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September 25, 1998

Zusammenfassungen der Vorträge und Poster

Abstracts of oral communications and posters

MINERALOGY

G.G. Biino (Bern):

The oxidation states of ad atoms and main components in the surface layers of pyrite, chalcopyrite and Mn-bearing minerals.

The principal method for carrying surface investigation is x-ray photoelectron spectroscopy (XPS). In XPS, one measures the kinetic energy of photoelectrons emitted from a surface. The kinetic energy of the electrons gives direct information on the energy of binding (final state), the chemical composition of the outermost layers of the sample, the oxidation state, and indirectly also the coordination environment of an element. Finally, atomic structure information is contained in photoelectron diffraction effects due to elastic scattering of electron by atoms neighbouring the emitter. The surface chemical environments of twenty Mn-bearing minerals were investigated by means of XPS. Peculiar satellite features in the Mn 2p peak make possible to characterise the complex Mn chemical environments.

Sulphide minerals have an active role in the geochemical cycles of elements. Pyrite and chalcopyrite are key agents of redox reactions in the near-surface environment, being responsible for severe environmental pollution associated with the products of sulphide oxidation, but also for stabilising metals (e.g.: by speciation and/or precipitation). The evolution of the chemical environment of Fe, Cu and S in chalcopyrite surface was traced over a time span of one year by means of XPS. Two independent sets of experiments were performed. In one set of experiments chalcopyrite was exposed to distilled water and in the other one to contact with the atmosphere of Bern

(CH). Atmosphere-chalcopyrite results in N, C and O sorption, complete oxidation of Fe, Cu and S, and passivation of the surface. Chalcopyrite was also exposed to solution containing different heavy metals (Cr, Se) at different pH (pH 4,7 and 10), temperatures (25 and 95 °C) and time span. Sorption and redox processes were therefore characterised. BIINO et al. (1998) used the MicroXPS at the Advanced Light Source of the Berkeley National laboratory to investigate at micron scale the chemical composition of the outermost layers of pyrite. The natural (100) crystal face of pyrite was exposed, for different time span, in buffered solutions at pH 4 and 7. The aquatic solution was containing Cr, Cu, Pb, and Se. Several oxidation states of sorbed and primary elements were observed in the same microspot of pyrite surface. We also observed, surprisingly, that some microspots are dominated by only one of the possible oxidation state. At the scale of observation, it was not possible to evidence any difference between microspots dominated by different oxidation states. For the first time, space-resolved XPS data allows to characterise heterogeneity in the oxidation state of sorbed elements on a mineral surface.

(This research was supported by U.S. Department of Energy.)

BIINO, G.G., ACKERMAN, G.D., YNZUNZA, R., LEWIS, C., PERRY, D.L. and HUSSAIN, Z. (1998): Mapping the oxidation states of absorbates on (100) pyrite by MicroXPS at the ALS (submitted).

C. Ferraris (Fribourg):

Mineralogic, petrologic, and crystallographic considerations about α-quartz and talc exsolution domains in phengite 3T from the Dora-Maira massif (Western Alps): HRTEM and AEM data.

A systematic HRTEM and AEM study of phengite 3T crystals $(K_{0.94}Na_{0.02})(Al_{1.42}Mg_{0.57}Ti_{0.01})[Al_{0.45}Si_{3.55}]O_{10}(OH_{1.93}F_{0.07})$, a = 5.215(1), c = 29.755(5) Å from the Dora-Maira massif were carried out to explain the presence of quartz and talc peaks in X-ray powders diffraction and of Mg^{2+} and Si anomalies in Electron Microprobe EDS chemical analyses. HRTEM images shows the presence of quartz domains associated with talc layers in close proximity. The quartz domains show a tabular form elongated in the clevage direction with arounded edges where a preferential orientation of crystallographical axes is absent. The talc interlayers are present like continuos' domains of 18.9 Å of thickness (double layers). The absence of phengite layer deformation around the quartz inclusions, the direct contact between quartz and phengite and the contemporary presence of talc, suggests the exsolution origin from a richer Si–Mg phengite. The present phengite composition (Ph2) with quartz (Qz), talc (Tc) and an hydrous phase like KOH, are the products of the Si–Mg richer phengite (Ph1) destabilisation during a rapid decompression in the α-quartz stability field:

$$4.4\ \mathrm{Ph2} + 0.2\ \mathrm{Tc} + 2.1\ \mathrm{Qz} + 0.6\ \mathrm{KOH} \Rightarrow 5\ \mathrm{Ph1}.$$

A. Griesser und L. Eggimann (Zürich):

Untersuchung von Zerrkluft-Fluiden in der Val Piora, Tessin.

Im Rahmen von zwei laufenden Diplomarbeiten im östlichen Talende der Val Piora wurde eine geologische Kartierung vorgenommen, um anhand von Flüssigkeitseinschlüssen in Quarzkristallen die zeitliche Entwicklung der Fluideigenschaften in Bezug zur regionalen Metamorphose zu rekonstruieren. Die Untersuchungen basieren auf folgenden Fragestellungen: Nimmt der Salzgehalt in den Flüssigkeitseinschlüssen mit zunehmender Entfernung zu den Sedimenten der Pioramulde kontinuierlich ab? Gab es in den verschiedenen lithologischen Einheiten zur selben Zeit unterschiedliche Fluide oder sind diese über das ganze Gebiet mehr oder weniger gleichartig? Welche Elemente wurden dem Gestein durch das Fluid zugeführt, welche reagierten mit dem Gestein und welche wurden durch ein Restfluid abgeführt?

Zunächst wurde als Grundlage eine Kartierung der geologischen Einheiten vorgenommen, mit Schwerpunkt auf der Kartierung von Zerrklüften, mineralisierten Klüften und den damit verbundenen Auslaugungszonen. So entstand ein Datensatz von über 100 verschiedenen Klüften. Angaben über Kluftausdehnung, Kluftorientierung, Minerale des Nebengesteins, Art der Auslaugungszone, Kluftmineralien (Chlorit, Muskovit, Albit, Adular, Quarz, Pyrit, Limonit) und zeitliche Beziehung zur Hauptschieferung (prä, syn, post) wurden systematisch aufgenommen.

Im untersuchten Gebiet gibt es zwei Gruppen von Klüften mit verschiedener Orientierung und Form. Die ältere Kluftgeneration entstand vor oder während der steilstehenden Hauptschieferung. Sie ist meist nicht planar und fällt nach Süden ein. Die jüngere entstand nach der Hauptschieferung, ist planar ausgebildet, steht senkrecht und streicht in nordsüdlicher Richtung. Die Längsausdehnung der jüngeren Klüfte kann bis zu 30 Meter betragen. Das häufige Auftreten von Chlorit in Amphibolitklüften zeigt, dass zumindest in diesem Fall die Kluftmineralogie von der

Mineralogie des Nebengesteins abhängig ist. Laufende Untersuchungen deuten darauf hin, dass die Fluideinschlüsse an einer Lokalität ausserhalb der mesozoischen Schichten schwachsalin sind, jedoch in den Bündnerschiefern Halit als Tochterkristalle enthalten, d.h. hochsalin sind. Je jünger die Fluidgenerationen werden, umso grösser wird das CO_2/H_2O-Verhältnis der Phasenzusammensetzung in den Fluiden, wobei eine letzte Generation in einem der untersuchten Dickschliffe nur noch Wasser und kein CO_2 mehr enthält.

Die Daten aus Petrographie und Strukturgeologie dienen als Grundlage für weitergehende Untersuchungen von Auslaugungszonen mittels Gesamtgesteinsanalyse, sowie der Flüssigkeitseinschlüsse mittels Mikrothermometrie und LA-ICP-MS (FRISCHKNECHT et al., p. 342 in diesem Heft). Besonders die LA-ICP-MS ist in den letzten Jahren als bevorzugte Methode für quantitative Analysen von Flüssigkeitseinschlüssen entwickelt worden (AUDÉTAT et al., 1998) und soll eingesetzt werden, um die Skala von Fluidtransport und Austauschreaktionen zwischen Zerrkluft-Fluiden und ihren Nebengesteinen zu quantifizieren.

