatible files.

PEPITA is distributed as freeware and available from the first author (ID) upon request.

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IN-SITU AND IN-SYNCH: TYING ACCESSORY CHRONOLOGY TO MAJOR PHASE GROWTH DURING HI-T METAMORPHISM

Perhaps the ultimate goal of obtaining age estimates from metamorphic rocks is to pin down the timing of specific mineral reactions along the P-T path of a metamorphic event. This is not easy, since most datable minerals occur as sub-mm grains without clear paragenetic associations with major phases. Recent breakthroughs in understanding garnet-zircon (e.g. Rubatto, Hermann 2007; Kelly, Harley 2005) and garnet-monazite equilibria (e.g. Pyle, Spear 2001) have greatly enhanced the promise of petrogenetically-constrained mineral chronometry. Microbeam (EMP, SHRIMP, and LAICPMS) analysis of accessory minerals in polished, thin-sectioned samples is taking the lead in such studies. At this workshop, two examples of *in-situ* microbeam geochronology will be presented.

In the first example (Fig. 1), zircon grains from metapelitic migmatites of the Lützow-Holm Complex, east Antarctica have a broad range of textures and ages. Whereas previous SHRIMP ages from separated zircon grains concentrate around 530-550Ma, and were interpreted as timing peak metamorphism, new analyses yield a spread of age estimates from 510 to 610Ma. In-situ analysis and isotope mapping of zircon preserved in a garnet megacryst, grown in anatectic pegmatite that fills boudin necks in a metapelitic layer, reveals multiple stages of zircon growth, with c.600Ma flat H/MREE cores, c.570Ma rims with outwardly decreasing H/MREE growth zoning. One interpretation is that the zircon core grew in equilibrium with garnet during prograde or peak metamorphism, prior to a stage of dissolution in anatectic melt. The graded rim grew along with garnet during cooling of the melt, growth, and the zircon was incorporated into the garnet megacryst prior to the final crystallization of the felsic pegmatite at c.550Ma. Although the 80Ma spread of metamorphic zircon ages from Lützow-Holm metapelites could be interpreted as recording separate events, textural and chemical associations between zircon, garnet and anatectic leucosome suggest that zircon growth progressed through prolonged metamorphism, with a large proportion of zircon growth at 530-550Ma occurring at a retrograde stage.

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Fig. 1.



Fig. 2.

In the second example (Fig. 2), monazite in a thin-section of metapelitic migmatite from the Higo Terrane of western Japan reveals a wealth of associations with metamorphic and deformational textures in the major phases. Monazite with euhedral growth zoning is found in high-Ca, low-Mg garnet cores. In the matrix, flattened grains and trails of low-Th monazite are aligned with sillimanite and biotite, to define an axial-planar foliation to crenulations that deform both melanosome and leucosome. Euhedral and foliated growth are interpreted as

occurring during anatexis and retrograde metamorphism, respectively. Both types of monazite grain commonly have embayed and recrystallized rims with Th enrichment. This is also seen in garnet-included monazite, where the host garnet has numerous inclusions and is locally modified adjacent to cross-cutting sheets of Ti-free biotite. Embayment and recrystallization is attributed to low-T fluids, possibly of high pH, similar to Th-enrichment produced experimentally (Harlov et al. 2006). EMP isochron (CHIME) ages of the monazite growth stages cannot be resolved; CHIME monazite and zircon and SHRIMP zircon ages from a variety of Higo lithologies restrict the timing of major mineral growth to 110-130Ma. Results from other dating methods which suggest that peak metamorphism occurred at c.250Ma appear to be influenced by isotopic inheritance.

In both examples, age data cannot be used to constrain the timing of major phase growth (or peak metamorphism, for that matter) without careful examination of the paragenetic relationships between minor and major phases. In terranes with complicated metamorphic histories, petrographically-constrained geochronology through microbeam techniques is essential.

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PHASE IDENTIFICATION BY USE OF ELECTRON BACKSCATTER DIFFRACTION APPLIED TO NON-CONDUCTIVE SAMPLES

In recent years Electron BackScatter Diffraction (EBSD) has become an enormously important technique for the characterization of polycrystalline microstructures in materials science and engineering. This method applied in the scanning electron microscope (SEM) enables to measure the full crystallographic orientation of lattice volumes as small as 50 nm in diameters.

Geological samples are polycrystalline and multiphase materials which grain size varies from 0.1 μ m up to several milimeter. Orientations of grains and microstructure of grain boundaries have a large influence on the properties of these materials. A classical X-ray diffraction (XRD) is generally used to determine global orientations but it cannot be applied to characterize changes of local orientations. A routine transmission electron microscopy (TEM) can be used to establish crystallographic relationships between several adjacent grains by studying selected area diffraction pattern (SAED). However, the TEM limits observation areas to a few grains only. Thus it makes difficult to gather statistical data from much larger volume of the sample. Therefore, it is essential to have to disposal a characterization technique that can provide detailed, reliable information about grain size, orientation and phase identification not only in nano- but also in micro-and mezoscopic scale.