AUDÉTAT, A., GÜNTHER, D. and HEINRICH, CH.A. (1998): Formation of Magmatic-Hydrothermal Ore Deposits: Insights with LA-ICP-MS Analysis of Fluid Inclusions. Science 279, 2091–2094.

C. J. Hetherington, St. Graeser and R. Gieré (Basel, Purdue):

Armenite in metamorphic rocks from the Simplon area, Switzerland.

The occurrence of the rare barium-containing mineral armenite, ($BaCa_2Al_6Si_9O_{30} \cdot 2\ H_2O$), at Wasenalp in the Berisal nappe, Simplon area of Switzerland (SENN, 1989) is one of only seven known localities world-wide (GRAESER, 1993). The Simplon occurrence is associated with a small (20 × 60 metres) outcrop of augen-gneiss which is cut by three generations of hydrothermal veins. Armenite is found in the youngest veins, and these are zoned so that quartz occupies the central section in each case and armenite the periphery. The armenite-bearing veins exhibit a sub-perpendicular relationship to the dominant foliation of the augen-gneiss. Quartz and armenite account for most of the mineral content in these veins, but minor amounts of rutile and white mica are also present. Armenite is fine-grained close to quartz, but more coarse-grained near the contact between vein and host rock. It occurs also in a reaction zone within the adjacent augen-gneiss.

Three distinct mineral assemblages may be observed in the augen-gneiss host rock. Two of these are found throughout the Berisal nappe and are characteristic for the augen-gneiss. The minerals in these assemblages are: (1) quartz, zoisite-clinozoisite, orthoclase, white mica, and accessory rutile; and (2) quartz, albitic feldspar, chlorite, garnet, and white mica. The two assemblages have the same multi-deformational history and both are cut by the armenite-bearing veins. At the armenite locality, however, the first assemblage is much more abundant, with the second occurring only in thin bands or lenses parallel to the dominant foliation. In general, the two groups are similar in texture, with porphyroblasts of quartz or garnet in a fine-grained matrix, and a pronounced foliation depicted by the white micas. The foliation is less marked, however, where assemblage (1) is particularly rich in zoisite-clinozoisite and relatively poor in mica .

The third mineral assemblage found in the augen-gneiss occurs only adjacent to the armenite-bearing veins (in a reaction zone) and is characterised by armenite, celsian, a Ba-bearing white mica, and zoisite-clinozoisite. It appears that zoisite-clinozoisite was partially replaced by armenite, whereas orthoclase and white mica were overgrown by celsian and the Ba-bearing mica, respectively. This is indicated by optical heterogeneities in the feldspar minerals and by the presence of armenite and celsian blasts which contain variable amounts of sub-millimetre zoisite-clinozoisite and white mica crystals. The distinctive poikilitic texture observed in the reaction zone could be interpreted as having been formed through metasomatic alteration of assemblage (1).

GRAESER, S. (1993): Armenit vom Simplon – ein sensationeller Neufund. Mineralien Welt, 6, 39–43.
SENN, T. (1989): Barium Mineralisation und Barium-Gneise/Wasenalp (VS). Diplomarbeit, unpubl. Universität Basel.

A. Peretti, P. Amacher und J. Mullis (Altdorf, Basel):

Vorkommen und chemische Variabilität der Mikromineralien im Bereich des Kraftwerkbaus von Amsteg: Mobilisation von chemischen Elementen (U, Ag, Pb, Bi, Fe, Cu, Zn, F, Ti, P, As, S und Seltene Erden) während der alpinen Metamorphose.

Während des Kraftwerkbaus von Amsteg konnte im Auftrag des Kantons Uri die Mineralienaufsicht durchgeführt werden. Es wurden insgesamt 230 Klüfte untersucht. Die hier vorgestellte Studie beinhaltet die Untersuchung der Mikromineralien in den alpinen Klüften mit dem Raster-Elektronen-Mikroskop, der modalen Gesteinszusammensetzung im Nebengestein und der Zusammensetzung und Dichten der Fluideinschlusspopulationen mit der Mikrothermometrie.

Der untersuchte Stollenbereich liegt im nördlichen Aarmassiv. Klüfte sind je nach Gesteinstyp (Biotitgneise, Hellglimmergneise, Amphibolite, Chlorit-Sericitschiefer, Chlorit-Biotitschiefer, Erstfeldergneise) und deren Orientierung zum tektonischen Spannungsfeld als Scher- oder Zerrklüfte ausgebildet. Die Nebengesteine, teilweise erzführend (Fe, Cu, Zn, Pb, Ag, Bi, As, S), weisen eine prä-alpine Metamorphose der Amphibolitfazies auf, die durch die retrograde alpine Grünschieferfazies überprägt worden ist.

In den Klüften wurden über 40 verschiedene Mineralien festgestelt (z.B. Synchisit, Xenothim, Monazit, Apatit, Fluorit, Titanit, Amiant, Anatas, Brookit, Rutil und verschiedene weitere Mineralien). Die Paragenesen wechseln je nach dem Nebengesteinstyp und dem Grad der metamorphen Umwandlung. Die Studien der Dünnschliffe aus den Alterationszonen der Klüfte belegen den Zusammenhang der Kluftmineralbildung mit der alpinen grünschieferfaziellen Überprägung der Nebengesteine. Die retrograde Umwandlung von amphibolitfaziellen Mineralien (Ti-reicher Biotit, Hellglimmer und Feldspäte) in grünschieferfazielle Mineralien (Chlorit und Serizit) führte unter Einfluss von fluiden Phasen in der Zone der stark chloritisierten Schiefer (Gesteinsübergangszone im Bereich Unterwasserkanal, Druckstollen) zur Mobilisation von Titan, Fluor, Uran und Seltenen Erden (Ce, La, Nd, Sm, Eu, Gd, Er, Dy, Yb) und somit zur Bildung von seltenen Mineralien in den alpinen Klüften.

Eine grosse Variabilität an Mikromineralien ist auch in denjenigen Klüften vorzufinden, die im Bereich vererzter Nebengesteine liegen (Fe-Cu-Zn-S-Mineralien, Fe-Cu-Bi-As-S-Mineralien, Fe-Cu-Zn-Pb-S-Mineralien). Sie lässt sich durch die Remobilisation bereits vorhandener Erzvorkommen erklären.

Mikrothermometrische Analysen der Flüssigkeitseinschlüsse wurden in der Zone der Ti-F-Seltenen-Erden-Mobilisationen und der remobilisierten Erze durchgeführt. Sie bestätigen, dass die Kluftmineralbildung und die Mobilisation von chemischen Elementen unter retrograden grünschieferfaziellen Bedingungen stattgefunden haben (retrograde P-T-Entwicklung) und belegen, dass wasserreiche Fluide anwesend waren.

MAGMATIC AND METAMORPHIC PETROLOGY

C. Ambrics and J. Bertrand (Genève):

Petrological features of the Pelvas d'Abriès massif (northeastern Queyras, French-Italian Alps) (Poster).

The Pelvas d'Abriès massif (2929 m) is an ophiolitic mass of the Piemont Ligurian Schistes Lustrés zone (LAGABRIELLE, 1982, 1987) which is located at the French-Italian border, on the NE side of the Guil Valley. The Pelvas unit consists of a klippe comprising mainly cpx-gabbro, minor Fe–Ti gabbro, and peculiar ultrabasic intercalations concentrated in the east and southeast flanks of the massif. The relationship of the latter with the gabbro is still unclear. Ultrabasic cumulate layers (BEARTH et al., 1975), ultrabasic intrusions, or peridotitic tectonic slices are possibilities.

Some remnants of the primary supra-ophiolite sedimentary cover are preserved. At the Col d'Urine, the inverted position of the Jurassic marbles of this cover indicates that the klippe is overturned. This attitude was explained by LAGABRIELLE et al. (1985) and LAGABRIELLE (1987) as corresponding to parts of the inverted limb of a folded megastructure. Field and microscopic observations demonstrate that the high level-type gabbro sometimes preserves signs of oceanic flaserization overprinted by Alpine deformation. Incipient magmatic layering is rarely observed. Mylonite zones occasionnally crosscut the gabbroic body. Contrasting with these textural features, the primary cumulate textures of the ultrabasic intercalations, mostly undeformed, are still recognizable except in shear zones along contacts between both rock types.

Mineral assemblages were investigated by microscopy and X-ray diffraction. In gabbro, the constituents are diopsidic-augitic pyroxene, magnesio-hornblende, actinolite-tremolite, crossite-ferroglaucophane, sometimes aegyrinic pyroxene, albitic saussuritized plagioclase, epidote, chlorite, carbonate, Fe–Ti oxides, apatite, rare pumpellyite, lawsonite and tourmaline. In ultrabasic intercalations, olivine is the dominant cumulus phase, with rare or absent orthopyroxene; plagioclase, often including chromiferous idiomorphic to subidiomorphic Cr-spinel, appears as an intercumulus phase (< 3% up to 30% locally). Except spinel, the primary minerals are almost completely serpentinized and chloritized. Remnants of amphibole-bearing reaction rims and ghosts of rodingitic Ca-silicates are preserved. Carbonate, talc, and rare brucite are also observed.

Alpine metamorphism is recorded in gabbro by a greenschist to moderate blueschist facies imprint, nevertheless magmatic and oceanic metamorphic relics are still observable. Blueschist parageneses are preferentially developed within Fe–Ti varieties. The peridotite did not record a well characterized Alpine metamorphic overprint having preserved its oceanic serpentinization and associated recrystallizations.

Bulk-rock chemical analyses (major and trace elements by XRF, Centre d'Analyse Minérale, University of Lausanne), were made on gabbroic and ultrabasic rocks. Binary and ternary diagrams permit a comparison with data from the Montgenèvre ophiolite (Bertrand et al., 1982, 1987) and from Rocciavré (Pognante et al., 1982). For the gabbros, the evolution from Ca–Mg to more evolved members is clear. The comparable distribution patterns of the representative points from the Pelvas (greenschist to blueschist facies), the Montgenèvre ophiolite (pumpellyite-prehnite facies) and Rocciavré (blueschist to eclogite facies) shows that the Alpine metamorphism did not significantly change the chemistry. For the serpentinized peridotites, a linear correlation and two distinct fields clearly appear for the ultrabasic rocks from Pelvas and Mongenèvre. This difference may be partly explained by the presence of chromiferous spinel and interstitial chloritized plagioclase within the Pelvas samples.

The strong textural contrast between gabbroic and ultrabasic rocks is consistent with an intrusive character of the latter. The injection of the ultrabasic crystal mush seems to post-date oceanic deformation of the gabbro. Moreover, taking into account the type of contact between the two rock types, part of the peridotite appears to have intruded the gabbro at an early magmatic stage, whereas later intrusions could have been emplaced in a colder environment thereby explaining brittle behavior in the gabbros.

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Lagabrielle, Y., Lemoine, M. and Tricart, P. (1985): Paléotectonique océanique et déformations alpines dans le massif ophiolitique du Pelvas d'Abriès (Alpes Occidentales-Queyras-France). Bull. Soc. Géol. France, t.1, 4, 473–479.

Pognante, B., Lombardo, B. and Venturelli, G. (1982): Petrology and geochemistry of Fe–Ti gabbros and plagiogranites from the Western Alps ophiolites. Schweiz. Mineral. Petrogr. Mitt., 62, 457–472.

L. Bolou and J. Bertrand (Genève):

Magmatic and metamorphic evolution of ophiolitic and oceanic gabbros (Montgenèvre Ophiolitic Complex, Vema and Romanche Fracture Zones) in the vicinity of the Moho transition zone: geochemical and microstructural constraints.

The petrological Moho transition zone is a place where important magmatic and subsequent metamorphic processes occur. By comparing present-day oceanic rock types with their equivalents in Alpine ophiolitic successions it should be possible to understand more precisely how transition zones acquire their magmatic and metamorphic petrological features.

Mantle tectonites and ultrabasic to basic plutonic rocks from the Liguro-Piemontais Montgenèvre Ophiolitic Complex (MOC) and the Equatorial Mid-Atlantic Ridge (MAR) Vema and Romanche fracture zones have been compared. Both environments are assumed to be expressions of slow spreading systems. The MOC is largely unperturbed by Alpine metamorphism which improves the validity of the comparison (Bertrand et al., 1982). Both localities contain peridotitic tectonite, whether impregnated or not, as well as the members of a strongly differenciated cumulate gabbroic sequence, from troctolite to Fe–Ti gabbro, with the Ca–Mg high level-type dominant (Bertrand et al., 1987; Cannat et al., 1992).

Microprobe analyses of primary and secondary amphiboles, plagioclases, and clinopyroxenes have been performed particularly in order to better constrain the effective part of Alpine metamorphic imprint within the MOC. The plagioclases from oceanic gabbros, often porphyroclastic, show a composition dominantly of Ab$_{60}$ within a compositional range of Ab$_{50-70}$. Sometimes more albitic (Ab$_{80}$) crosscutting recrystallized veins are observed. Such compositions are found from slightly to strongly deformed plagioclases which have undergone pervasive hydrothermal alterations. These results are therefore not strictly representative of a primary composition. The neoblastic secondary plagioclase associated with the porphyroclastic plagioclase have almost the same composition.

In the ophiolitic equivalent gabbros, plagioclase compositions are Ab_{85-95} with again no significant variation between porphyroclastic crystals and their associated neoblasts. In this case a more drastic pervasive albitization is implied. The style of deformation is similar to that observed in the oceanic gabbros. Either in oceanic or ophiolitic gabbros, amphiboles frequently occur as complex intergrowths with pyroxene, other amphiboles, or chlorite. Therefore it is often difficult to clearly discriminate between primary, hydrothermal, or metamorphic amphiboles, which have often developed during the oceanic stage. Nevertheless there are some evidences for the origin of differing amphiboles. In Fe–Ti gabbro types, the common brownish to dark brown amphibole are considered to be primary, magmatic or late-magmatic. In the Na + K vs Si classification diagram of LEAKE et al. (1997), they are characterized by an edenitic composition, close to the pargasitic end-member, along a trend between pargasite and tremolite. In the other gabbros, mostly of Ca–Mg type, colorless or greenish calcic amphibole are generally observed. In the same diagram, they plot in the ferro-actinolite to actinolite (rarely tremolitic) and ferro- to magnesio-hornblende fields. Most of these varieties are secondary, which is clearly evidenced by the textural intergrowth with relics of clinopyroxene or earlier developed amphibole. These data do not provide significant discrimination features between oceanic and ophiolitic amphibole. These amphiboles display a wide range of chemical and textural variations that result from non-equilibrium crystallization conditions.

Microprobe analyses on relics of primary pyroxene indicate diopsidic clinopyroxene composition with no detectable Cr, about 0.5–1 wt% Ti, and 0.2 wt% Cr, 0.5–1 wt% Ti contents, respectively in ophiolitic and oceanic clinopyroxene. In both environments, these pyroxenes have very often been stretched and partially recrystallized. From microprobe data no chemical difference between porphyroclasts and associated neoblasts is found; the only difference between the two generations is textural, with the presence of both an undeformed neoblastic and a deformed porphyroclastic diopsidic pyroxene. All of these textural and microprobe chemical data do not point to any evidence for clearly distinct Alpine recrystallizations, with the possible exception of the severe albitization of the ophiolitic plagioclase.