Electron BackScatter Diffraction can make extensive contribution to the crystallographic and structural analyses of geological samples by providing data about the absolute and relative grain orientation, misorientation angles, planes of grain boundaries and identification of unknown phases from the range just in the middle between the XRD and TEM capabilities.

In addition, three-dimensional studies can be performed by in-situ sectional in the SEM equipped with both electron and focused ion beams (EB and FIB). EBSD provides also a robust and relatively simple way to identify unknown crystalline phases in bulk samples from their crystallography and chemistry. Special procedures (PHASE ID, DELPHI Phase Identifications) have been developed that permit automated identification of unknown phases in the SEM provided that a suitable crystallographic database is available. The phase identification using the EBSD technique can be applied to unprepared bulk samples, fracture surfaces and particles.

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Combination of the Scanning Electron Microscope with Variable Pressure (E-SEM) with the EBSD and EDS systems allows to analyze non-conductive specimen (including geological samples) without applying any conductive coating. Such a sophisticated facility system allows to obtain the wealth of information needed to determine the relationships between its physical properties, morphology, chemistry and crystallography.

In the following presentation the author describes the basics of EBSD technique, its unique application to non-conductive specimens (ceramics, geological samples) and phase identification procedures. A special attention will be drawn to the problems arising during such measurements.

Recent developments and new trends in automatic crystal orientation microscopy (ACOM) with in-situ sectioning (3D EBSD) will be also discussed.

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METASOMATIC ALTERATION AND RE-EQUILIBRATION OF ORTHOPHOSPHATE MINERALS: TEXTURES, FLUIDS, AND MASS TRANSFER

In nature, total re-equilibration of minerals and mineral assemblages under prevailing P-T-X conditions is greatly enhanced when suitably reactive fluids are involved. Oft times, however, re-equilibration is only partial and limited to those areas of the grain in immediate contact with the fluid. This can be due to a variety of factors including limited amounts of fluid, a limited reactivity between the fluid and the mineral and/or sufficiently low P-T conditions thus guaranteeing very low reaction rates. In general re-equilibration, whether localised or total, occurs as a result of dissolution-reprecipitation processes which can also allow for the nucleation and growth of mineral inclusions of one phase within minerals of another phase.

Here a series of different orthophospate mineral textures with or without mineral inclusions will be described and interpreted. Each of these textures is the direct result of fluid-induced dissolution-reprecipitation processes and represents the re-equilibration of the orthophosphate mineral on a localised scale. Such re-equilibration textures can have profound implications with regard to dating metasomatic events as well as allowing for P-T-X conditions to be estimated.

From a broader perspective, these fluids have not only interacted with the orthophosphate minerals but also potentially with the rock as a whole. As a consequence, the documentation and interpretation of metasomatically induced alteration in orthophosphate minerals has broader implications with respect to obtaining deeper insights into the nature and role of fluids in the crust and upper mantle.

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THE MINERALOGY AND PETROLOGY OF XENOTIME: A BRIDGE BETWEEN MONAZITE AND ZIRCON

Xenotime, like monazite and zircon, has an ideal formula of ATO₄, where A represents yttrium (Y) in an eight-oxygen coordinated polyhedra, and T a tetrahedrally coordinated atom of P. Its crystallographic arrangement is iso-structural with zircon (and thorite). The A-site in xenotime may also be filled by the rare earth elements (REE). The smaller, heavier rare earth elements (Gd to Lu), are favoured in the xenotime structure, but compositional solid-solution with the larger, lighter rare earth elements (La to Eu), typically favoured in monazite is also possible providing a direct link with that mineral. Despite these relationships, xenotime is less commonly included in petological studies. This is not a reflection on the range of data that can be gleaned from xenotime, but to its smaller stability range in PT space, and subsequent lower rate of occurrence. Nevertheless, its rarity is also part of its beauty in petrological studies for its presence commonly coincides with conditions where monazite and zircon may be unstable, or provide little meaningful information. Some examples of these conditions include: diagenetic and low-grade metamorphic conditions where xenotime growth is favourable over both monazite and zircon; high Ca environments where monazite is unstable relative to apatite or allanite; low- to mid-amphibolite facies conditions where prograde growth of zircon may be minimal; hydrating retrograde conditions where monazite may be unstable and the breakdown of HREE-bearing phases such as zircon and garnet may result in the growth of xenotime; and, in selected hydrothermal environments, where xenotime may be more stable than either monazite or zircon.

To maximise the potential of xenotime, a complete understanding of its composition and relationships to a rock-forming assemblages is essential. Electron-beam techniques are ideally suited to this task, providing micron-scale resolution of composition and textural variation, as well as yielding precise ages for individual micro-volumes in multi-domain grains. A method for accurate trace element analysis adapted from the optimised methodology for monazite analysis using the "*Ultrachron*" electron microprobe at the University of Massachusetts is advocated. As with monazite analysis, careful characterisation of background curvature, background interference, and peak-to-background ratios is required. In contrast to monazite, analysis of Pb is made on the M β -line in order to avoid the

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significant overlap of Y-L $\gamma_{2,3}$ on Pb-M α . In some respects, the analysis of xenotime is simplified because of the reduced influence of complex LREE overlaps on Th, U and Pb. However, the imperfect exponential curvature of the background wavelength scan in the Pb-region of the spectra must also be considered.

Using a series of examples, it will be shown that xenotime provides an alternative target for electron microprobe analysis, and can be used to complement, or as an alternative, to monazite and/or zircon depending on the nature of the geological problem. The analysis and integration of xenotime composition, texture, and geochronology represents a powerful tool for extracting information from exotic mineral assemblages, and deciphering geochemically complex metamorphic and metasomatic histories.

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REVIEW OF LASER ABLATION U-TH-PB ICP-MS DATING METHODS AND RECIPES FOR STATE OF THE ART BEST PRACTICE IN DATA ACQUISITION, ACCURACY, PRECISION AND ERROR ESTIMATION

LA ICP-MS U-Pb dating is now a common-place method utilised to determine the age of mineral grains both in-situ in petrographic thin sections and from those grains separated from a rock and mounted in polished blocks. Three types of mass spectrometer, quadrupole ICP-MS and single and multiple collector sector field ICP-MS, are commonly used to acquire this data using various types of laser ablation systems.

All of these variants have the ability to offer similar quality data such that, from the point of view of the field geologist, all methodological approaches have the potential to offer Pb-U data in the region of 2-3% (2SD). However, detailed analysis of the data commonly shows higher quality from sector field instruments coupled to shorter wavelength laser systems. Improvements in data quality can be achieved by optimising the set-up, acquisition and handling of this data and the mineral grains prior to analysis. For zircons, this means that concordant analyses can routinely be achieved at a spatial resolution (x-y-z) of c.25x25x15um for a Palaeozoic crystal with a concentration of c.50ppm U. Higher uranium zircons around 25Ma can equally be targeted when containing a few thousand ppm U.

Other mineral phases such as monazite and xenotime can offer significantly more information about metamorphic processes and these phases can also be targeted and successfully analysed to the same or even higher levels of data quality by LA ICP-MS. Much higher spatial resolution, on the order of 10um, for much younger crystals can be achieved for these minerals due to their higher U contents. Common-Pb which commonly complicates these analyses, can also be corrected either on-line during the analysis or graphically. Standardisation although a perennial problem for laser ablation methodologies, is possible using pre-existing well-characterised mineral standards and a dynamic ablation protocol to avoid or minimise inaccuracies related to non-matrix matching. Th-Pb data can also be collected along with U-Pb data to provide a more complete understanding of the U-Th-Pb history of the mineral and to consider the degree of concordance in each of the systems. However, to date LA-ICP-MS Th-Pb data appear less reliable than U-Pb data with Th-Pb behaviour during ablation being poorly characterised.

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Fig. 1. LA-MC-ICP-MS analyses of monazites occluded in garnets and separate rim and core analyses of those in the rock matrix after imaging to demonstrate chemical variations (scale bars are 50μ m).

Coupled with the textural, trace element and P-T information that can be determined from these and other accessory phases, LA ICP-MS dating can be demonstrated to be an essential tool in helping decipher the tectono-thermal history of a region. Examples will be discussed to demonstrate the complexities in acquiring, handling and interpreting such data, but which ultimately allow complex geological histories to be elucidated (e.g. Figure 1).

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MONAZITE AND ALLANITE PHASE RELATIONS IN LOW-GRADE METAPELITES

Among the successfully used radiometric techniques those involving the U-Th-Pb isotopic systems are among the most powerful. A variety of chemically robust minerals such as monazite LREEPO₄, zircon ZrSiO₄, xenotime HREEPO₄, allanite (REE-epidote), and titanite yields high-precision ages of geological events in sedimentary, metamorphic or magmatic rocks. To interpret geochronological data derived for metamorphic rocks, it is critical to consider whether these minerals record the time of their formation (under what conditions) or closure upon cooling (and below what temperature). To correlate ages with P-T conditions, U-Th-Pb geochronology has made considerable progress by combining new *in-situ* isotopic measurements with detailed petrological characterization of the behavior of accessory minerals during metamorphism. Insufficient thermodynamic properties for REE-minerals prevents the reliable calculation of stable phase relations involving monazite and allanite; these have thus been mostly inferred indirectly from in-situ U-Pb and Th-Pb age data from mineral assemblages that evolved along metamorphic transects (e.g. Wing et al. 2003, Janots et al. 2006). In metapelitic rocks, monazite stability (and geochronology) has long been thought to be restricted to medium and high-grade metamorphism, typically beyond greenschist facies conditions, where allanite is the dominant REE-mineral (see Spear and Pyle 2002 for a review). At lower grade (including diagenesis), monazite where present is usually considered detrital but metastable. However, recent studies show that monazite can crystallize under subgreenschist and low-temperature blueschist conditions (Rasmussen, Fletcher et al. 2001; Bollinger and Janots 2006; Janots et al. 2006, Krenn and Finger 2007) or even during diagenesis (Evans and Zalasiewicz 1996, Evans et al. 2002). Here, we address the phase relations between monazite and allanite at low-grade conditions, by combining petrological and thermochemical studies. Monazite and allanite occurrences have been investigated in low-grade metapelites collected in the Lesser Himalaya (Nepal), the Rif (Morocco) and the Central Alps (Switzerland). Our strategy has been to characterize texturally and chemically the REE-minerals at the micrometer scale, document their assemblages, and deduce mineral reactions that occurred with increasing regional metamorphism. Data were collected along metamorphic transects from anchimetamorphic to lower amphibolite facies or blueschist facies conditions. At diagenetic grade, detrital REE-minerals (monazite or alumino-