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R. Ferreiro Mählmann (Basel):

Das Diagenese-Metamorphose-Muster in Mittelbünden: Geochronologie und Metamorphosegeschichte.

Metamorphoseuntersuchungen in der Arosa-Zone (Reste der kreidezeitlich aktiven Plattengrenze von der ozeanischen Piemont-Liguria- und der kontinentalen Austroalpin-Apulia-Platte) und im überlagernden Austroalpin (Oberostalpin) zeigen auf, dass das Metamorphosemuster in diesem Abschnitt der West-Ostalpengrenze sehr heterogen ist. Mit Hilfe der auf Temperatur sensibel reagierenden Parameter, der Vitrinitreflexion und der Illit-Kristallinität, konnten eine detaillierte Metamorphosekarte erstellt und, gegenüber den bisherigen Kenntnissen aus Mineral-Paragenesen, weitreichendere Schlussfolgerungen gezogen werden. Zusätzliche thermobarometrische Untersuchungen mit dem Chlorit-Thermometer, dem Phengit-Barometer, dem druckabhängigen Illit-b_0-Parameter sowie einigen Flüssigkeitseinschlussuntersuchungen an Faserquarzen aus Extensionsklüften vervollständigen das Metamorphosebild, das durch T-t- und P-T-t-Modellierungen der Gesteinsmaturität ergänzt wird. Die genaue Bestimmung der thermischen Überprägung ermöglichte es auch, K/Ar- und Rb/Sr-Altersdaten besser zu interpretieren.

Im *Oberostalpin* liegt ein präorogenes Metamorphosemuster vor. Mehrere Aufheizungen im Perm, in der Trias und im Jura konnten belegt werden. In den post-variszisch nur anchizonal aufgeheizten Bereichen im NW der Silvrettadecke kommen Mischalter zwischen 423 bis 299 Ma vor. Fraktionsabhängige Verjüngungen in Glimmern aus dem Grundgebirge tendieren auf einer

SW–NE-Achse zu Karbon- bis Perm-Altern (303 bis 263 Ma). In den epizonalen, auflagernden Trias- und Jurasedimenten sind in den Tonfraktionen Alter um 128 bis 84 Ma typisch. Die höchste Gesteins-Maturität wird für die Periode Jura-Unter-Kreide modelliert, weshalb diese Alter als kreidezeitliche Abkühlalter gedeutet werden. Die Abkühlung erfolgte mit dem Beginn der Deckentektonik (Störung des geothermischen Regimes). In Gesteinen, in denen während der zweiten Deformation an der oberostalpinen Basis Glimmer neu gebildet wurden, weisen Tonfraktionen ein Alter von 74 bis 52 Ma auf. Mit Maturitätsmodellen und mit dem Chlorit-Thermometer wird gezeigt, dass vor und während D2 noch einmal Temperaturen bis 300 °C erreicht wurden, während im N und in strukturell höheren Bereichen Zirkonalter zur selben Zeit eine Abkühlung unterhalb dieser Temperaturen belegen. Drücke unter 2.0 kbar während D1 und D2 sind mikrothermobarometrisch und durch den Si-Gehalt der Phengite nachgewiesen. Die Illit-b_0-Werte sind typisch für Gesteine, die niedrige Drücke erfahren haben.

In der *Arosa-Zone* wird das Bild deutlich uneinheitlicher. In den Fragmenten der Tschirpen-Dorfbergdecke (Unterostalpin) sind die Glimmeralter im Kristallin deutlich verjüngt (214 bis 129 Ma), während Kristallinblöcke des Oberostalpins wieder Glimmeralter zwischen 323 und 282 Ma aufweisen. In den max. epizonal aufgeheizten unterostalpinen Sedimenten (250 bis 320 °C, 3 bis 6 kbar) weisen Tonfraktionen homogene Alter auf (123 bis 98 Ma). Diese werden als Bildungsalter während des Höhepunktes der Metamorphose gedeutet. Spaltspurenalter an Zirkonen variieren zwischen 111 und 93 Ma. Diese sich überschneidenden Alter werden mit einer schnellen Exhumation nach der Subduktion erklärt. In grünschieferfaziellen Gesteinen werden in der Tonfraktion Alter von 79 bis 73 Ma als Abkühlalter gedeutet, die sich mit den D2-Altern der nördlichen unterostalpinen Decken (Ela, Carungas) vergleichen lassen (77 bis 67 Ma). Auch hier lassen sich diese Alter mit thermischen Modellierungen als Abkühlalter deuten. In Bereichen, in denen in den Ophiolithen eine ozeanische Prh-Pmp-, Pmp-Act- und Hornblende-Hornfelsfazies gefunden wird, stehen zwei Alter von 165 und 177 Ma in Zusammenhang mit der Bildung der Ozeankruste. Aufgrund der schwachen tertiären Temperaturüberprägung (< 250 °C, < 3 kbar) der Kreidesedimente der Mélange müssen die absoluten Alter aus diesem Bereich (152 bis 53 Ma) als geologisch insignifikant bewertet werden.

M. Jaboyédoff, B. Kübler and Ph. Thélin (Lausanne, Neuchâtel):

La cristallinité de l'illite: les probables raisons d'un succès.

Pour quelles raisons la cristallinité de l'illite (IC) s'est-elle montrée si efficace depuis trois décennies? Ce succès est très certainement lié à des propriétés physiques particulières, malgré la probable origine "polyphasée" du premier pic de diffraction de l'illite (LANSON, 1997). Par conséquent une interprétation physique de la méthode de mesure traditionnelle de l'IC semble possible (EBERL et VELDE, 1989 n'ont pas utilisé cette manière de mesurer). En utilisant le programme Newmod© (REYNOLDS, 1985), on peut créer des abaques qui permettent de définir le nombre moyen de feuillets (N) par domaine cohérent de diffraction et le taux moyen de couches smectitiques (%S) grâce aux mesures des largeurs de Scherrer du pic à 10 Å des diffractogrammes des essais séchés à l'air (LSSA = IC) et glycolés (LSG). Les distorsions du réseau ne sont ici pas prises en compte. Ces abaques sont établis pour les empilements de Reichweite R0, R1 et R3.

Grâce à ce modèle on peut tenter d'interpréter les deux limites de l'anchizone. Il apparaît que ces limites sont très similaires aux courbes que suivent des empilements de MacEvan qui contiennent des particules fondamentales (fundamental particles) constituées d'un nombre moyen constant de feuillets (NFP). La limite diagenèse-anchizone correspond à NFP ~ 20 et celle de l'anchizone-diagenèse à NFP ~ 60, ceci est un ordre de grandeur correct, car même si les micas détritiques peuvent influer l'IC, dans le domaine de l'anchizone ce sont les néoformations qui dominent. L'augmentation des épaisseurs des particules fondamentales avec le faible métamorphisme n'a pas de signification directe du point de vue de la croissance cristalline (ALTANER et YLGANG, 1997).

Dans les abaques LSSA et LSG, les empilements de MacEvan constitués de NFP constants suivent des trajectoires d'IC de valeurs presque constantes. Plus on s'éloigne de l'anchizone, moins cette relation entre IC et NFP se vérifie. Par conséquent l'anchizone et ses abords apparaissent comme l'unique zone où l'échelle est précise, si l'on suppose que cette échelle s'identifie aux épaisseurs des particules fondamentales. Ceci permet d'expliquer, en partie, la dispersion des mesures dans la diagenèse et le manque de finesse de la méthode de l'IC dans l'épizone.