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phosphate) contain the LREE, but minor newly formed monazite appears at the lowest metamorphic grade. At temperatures of ~450°C, monazite is replaced by allanite (over large range of pressures (4-15 kbar), Rif and Central Alps). Under these conditions, monazite growth has only been observed to occur in retrograde replacements of allanite involving fluids interactions (Rif and Himalaya). At temperatures >550°C, allanite is partially replaced by monazite and xenotime, both associated with plagioclase, biotite and/or staurolite, in the Central Alps. In these samples, the presence of epidote relics, which preserve their characteristic chemical and textural zoning, indicates that they did not experience reequilibration following their prograde formation (Fig. 1).



Fig. 1. Elemental map of La, Nd, Th and Y of the insitu breakdown of allanite into monazite and xenotime. The presence of the allanite with an epidote rim rich in HREE show that the phases of the epidote group did not experience reequilibration from their formation up to their destabilization in monazite and xenotime.

Hence the partial in-situ breakdown of allanite to monazite offers the unique possibility to obtain ages representative of two distinct crystallization stages. SHRIMP Th-Pb and U-Pb dating on allanite and monazite from the Central Alps yields ages of 31.5 ± 1.3 Ma and 18.0 ± 0.1 Ma, respectively. Considering that the difference of 13.5 Ma between the two ages represents the time elapsed between 450° C and 570° C, an average heating rate of $8-10^{\circ}$ /Ma can be calculated.

Thermochemical properties have been either measured or estimated for synthetic monazite, LaPO₄, and dissakisite, CaLaMgAl₂(SiO₄)₃OH, the Mg-equivalent of allanite (Janots et al. 2007). A dissakisite formation enthalpy of -6976.5 \pm 10.0 kJ.mol-1 was derived from high-temperature drop-solution measurements in lead borate at 975 K. A third-law entropy value of 104.9 \pm 1.6 J.mol-1.K-1 was retrieved from low-temperature heat capacity (Cp) measured on synthetic LaPO₄ with an adiabatic calorimeter in the 30-300 K range. Cp was

measured in the 143-723 K range by Differential Scanning Calorimetry. Pseudosections were calculated using the DOMINO software, based on the thermochemical data retrieved here for a simplified metapelitic composition (La = Σ REE+Y) and considering monazite and Fe-free epidote along the dissakisiteclinozoisite join, as the only REE-bearing minerals. Calculation shows a stability window for dissakisite-clinozoisite epidote (T between 250-550°C and P between 1-16 kbar), included in a wide stability field for monazite (Fig. 2). The P-T extension of this stability window depends on the bulk rock CaO content. Assuming that synthetic LaPO₄ and dissakisite-(La) are good analogues of natural monazite and allanite, these results are consistent with the REE-mineralogy sequence observed in metapelites, where (1) monazite is found to be stable below 250°C, (2) around 250-450°C (depending on pressure) allanite forms at the expense of monazite, and (3) at the transition to amphibolite facies conditions, monazite reappears at the expense of allanite.



Fig. 2: DOMINO phase diagram of simplified metapelite composition highlights the stability fields of monazite (Mnz) and dissakisite-clinozoisite solution (Epd). Dissakisiteclinozoisite isopleths are represented by the lines labelled by the mole fraction of the dissakisite component (X_{Dsk})

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BEHAVIOR OF MONAZITE DURING METAMORPHIC PROCESSES

Monazite is an important metamorphic mineral in rocks of pelitic or granitic composition. Current studies in the Alpine and the Variscan orogen show that monazite can grow over the whole metamorphic PT range, including anchizonal as well as granulite and eclogite facies conditions.

During very low-grade and low-grade regional metamorphism (~250-450°C) monazite readily forms at the expense of allanite, which is obviously unstable and reactive at these low-T conditions (Krenn and Finger 2007). The fact that monazite often replaces allanite in-situ, indicates a certain mobility of phosphorous in low-T fluids. In contrast, protolithic rocks without allanite, but with detrital or relictic monazite, are generally unfertile for the growth of a new, low-T metamorphic monazite generation. In such series the old monazites commonly survive during a low-grade metamorphic event (Finger et al. 2003), sometimes even up to the amphibolite facies.