Thanks to this model one can try to interpret the two limits of the anchizone. It appears that these limits are very similar to the curves which follow of stackings of MacEvan which contain of the fundamental particles (fundamental particles) made up of a constant average number of layers (NFP). The limit diagenesis-anchizone corresponds to NFP = 15–20 and that of the anchizone-diagenesis with NFP = 30–50, this is a correct order of magnitude, because even if the detrital micas can influence the IC, in the field of the anchizone in fact the neo-formations dominate. The increase thicknesses of the fundamental particles with the weak metamorphism does not have direct significance from the point of view of the crystal growth (ALTANER et YLGANG, 1997).

ALTANER, S.P. and YLGANG, R.F. (1997): Comparison of structural models of mixed-layer illite/smectite and reaction mechanisms of smectite illitization. Clays and Clay Minerals, 45, 517–533.

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J. Mullis (Basel):

Fluid evolution and mineral precipitation in extensional fissures during neo-Alpine compressional tectonics and metamorphism along the Gotthard Alp-Transit.

Fluid evolution and mineral precipitation during neo-Alpine tectonic and metamorphic events were studied in Alpine extensional fissures (MULLIS et al., 1994). Samples were collected in more than 50 localities at the surface, close to the planned Gotthard railway tunnel. The methods applied include microthermometry, micro-Raman spectroscopy, K/Na thermometry, stable isotope and X-ray analyses.

Early fluid inclusions provide information on temperatures close to the peak of the Late Tertiary or neo-Alpine metamorphic event. Spacial distribution of the main volatile components are at increasing temperature from north to south: heavy hydrocarbons, methane and water in the Helvetic and Ultra-Helvetic nappes; water in the Aar and northern Gotthard massifs; and carbon dioxide in the southern Gotthard massif and the Lepontine area. Retrograde fluid evolution is recorded in several cases by episodic enrichment of salt and volatiles (CO_2, N_2 and CH_4). Late inclusion populations are aqueous, with small amounts of salt and without any detectable volatiles.

Once the extensional fissures were opened by neo-Alpine compressional tectonics, the fissure wall rocks began to be leached. Dissolved minerals were transported into the fissure systems where they precipitated. Early fissure mineral assemblages evolved, from north to south, as a function of the chemical compositon of the host rocks, the increase in temperature and change in fluid composition. During retrograde conditions significant tectonic events affected some of the fissure systems causing repeated fluid pressure drops, fluid immiscibility and channeling of fluid through the massifs and nappe systems. CO_2-rich fluids increased within the fissure systems. Several minerals like epidote, ilmenite, sphene and chlorite were no longer in equilibrium with the CO_2-enriched fluid and thus dissolved and reacted to a late carbonate dominated mineral assemblage with siderite, ankerite, phengite and rutile.

MULLIS, J., DUBESSY, J., POTY, B. and O'NEIL, J. (1994): Fluid regimes during late stages of a continental collision: Physical, chemical, and stable isotope measurements of fluid inclusions in fissure quartz from a geotraverse through the Central Alps, Switzerland. Geochim. Cosmochim. Acta. 58, 2239–2267.

Th. Nagel (Basel):

Die Zentralalpen als ein mitteloligozäner "Metamorphic Core Complex" – Hinweise aus der unteren Valle Mesolcina.

Isothermen der amphibolitfaziellen Metamorphose im Lepontin zeigen nach S zunehmende Metamorphosebedingungen an. Die Insubrische Linie als südliche Begrenzung des Lepontins stellt einen bedeutenden Metamorphosesprung an der Oberfläche dar. Das heute vorliegende Metamorphosemuster wird im allgemeinen als das Produkt der ab 30 Ma stattfindenden Rücküberschiebung des nördlichen Blocks an der I.L. gedeutet (z. B. SCHMID et al., 1989). Die Geometrie der Isograden in den Zentralalpen ähnelt andererseits denen eines *Metamorphic Core Complex* (BRADBURY and NOLEN-HOEKSEMA, 1985). In diesem Beitrag soll ein erweitertes Modell zur Diskussion gestellt werden, nach dem die Exhumation des nördlichen Blocks teilweise schon vor 30 Ma an einer südfallenden, sinistral transtensiven, duktilen Abschiebung stattfand, die heute in der südlichen Steilzone und unmittelbar nördlich davon aufgeschlossen ist.

Das Arbeitsgebiet liegt im südöstlichen Lepontin und gehört strukturell zur Adula- und zur unterlagernden Simano-Decke. Es beinhaltet den Übergang von flach NE-fallendem Deckenbau in die südliche Steilzone. Von N nach S findet ein bemerkenswerter Wechsel des strukturellen Baus statt:

- Im N fällt die Hauptfoliation (S2) flach bis moderat nach NE, die dazugehörende Streckungslineation (L2) nach NNE ein. Schersinne zeigen "Top nach N" gerichtete Bewegung an.
- Gegen S biegen die Streckungslineare gegen den Uhrzeigersinn nach E um. Schersinne sind "Top nach SE" bzw. E gerichtet. Eine ausgeprägte Rückfaltung, deren Faltenachsen parallel zum Streckungslinear orientiert sind, bringt diese Foliation in die südliche Steilzone, ohne eine neue Achsenebenenschieferung auszubilden. Die S2-Foliation im N wird in Metapeliten hauptsächlich von Hellglimmern definiert. Weitere stabile Phasen sind u.a. Qz, Grt, Bt, ± Ky. Staurolith überwächst S2. Im S sind die Metapelite modal reicher an Biotit. Die SE-gerichtete Scherung überprägt S2-Disthen. Später als Disthen und Staurolith gewachsener Sillimanit ist verbreitet im Streckungslinear stabil. Die D2-Strukturen im N werden demnach als älter als die SE-Scherung (D3, L3) und folgende Rückfaltung (D4) im S angesehen.

Kartierung von Isograden und die Bestimmung von Mineralreaktionen im DS zeigen, dass zwischen D2 und D4 eine Dekompression des Arbeitsgebietes stattgefunden hat. Jüngere Untersuchungen haben gezeigt, dass die Basis des ostalpinen Deckenstapels und der höhere Teil der penninischen Decken in Graubünden im mittleren Oligozän eine Phase bedeutender SE-Scherung (Turba-Phase) erfahren haben (z.B. Nievergelt et al., 1996). Die SE-gerichtete Scherung im Arbeitsgebiet (D3) im gleichen strukturellen Niveau unter der ostalpinen Tonale-Serie interpretiere ich als die Fortsetzung der Turba-Scherzone (Abb. 1). Die Steilstellung dieses Scherhorizontes in die heute nordfallende Orientierung erfolgte in einer Phase wiedereinsetzender Kompression unter andauernder E-W-Dehnung (D4), in deren Zuge die Rücküberschiebung an der Insubrischen Linie einsetzte.

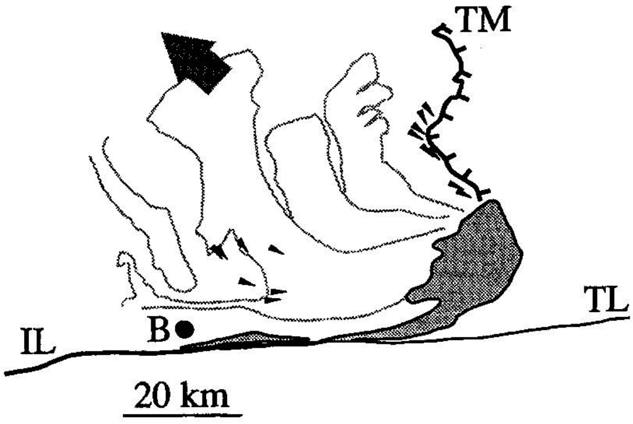

Abb. 1 Skizze des südöstlichen Lepontins: Die kleinen Dreiecke zeigen die Bewegungsrichtung des Hangenden unterhalb des Turba-Mylonits (Nievergelt et al., 1996) und im Süden des Arbeitsgebietes an. (TM: Turba-Mylonit; IL: Insubrische Linie; TL: Tonale Linie; B: Bellinzona).