While the significance of monazite formation at low-T metamorphic conditions was previously often underestimated (see discussion in Krenn and Finger 2007), there is wide agreement in the existing literature that monazite growth frequently takes place at upper amphibolite facies and granulite facies conditions (Parrish 1990, Spear and Pyle 2003 and references therein). Interestingly, at intermediate metamorphic grades (upper greenschist to lower amphibolite facies), it is often (although not always - Franz et al. 1996) the case that monazite reacts to allanite (Wing et al. 2003). Thus, there is a certain "window" in the PT space between ~450 and ~550 °C, where monazite is less abundant and where allanite is stable in most lithologies including many metapelitic and metagranitic rocks. A characteristic microstructural feature of this intermediate PT range is the development of "corona monazites", i.e. monazites mantled by a secondary corona of apatite, allanite and epidote (Broska and Siman 1998, Finger et al. 1998). If the host rock undergoes a renewed later stage of metamorphism at higher (> 550°C) or lower T (< 450°C), it may happen that these apatite-allanite coronas can spawn another generation of small monazite grains. These have been named "satellite monazites" by Krenn and Finger (2006), because they arrange themselves like satellites in some distance from the older monazite core.

While at $T < 600-700^{\circ}C$ metamorphic monazite often forms from an allanite source, it would appear that at higher T new monazite preferentially forms through recrystallization (dissolution-reprecipitation) from previous amphibolite-facies monazite. Dissolution starts marginally or along cracks, and new monazite

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substance is stepwise reprecipitated more or less in the same places. This high-T replacement of monazite through monazite often leads to significant element fractionations on a small scale (comparable to a chromatographic column) creating composite grains with complex zoning patterns (Harlov et al. 2007). Additionally unreacted domains can remain as relictic cores (Finger and Krenn 2007).

One reason that triggers such monazite recrystallization at high PT is the partitioning of LREEs from monazite into apatite. This favours the formation of a particularly Th (U)-enriched peak-PT monazite (Finger and Krenn 2007). Vice versa, the retrograde annealing of a high-PT rock at T > 600-700 °C often results in the formation of a late monazite generation derived from (formerly) LREE-enriched peak-PT apatite. These late monazites grow mostly parasitic within the apatite. They form needles, which look like exsolutions, or in other cases larger rim grains, that replace the apatite. Monazites derived from an apatite source are generally characterized by a Th-poor composition with ThO₂ mostly < 1 and ThO₂/UO₂ often < 1.

Another situation that can effectively stimulate the recrystallization of monazite at high-T is the liberation and availability of yttrium during retrograde garnet breakdown. This often occurs when a high-pressure metamorphic rock passes a near-isothermal decompression path. The typical result are zoned monazites with remnant and resorbed low-Y cores representing the peak PT stage and (reprecipitated) high-Y rim zones, that formed during decompression.

The fact that monazite grains in high-grade metamorphic rocks often grow stepwise, and not just wholesale close to the PT peak, opens the important possibility for precisely dating individual stages of a metamorphic PT loop by high-resolution U-Pb geochronological methods.

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MONAZITE DATING USING MICRO-PIXE

Nuclear microprobe delivers an ion beam, produced typically in a small Van de Graff accelerator and magnetically focused down to a diameter of few micrometers, to a target specimen. As a result, several physical effects take place, from backscattering of the bombarding ions to emission of secondary electrons. characteristic X-rays, gammas, or even light. From many nuclear techniques basing on such facility, the Proton Induced X-ray Emission (PIXE) plays a particularly important role in many applications in biomedicine, material science, earth sciences, or even archeology. The detected characteristic X-rays, used for elemental analysis of the sample surface and subsurface regions, deliver results with limits of detection in the single ppm range and produce elemental maps with resolution of single micrometers. Though the experimental basics are quite similar to an electron probe, one has to take into account few important differences of the involved physical processes. The high mass of the proton causes that the bombarding particle looses only a small fraction of its energy in an interaction with electrons in the target (at energies of few MeV, typical for the application discussed, the energy loss due to nuclear interactions is much smaller and may be neglected). As a consequence, the trajectory of the proton in a target is not much changed during a single encounter and, even at significant depths, is still close to linear. In example, the projected range of 2 MeV protons in a quartz crystal is about 44 µm while the average longitudinal and lateral deviations at the end of proton trajectory are below 2 µm. However, a relatively high effective depth of the analysis (typically several tens of µm) must be taken into account in order to avoid analysis errors stemming from interaction with elements in the underlying substrate. Another effect is the decrease of the X-ray production cross-sections with the loss of proton energy inside the sample volume, accompanied with the attenuation in the target material. Generally, most of X-ray signal comes from regions close to a surface while the origin of a registered X-ray is well defined and corresponds to a momentary position of the beam. Major analytical advantages of the proton microprobe over the electron microprobe are higher spatial resolution and a lower X-ray background (and thus lower detection limits). From the other hand, the high technical requirements accompanied with the running the accelerator and maintaining a well-focused proton beam, must be considered as the

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disadvantage of the method. As a consequence, for geological materials, the method is not used as often as electron microprobe.