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T. Petrova, W.B. Stern and M. Frey (Basel):

Metamorphism of carbonaceous material in the Bündnerschiefer of eastern Switzerland: application of X-ray diffraction and thermal methods.

Dispersed carbonaceous material is a common constituent in sedimentary and metasedimentary rocks. With increasing grade of metamorphism, its chemical composition, thermal behaviour and crystal structure change systematically, a transformation referred to as "graphitisation". Because the graphitisation process is considered to be irreversible, the extent of graphitisation is a useful indicator of the maximum metamorphic grade attained. In this study the metamorphic profile in Bündnerschiefer of eastern Switzerland has been sampled (40 samples) to trace the graphitisation and correlate its stages with metamorphic degrees.

The Bündnerschiefer series of eastern Switzerland consist of low-grade metamorphic shaly-calcareous-terrigenous sediments. Metamorphic grade in the "Prättigau-Schiefer" increases from the greenschist facies in the West to "anchizonal grade" towards the East (Weh et al., 1996). Teutsch (1982) did a systematic metamorphic study on the various lithologies from the Misox zone south of the Hinterrhein valley. Metamorphic grade increases continuously from Hinterrhein to Passo della Forcola, and the limit between greenschist and amphibolite facies was mapped near Mesocco. Thus, in the chosen metamorphic profile in Bündnerschiefer metamorphic grade increases to the south.

The graphitisation process is characterised by transition from the two-dimensional aromatic structure to the three-dimensional crystal growth of graphite. At low metamorphic grade up to greenschist facies, the organic composition of the precursor material will control the process of graphitisation (DIESSEL et al., 1978). Carbonaceous material has been extracted from the whole rock samples after long multi-acid treatment. The extracted powder included the insoluble accessory phases as well, such as rutile, zircon, pyrite, and turmaline. XRD diffractograms of the carbonaceous matter from low-grade northern parts of Bündnerschiefer still exhibit no clear graphite peaks, but an amorphous area corresponding to the coaly material. However, diffractograms for the higher grade carbonaceous matter concentrates display better morphology and already visible peaks of graphite (relatively well-ordered).

The same extracts of carbonaceous material have been studied with differential thermal-thermal gravitational and combustion analyses under O_2 and N_2 atmospheres. In general, higher intensity of regional metamorphism parallels higher temperatures of exothermal peaks of CO_2 on the heating curves during thermal analysis of carbonaceous and graphite material, the peaks for successive facies being separated by roughly 100 °C. This shift of exothermic CO_2 peaks due to oxidation of carbonaceous and graphite material is explainable by different degrees of graphite ordering during the graphitisation process. Well-ordered graphite is oxidised at higher temperatures (650–800 °C) than the poorly ordered one or the coaly material (400–550 °C).

Presence of different types of carbonaceous matter with various degrees of ordering in the same samples is detected in some cases with help of combustion analysis and partly X-ray diffractometry. For example, several extracts of carbonaceous material produce different peaks of CO_2 with peak temperatures ranging from 300 to 600 °C (in these cases no calcite is present). This may be due to detrital graphite occurrence in the samples or different behaviour of certain coal particles during oxidation under O_2 atmosphere.

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M.K. Rahn and **M.T. Brandon** (Freiburg i. B., New Haven):

Insights into very low-grade metamorphism and exhumation of an active accretionary wedge: the Olympic subduction complex, Washington State, USA.

The Olympic Subduction Complex (Olympic peninsula, Washington State) is the only subaerially accessible and deeply exhumed part of the Cascadia accretionary wedge which formed over the last 35 m.y. due to subduction of the Juan de Fuca plate beneath North American. The complex is mainly composed of volcaniclastic sandstones (graywackes) with subordinate shales and minor basalts. The exposed part of the complex was accreted from Late Eocene through early Miocene time.

Thin sections of more than 400 graywacke and basalt localities were investigated petrographically, and selected samples analyzed by microprobe and bulk rock chemistry. Different from previously published metamorphic zonation (TABOR and CADY, 1978), but concordant to existing apatite and zircon fission track (FT) pattern (BRANDON et al., 1998), a concentric increase of metamorphic grade from zeolite facies (assemblage lmt-ab-chl), only found in the western part) to prehnite-pumpellyite (pmp-prh-ab-chl-ep) along the bordering Hurricane ridge fault, and pumpellyite-actinolite (pmp-act-ab-chl) in the basalts of the central region is proposed. The fact that the area of greatest topographic elevation coincides with the highest metamorphic rocks is explained by strong post-metamorphic updoming of the central region. The concentric rather than linear metamorphic pattern is compatible with an erosion-driven exhumation rather than a tectonically driven denudation by normal faulting along the limiting faults.

Several samples from the area of reset zircon FT ages reveal actinolite (act) growing epitactically on relict clinopyroxenes in basalts and graywackes. The breakdown of former plagioclase (plag) into albite (ab) and pumpellyite (pmp) can be formulated by a reaction

$$\text{plag} + H_2O + (\text{Mg,Fe})^{2+} = \text{ab} + \text{pmp} + \text{qtz}.$$

The resulting pmp forms isolated aggregates within ab, and is very Al-rich. Fe-rich pmp forms at the expense of former glassy particles. The coexistence of prehnite and pmp and absence of act is restricted to samples from the rim and outside of the zircon reset zone inferring a close temperature relationship between the onset of the pmp-act facies and the complete reset of the zircon FT system. Preliminary temperature estimations for this parallel transitions on the basis of chlorite Al^{IV} thermometry suggest a range of 300–320 °C which is in agreement with latest statistical treatment of zircon annealing experiments (GALBRAITH and LASLETT, 1997) for the zircon partial annealing zone boundary.

Both, P-T estimations on existing mineral assemblages and the absence of phases such as lawsonite, glaucophane, or aragonite indicate that the Cascadia accretionary wedge, different from other and older accretionary wedges along the U.S. West coast, did not undergo HP metamorphism.

BRANDON, M.T., RODEN-TICE, M.K. and GARVER, J.I. (1998): Late Cenozoic exhumation of the Cascadia accretionary wedge in the Olympic Mountains, NW Washington State. Geol. Soc. Amer. Bull. 110, 985–1009.

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CONTINENT-OCEAN INTERACTION

G.W. Bianchi, G. Martinotti and R. Oberhänsli (Potsdam, Torino):

Evidence for an early Tethys phase of rifting in the western Alps: a comparison between two case studies.

Despite their complex tectonic-metamorphic evolution, evidences of the early Tethys phase of rifting are in places well recorded within the cover sequences of Permian-Liassic age in the Western Alps. Two different sequences have been studied in order to reconstruct the evolution of the rifting events. The first area is located in the Ossola-Ticino structural domain, and it includes part of Monte Leone and Antigorio cover sequences as well as part of the Gotthard massif Mesozoic cover. The second area is located in the Southern Cotian Alps, within the Piemontese Zone of ophiolitic calcschists.

Detailed field studies have allowed the recognition of a stratigraphic continuity between dated Permian-Triassic rocks (mainly local quartzites and gypsum lenses and calcareous-dolomitic marbles) and the associated heterogeneous calcschists: critical lithological associations, datable fossiliferous horizons and rifting paleostructures can be observed within these metasediments. Breccia horizons outcropping at different structural levels within the sequences, metabasite and serpentinite bodies as well as syn-sedimentary faults provide evidences for the rift activity, lasting at least between the middle Trias and the beginning of the Dogger. Chemical analyses suggest a basaltic-tholeiitic trend and a WPB affinity for the basalts, supporting a rift setting for the emplacements of these rocks. Nevertheless, the presence of phyllitic black schists, ammonite-bearing horizons, metapelites and metasandstone bands suggest a low energy depositional environment in more external sectors of the basin.

Based on these observations, a model first defined for the Monte Leone cover sequence (BIANCHI et al., 1998) has been extended to describe the evolution of the continental margin in the Central Alps area during the upper Permian through the lower Jurassic. Lithologic similarities suggest the applicability of this model to the Cotian Alps area. Although further studies are needed to better define the entire rift evolution, the data suggest a structurally complex basin: the presence of smaller, more external basins active since the middle-upper Trias, and isolated by structural highs from the rift axis can be hypotesized.

BIANCHI, G.W., MARTINOTTI, G. and OBERHÄNSLI, R. (1998): Metasedimentary cover sequences and associated metabasites in the Sabbione Lake zone, Formazza Valley, Italy, Northwest Alps. Schweiz. Mineral. Petrogr. Mitt., 78, 133–146.

MICHARD, A. (1967): Etudes géologiques dans les zones internes des Alpes Cotiennes. CNRS, Paris, 447 pp.

K.B. Föllmi, Th. Adatte, Ph. Steinmann, F. Tamburini, B. van de Schootbrugge, E. Szücs, C. John, Ch. Badertscher, Ph. Veuve, M. Benbrahim (Neuchâtel):

Continent-ocean interactions and their geological records.

At the Geological Institute, University of Neuchâtel, a new, long-term, research program is being developed, which is entitled "continent-ocean interactions and their geological records". The rationale behind this program is to trace continental weathering by all means, and establish feedback mechanisms between continental weathering, productivity, and (paleo-)climate. A major goal is to identify the direct and indirect impact of glaciation on weathering and compare it with ice-free areas and time windows. Prime target areas and time windows are (1) present-day biogeochemical weathering in glaciated areas (T. Adatte, P. Steinmann, E. Szücs); (2) Pleistocene variations in continental weathering based upon phosphorus burial records in selected ODP cores (F. Tamburini, T. Adatte, P. Steinmann); (3) Miocene deposition of marine organic matter

(Monterey Formation, California; C. John, C. Badertscher, T. Adatte) and continental organic matter (lignites, Europe); (4) continental weathering and ecological change in the early Cretaceous (Helvetic carbonate platform, Alps; B. van de Schootbrugge, T. Adatte); and (5) iron and phosphate-rich deposits of the early and middle Jurassic, documents of intense continental weathering (central Europe; P. Veuve, M. Benbrahim, T. Adatte, P. Steinmann).

We use a series of key proxies in tracing weathering records, such as carbon, nitrogene, oxygen and strontium isotopes, P, Ti, Cd, Ba, and Al as trace elements, and composition and distribution of clay minerals. A preliminary data set based upon a globally averaged marine phosphorus burial record indicates two tendencies, which are to be tested in the course of our research program: (1) changes in total weathering rates are closely associated with changes in chemical weathering rates; (2) in an ice-free world, continental weathering appears to be driven by a combination of warm and humid climates; in an "icehouse" world, continental weathering appears to be driven by glaciation. Weathering is the important source of biophile elements and a change in its driving mechanism may have changed feedback mechanisms between productivity, carbon burial and the fixation of atmospheric CO_2, and climate development.

J. Meyer, J.D. Kramers and G. Früh-Green (Bern, Zürich):

Anomalous hydrothermal alteration in thin oceanic crust of the Jurassic Masirah ophiolite (Sultanate of Oman).

The Upper Jurassic Masirah ophiolite displays an unusually thin crust with only several 100 m of gabbros and sheeted dykes (PETERS et al., 1995). Ridge-related hydrothermal metamorphism is unusual. In the pillow lavas, altered rock volume is estimated at about 20–30%, and fluid appears to have percolated mainly along microbrecciated hyaloclastitic rims. The usual alteration paragenesis is chlorite-titanite-albite-muscovite/illite-celadonite-calcite-prehnite (± pumpellyite, epidote and actinolite). Microfossils in interpillow sediments (mainly radiolaria) and in the lowermost few m of overlying sediments are completely calcitified, and interpillow sediments may be epidotised. In the sheeted dyke complex, 35–40 vol.% is altered. The mineralogy, chlorite – clinozoisite / epidote – actinolite / actinolitic hornblende – titanite – (± sericite / muscovite, albite) is the same throughout the sheeted dyke complex. Microcracks, incomplete reactions and armoured relics indicate rapid reaction under a low water/rock ratio. In the upper parts of the gabbro sequence swarms of < 1 mm thick parallel veins of green hornblende, associated with c. 1 cm wide metasomatic alteration zones and locally larger pegmatoids, are common. At a later stage, mm- to cm wide prehnite-filled fractures and networks of cataclastic, prehnite-impregnated zones were formed at all levels of the oceanic crust, most intensely (up to 10 vol.%) in the sheeted dyke complex. The mineralogy of the veins (prehnite ± quartz, calcite, epidote) documents prehnite-pumpellyite facies conditions throughout the crustal profile. The pillow lavas alone are crosscut by networks of mm – cm thick quartz veins. Hydrothermal breccias and voids are common. Traces of epidote and of ore minerals (pyrite, chalcopyrite) can be present. Massive sulfide formations were not found. The veins are mainly oriented parallel to the pillow stacks, in contrast to what might be expected in the case of a black smoker type fluid exit into the ocean.

Sr and O isotope patterns are also unusual. Gabbros and one of three sheeted dyke samples range in $\delta^{18}O$ from +6 to +0.5, with lowest values shown by hornblendised gabbros. Meanwhile $^{87}Sr/^{86}Sr$ values remain between 0.7035 and 0.7041, thus displaying little apparent effect of seawater interaction. Two samples of sheeted dykes and all pillow lavas have $\delta^{18}O < 5.5$ and $^{87}Sr/^{86}Sr$ ratios between 0.7041 and 0.7055. Prehnites in veins occupy an intermediate position, while calcite veins within pillow lavas and sheeted dykes have $\delta^{18}O$ between 7 and 23 and $^{87}Sr/^{86}Sr$ between 0.7036 and 0.705. The O and Sr isotope systematics are thus decoupled and cannot be described by mixing, even if temperature effects are taken into account. Further, calcites in veins within pillow lavas and below have Sr concentrations less than 60 ppm, extremely low for calcite. These features can be explained by calcite precipitation from downward percolating seawater, whereby Sr was efficiently scavenged. The relatively low water-rock ratio could have led to fluids at deeper level having $\delta^{18}O < 0$, after which high temperature mixing could produce altered zones with $\delta^{18}O \approx 0$. Three quartz veins all have $\delta^{18}O$ between 8 and 11, whereas $^{87}Sr/^{86}Sr$ ratios vary from 0.7045 to 0.708. These veins can thus not represent exits from the hydrothermal system portrayed by the alteration described above. Rather, they represent a second, local fluid circulation system within the extrusive series. All anomalous features can be related to the fact that the oceanic crust of Masirah was very thin. As a result no large scale fluid circulation arose, the water-rock ratio remained low and the crust remained hot unusualy long up to high levels.

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GEOCHRONOLOGY AND GEOCHEMISTRY

E. Belluso, R. Ruffini, M. Schaller and I.M. Villa: (Torino, Bern):

Electron-microscopic and Ar isotopic identification of chemically heterogeneous amphiboles from the Palala Shearzone, Limpopo Belt, South Africa.