In geology, the PIXE method may be used for various purposes. The extensive overview of use of PIXE (and the other the ion beam techniques) in geology is given by Ryan (2004). Several successful attempts of the proton beam monazite dating have been reported there.

The method of the chemical dating by the elemental analysis has been developed on the basis of electron microprobe analyses by Suzuki and Adachi (1991). Its basis is the condition that the concentration of primary lead in mineral monazite is neglected and that after the mineral formation, the system has remained closed with respect to U, Th and Pb. If this condition is met, the determination of the elemental contents of the U–Th–Pb chain and subsequent solving of a balance equation gives the time of Pb accumulation and thus the age of a crystal. It is worth to notice that only relative data may be used and there is no need to determine the absolute concentrations.

In monazite crystals studied by PIXE, the useful X-ray signal (Pb, U, and Th Llines in region extending roughly from 10 to 20 keV) is accompanied with a very high, lower energy background from rare earths that must be supressed by a filter (typically 60–100 μ m of Aluminium).

If the detection system is well characterized, the PIXE method, in contrast to electron microprobe, may be carried out as a standardless technique, using theoretically calculated data. From several software packages used for the X-ray spectra evaluation the most frequently cited are GUPIX from the University of Guelph (pixe.physics.uoguelph.ca) and GeoPIXE from CSIRO (www.nmp.csiro.au). A considerably lower detection limits of about 10 ppm or less for Pb, Th, and U determination, an order of magnitude less than in electron microprobe, should also be noted. These low detection limits make the technique a standard tool for trace elements analysis in many research areas.

For absolute concentrations determination, parallel to the standard charge normalization of the beam current, a complementary RBS (Rutherford Backscattering) ion beam technique may be used. RBS provides also the additional information on the sample matrix composition what is useful in energy loss and X-rays attenuation calculations. In monazite dating, an error of calculated ages mainly depends on the Pb level, estimated usually with a few percent error. In practice, for monazites that are few hundred millions years old and Pb levels ranging from 100 ppm upwards, the typical, maximum error of the age calculation is in the range of about 5-10%. Due to nonlinear character of the equilibrium equation the age error cannot be calculated directly but is usually estimated by solving the equation for extreme elemental contents, thus producing the upper and lower limits for the age value.

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SYNCHROTRON MICROANALYTICAL METHODS IN THE STUDY OF TRACE AND MINOR ELEMENTS IN APATITE

Synchrotron X-ray facilities have the capability for numerous microanalytical methods with spatial resolutions in the micron to submicron range and sensitivities as low as ppm to ppb. These capabilities are the result of a high X-ray brilliance (many orders of magnitude greater than standard tube and rotating anode sources); a continuous, or white, spectrum through the hard X-ray region; high degrees of Xray columniation and polarization; and new developments in X-ray focusing methods. The high photon flux and pulsed nature of the source also allow for rapid data collection and high temporal resolution in certain experiments. Of particular interest to geoscientists are X-ray fluorescence microprobes which allow for numerous analytical techniques including X-ray fluorescence (XRF) analysis of trace element concentrations and distributions; X-ray absorption spectroscopy (XAS) for chemical speciation, structural and oxidation state information; X-ray diffraction (XRD) for phase identification; and fluorescence microtomography (CMT) for mapping the internal structure of porous or composite materials as well as elemental distributions (Newville et al. 1999; Sutton et al. 2002; Sutton et al. 2004).

We have employed several synchrotron based microanalytical methods including XRF, microEXAFS (Extended X-ray Absorption Fine Structure), microXANES (X-ray Absorption Near Edge Structure) and CMT for the study of minor and trace elements in apatite (and other minerals). We have also been conducting time resolved X-ray diffraction to study nucleation of and phase transformations among precursor phases in the formation of apatite from solution at earth surface conditions. Summaries of these studies are given to exemplify the capabilities of synchrotron microanalytical techniques.

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A MICROANALYTICAL STUDY OF FLUID-INDUCED ZIRCON AND ALLANITE RECRYSTALLIZATION

The recent advances in in-situ microanalysis have forced geochronology to become increasingly more multicomponent and linked to textures, mineral chemistry and petrology. Dating of a mineral is not anymore limited to the measurement of its isotopic composition, but requires imaging of the grain before dating, as well as chemical and isotopic analyses to support and correctly interpret the age measured.

An example is provided by the zircon and allanite from a deformed highpressure rock from the Lanzo Massif in the western Alps, Italy. Secondary electron imaging was the basic tool to identify zircon and allanite grains, and investigate the textural relationships with surrounding minerals. The investigation allowed the identification of unusual recrystallization textures consisting of a porous aggregate of small euhedral zircon grains with interstitial omphacite, which mimics the original zircon shape. The zircon grains were imaged by cathodoluminescence for detecting the different growth zones: magmatic oscillatory versus mosaic zoning in the recrystallized domains. High-contrast Back Scattered Electron imaging was additionally required to establish that chaotic zoning patterns were mainly due to chemical variations and did not reflect dislocations. Electron Back Scattered Diffraction was necessary to quantify the amount of deformation within crystals and its effect on chemistry. It could be established that the new zircon microcrystals substitute nearly epitaxially the original magmatic crystal. A slight misorientation of these microcrystals with respect to the original zircon is in line with a minor event of stress-driven deformation. U-Pb isotopic analysis performed via SHRIMP ion-microprobe revealed an age variation correlated to the internal structure of the grains with the magmatic domains preserving an age around 164 Ma, and the recrystallized aggregates yielding a 55 Ma age. The inclusions in the zircon aggregates consist of high-pressure minerals such as jadeite and allanite, which are also found in the rock matrix. The trace element composition of the different zircon domains obtained by Laser-Ablation - ICPMS indicates a progressive depletion in L-MREE, and a decrease in Eu negative anomaly and Th/U ratio from the magmatic to the recrystallized zircon. The chemical variations are in line with low temperature recrystallization and purging of trace elements. Tiin-zircon thermometry indicates temperatures of ~650°C for the recrystallization.

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The textural, structural, isotopic and chemical data suggest zircon recrystallization by a dissolution-precipitation process in the presence of metamorphic fluids at high-pressure conditions. Release of fluids from the surrounding serpentinites during prograde subduction is proposed as the likely source of fluids that caused zircon recrystallization.



Fig. 1. Back scattered electron and cathodoluminescence image of the recrystallized zircon from the Lanzo eclogite.

The zircons investigated are texturally associated to allanite found both as interstitial minerals in the zircon aggregates and as larger crystals in the rock matrix. U-Th-Pb dating of allanite via SHRIMP ion microprobe and Laser-Ablation – ICPMS has been recently developed at the ANU (Gregory et al. in press). Using a matrix-matched standard a precision of 1.4-2.8% (95% c.l.) can be reached with Laser-Ablation – ICPMS analysis at a spatial resolution of 32x32x20 μ m. Accurate (±1-3%) and precise (1-2%) SHRIMP Th-Pb ages can be measured directly on allanite samples with REE+Th > 0.5 atoms per formula unit, without additional matrix corrections at a spatial resolution of 17x21x2 μ m. Allanite from the Lanzo sample has a trace element composition characterized by high Sr contents, moderate depletion in HREE with respect to the LREE and lack of Eu anomaly, in line with growth at high-pressure conditions. SHRIMP measurements yielded an age of 45±4 Ma, significantly younger than the zircon. It is therefore suggested that the Th-Pb system in allanite recorded a later event in the high-pressure history of the Lanzo sample, arguing for a protracted permanence at depth.

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INTEGRATING TECTONICS AND GEOCHRONOLOGY IN MULTIPLY-DEFORMED TERRANES: HIGH-RESOLUTION MONAZITE GEOCHRONOLOGY AND GEOCHEMISTRY BY ELECTRON MICROPROBE

In-situ monazite geochemistry and geochronology provide critical constraints for illuminating the P-T-t-D history of tectonites. Monazite crystals typically contain multiple compositional and age domains, which can be linked to silicate textures, fabrics, and metamorphic reactions. The electron microprobe can yield precise compositions (trace and rare earth elements) from grains or domains far too small for in-situ isotopic techniques. New or modified analytical techniques are critical for accurate trace element analysis, especially background characterization and interference correction for both peak and background calculation. Spectrum modeling and regression are essential for accurate determination of background and associated uncertainty. Age precision is on the order of several m.y. to tens of m.y. even in very small, chemically-homogeneous domains. Results from the high-P-T Athabasca granulite terrane, Saskatchewan provide an example of the unique and essential contribution that microprobe monazite analysis makes to petrologic/geochronological investigations. Excellent U-Pb zircon data provide a high-(temporal)-resolution framework for the tectonic history. However, major questions persist about the timing and significance of regional fabrics, shear zones, and metamorphic assemblages that critically limit tectonic interpretations. Monazite textures and fabrics allow increments of monazite growth to be correlated with deformation events. In shear zones, monazite commonly grows at extensional quadrants of existing grains, allowing direct dating of deformation. Trace and REE compositions provide a link with silicate phases and allow direct dating of key metamorphic reactions. The Grease River shear zone is a superb example. Pre- syn, and post tectonic monazite, combined with metamorphic data and zircon data from cross-cutting dikes, have constrained the age of shearing, the P and T conditions (i.e. crustal depth), and the relationship to thrusting and melting in the adjacent terranes. The integration of monazite composition, texture, and geochronology, together with silicate petrogenesis, represents a new frontier for analysis of P-T paths and tectonic histories in complex tectonites.

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NANOANALYSIS OF GEOMATERIALS APPLYING FOCUSED ION BEAM (FIB) SAMPLE PREPARATION COMBINED WITH TRANSMISSION ELECTRON MICROSCOPY (TEM)

Meaningful interpretation of trace element analysis and isotope geochemistry data from accessory minerals such as zircon and monazite requires the characterization of the starting material with respect to structural and chemical homogeneity, radiation damage and microstructure prior to the analysis. Transmission electron microscopy (TEM) is an appropriate tool characterization starting materials on a nanometre scale with respect to internal texture, microstructure, chemical composition and crystal structure. Focused ion beam technique (FIB) is the appropriate TEM sample preparation method that allows the preparation of electron transparent foils with typical dimensions of 15 x 10 x 0.150 μ m from the locations of interest (Wirth 2004). FIB sample preparation consumes only a small volume of the sample (approximately 2300 μ m³), leaving most of the material completely unaffected.

Modern TEM facilitates the determination of the chemical composition with unsurpassed spatial resolution. High-resolution imaging and electron diffraction provide structural information from the same location. It is the combination of crystal structure, the chemical composition and the microstructure that fully characterizes the investigated volume of interest. High-resolution elemental mapping or line scan utilising drift correction acquire complete EDX spectra pixel by pixel. Subsequent data evaluation allows connecting the spectrum with the respective elemental map or line scan and the image, thus illustrating spatially resolved chemical composition.

Frequently, minerals enclose sub micrometer- or even nanometre-sized inclusions, which might give us information about the environment during mineral growth. Nanoinclusions are of peculiar significance because they might have preserved their original crystal structure thus providing a geobarometer. FIB/TEM are appropriate techniques to define the chemical composition and the structural state of inclusions on a nanometre scale. The unique capability of modern FIB/TEM is demonstrated with three examples of nanometre-sized inclusions in pyroxene, olivine and diamond.

Polycrystalline aggregates of nanometre-sized diamond were found in melt inclusions, which are enclosed in ortho- and clinopyroxene in a garnet pyroxenite xenolith from the mantle lithosphere beneath the Hawaiian island of Oahu. The melt inclusions are not related to the host magma, but represent CO_2 -rich melts

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possibly derived from the deep mantle. This finding documented the first observation of diamond in the oceanic mantle adjacent to recent hot spot volcanism (Wirth and Rocholl 2003).

TEM investigations of olivine grains from the kimberlite pipe Udachnaya, Siberia, revealed nanometre-sized inclusions of (Mg,Fe,Cr)TiO₃ perovskite together with ilmenite. The crystal structure of the perovskite inclusions is monoclinic with $a_0 = 1.095$ nm, $b_0 = 0.5169$ nm, $c_0 = 0.743$ nm and the monoclinic angle $\beta = 95^{\circ}$. This observation combined with the experimentally determined ilmenite/perovskite phase boundary allows the use of perovskite in olivine as a geobarometer. In this case the presence of perovskite in olivine suggests that the peridotite originated at pressures of 8 - 10 GPa, significantly higher than the pressure of last silicate equilibration (4.5 - 6.4 GPa) (Wirth and Matsyuk 2005).

In alluvial diamonds from Juina (Mato Grosso, Brazil) we observed a hydrous alumina silicate phase Egg (AlSiO₃(OH)) using transmission electron microscopy (TEM) and Raman spectroscopy. Phase Egg is present in diamond in several larger inclusions (a few hundred micron in size) as nanometre-sized, idiomorphic crystals (20 - 30 nm). Phase Egg is associated with a small volume fraction of stishovite and a significant amount of pore space, which was originally filled with a fluid or gas. The gas or fluid has been released during TEM sample preparation. The finding of phase Egg suggests the existence of an Al-phase in the lower mantle and Transition zone environment. The presence of OH-groups in phase Egg strongly supports the idea of subduction processes reaching the depth of Transition zone and lower mantle (Wirth et al. 2006).

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MINERALOGICAL WORK AT THE RECENTLY SET-UP MICROPROBE LAB OF THE INSTITUTE OF MINERALOGY AND GEOLOGY, UNIVERSITY OF MISKOLC, HUNGARY

A JEOL-JXA 8600 Superprobe electron-microscope is operating at the Microprobe Laboratory of the Institute of Mineralogy and Geology, University of Miskolc, equipped with an EDX- and three WDX-spectrometers. A digital imaging system was our own development to the machine last year, thus the secondary electron- (SE) and back-scattered electron (BSE) images can be saved directly to PC-compatible format.

The primary target of the laboratory is to serve the university work, such as teaching the technique for students and scientific research, but commercial projects are also run. The research fields of the laboratory cover a wide range:

- general mineralogy and petrology (Less et al. in rev.)

- topographical mineralogy of Hungarian and Transylvanian occurrences (Zajzon et al. 2006)

- environmental pollution in settling dust and soil (Márton et al.in press)

- mineralogy and microstructure of ceramics (Gorea, Kristály 2007)

- medical mineralogy (Weiszburg 2006)

- archeo-mineralogy (Mohai 2004).

As further development we would like to upgrade the computer control part of the microprobe.

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