Amphiboles from a retrogressed charnoenderbite and a metagabbro in and near the Palala Shearzone, a Proterozoic suture zone between the Central Zone of the Limpopo Belt and the Northern Kaapvaal Craton, South Africa, were analyzed by $^{39}Ar/^{40}Ar$. Their age spectra are discordant and several step ages are older than the most probable age of peak metamorphism at 2.02 Ga, as determined by Pb/Pb stepleaching on titanite. By using Cl/K vs Ca/K correlations obtained from Ar isotopes it is straightforward to identify different end-member trends (at least two in one sample, four in the other). Heterochemical amphiboles are intergrown at a sub-micron scale and can be recognized by transmission electron microscopy but neither by optical microscopy, nor by electron microprobe profiling. Extrapolating to pure endmember amphiboles, ages can be modeled. In the charnoenderbite amphibole, formed by pyroxene hydration, an excess radiogenic $^{40}Ar/^{36}Ar$ initial can be removed to give a 2.02 Ga age; in the gabbro sample, the step ages pertaining to tschermakite and Mg-hornblende give c. 2.02 Ga, with both minor chlorite alteration and late edenite overgrowths accounting for higher and lower outliers.

J.D. Kramers, V. Chavagnac, L. Holzer, F.Th. Nägler and I.M. Villa (Bern):

Trace element concentration contrasts, partition coefficients and resetting or non-resetting of mineral chronometers.

In the Mahalapye Complex, Botswana, high grade metamorphism at 2.0 Ga, leading to migmatization, is recorded by Sm–Nd in garnet and U–Pb in monazite of leucosomes (CHAVAGNAC et al., submitted). Two populations of euhedral apatite grains from paleosome yielded a Sm–Nd age of 1959 ± 47 Ma, whereas a third fraction (rounded grains) gave an age of 2400 ± 60 Ma, which is interpreted as a mixing age between Archean and 2 Ga. U–Pb ages of the same apatite fractions are concordant at 2 Ga, and Sr isotopes also appear to have equilibrated with the whole rock at that time.

Diffusivity of trace elements in a mineral lattice can be reasonably well predicted by ionic porosity calculations (DAHL, 1996, 1997). For instance, biotite is predicted to be unretentive for Sr and Ar, apatite intermediate for Nd and Sr, and monazite retentive for Nd and Pb. The apatite behaviour described above presents an apparent contradiction to such predictions. We investigate the possibility that Nd isotope exchange is not limited by the apatite grains, but by the material surrounding them. In considerations of closure behaviour it is generally assumed that trace element transport outside the mineral grain is not rate limiting, as fluid transport, e.g. along grain boundaries, is many orders of magnitude faster than diffusion in the crystal lattice. Aqueous fluids are present during greenschist and amphibolite facies metamorphism, but H_2O activity may be very low under high grade conditions if a H_2O undersaturated melt is generated. Diffusivity in minerals surrounding the dated grains may then be an important limiting factor, even if they are not "armoured".

This can be illustrated using Fick's and Henry's laws. If a grain of mineral A is embedded in a medium B, e.g. another mineral, then equilibrium exists for a trace isotope i if $^iC_A/^iC_B = {}^iK$, where ^iK is the (Henry's law) equilibrium partition coefficient for i between the two phases. Accessory minerals are (except in clastic sediments) normally in equilibrium with their surroundings when a rock is formed. If i is a radiogenic isotope produced in A, ^iC has increased in A over time and "disequilibrium" exists only for that isotope. During a thermal event, incipient diffusion will set up concentration gradients in A and B close to the interface for isotope i. These are related by $\partial C_A/\partial x = {}^iK\partial C_B/\partial x$. Thus a high value of ^iK leads to a weaker gradient in the surrounding medium B than in A. Since net diffusion, following Fick's law, of i in medium B depends on this gradient ($^iF = {}^iD_B\partial^iC_B/\partial x$ where D is the diffusion coefficient, ^iF is the rate of transport through a unit area perpendicular to x) isotope exchange is impeded by phase B if $^iK >> 1$, unless $^iD_B >> {}^iD_A$. If $^iK < 1$, diffusivity in the surrounding medium B will rarely be a limiting factor.

Sr in biotite among other silicates is generally a case of $^iK < 1$, a further reason why this system is so readily reset. In contrast, $^iK >> 1$ for Nd in apatite among silicates, which explains the apparent paradox outlined above. Speculations about zircon U–Pb retentivity are also interesting: Pb^{4+} has a ionic radius close to that of Zr^{4+}, and should thus be highly compatible in the zircon lattice. If radiogenic Pb is (as is likely) in the 4+ state, this would therefore explain the extreme retentivity of Pb–Pb and U–Pb systematics in zircon under high grade metamorphism.

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K. Kreissig and J.D. Kramers (Bern):

Weathering in the Archean and the early atmosphere.

Problems of particular importance in Archean research are the growth history of the continental crust and processes of its formation, the rate and mechanisms of weathering through time, the change in atmosphere composition, and ultimately, the appearance and evolution of life. A special question is whether oxidising or reducing conditions prevailed in the early to middle Archean. This is at present again controversial (e.g. OHMOTO, 1996).

One possible indicator of the oxidation potential of the early atmosphere are fine clastic sediments. Their geochemistry and isotope compositions can, apart from being useful in constraining the provenance, provide indications on the intensity and redox conditions of chemical weathering in the source area. The former can be assessed using the chemical index of alteration, CIA (NESBITT and YOUNG, 1982). Most Archean metapelites show intense chemical weathering in their source regions, although corrections have to be made in some cases for diagenetic K-metasomatism (FEDO et al., 1995). An estimate of redox conditions during Archean weathering can be made using trace elements whose mobility depends on their oxidation state. U in minerals has the 4^+, 5^+ and 6^+ valences. When oxidised to U^{6+} uranium is easily mobilised in surficial processes. Therefore the Th/U-ratios of pelites (measured directly or obtained from Pb isotope ratios), compared to their probable source rocks, provide an avenue towards assessing the redox conditions of the Archean atmosphere.

We have carried out such a study on intracrustal rocks (mainly tonalitic gneisses) and metapelites from two individual tectonic units of the Archean craton and the Limpopo Belt in southern Africa. The sampled gneisses and metapelites from the Southern Marginal Zone (SMZ) of the Limpopo Belt differ from those from the adjacent Kaapvaal Craton (KC) in terms of the metamorphic history. The SMZ underwent a granulite facies metamorphism 2690 Ma ago while the KC-samples are all greenschist or amphibolite facies rocks. Most metapelites from both provinces indicate significant chemical weathering in their source region (CIA-values between 64 and 97). Various geochemical indicators (e.g. Sm–Nd systematics) show that the metapelites derived from the gneisses. Th/U-ratios are remarkably uniform (between 2 and 4) within the different terranes as well as within the different lithologies. The similarity of the Th/U-ratios of granulite facies and greenschist/amphibolite facies samples contrast the earlier assumption (e.g. BLACK et al., 1973) that U mobilized during granulite facies metamorphism. Thus the approach appears robust even in high grade metamorphic provinces.

From the lack of U-loss it appears that no oxidisation of uranium to the soluble hexavalent state took place during the documented intense chemical weathering. Thus our results concur with many other indicators in pointing to an anoxic atmosphere in the late Archean.

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P. Oppizzi and U. Schaltegger (Lugano, Zürich):

Zircon-bearing plagioclasites from the Finero complex (Ivrea zone): dating a Late Triassic mantle hic-cup?

Introduction: The mafic-ultramafic Finero complex is situated in the eastern part of the Ivrea-Verbano Zone and consists of peridotite, serpentinites, pyroxenites and layered gabbros. The suite was probably emplaced in the lower crust ca. 270 Ma ago. Sm–Nd whole-rock and zircon U–Pb ages of 530 to 540 Ma ago (e.g. Lu et al., 1997) were first interpreted as emplacement ages but have been proposed to be due to mixing and inheritance (e.g. GEBAUER et al., 1992). The mafic-ultramafic rocks represent melts from a depleted mantle, which underplated amphibolitic-kinzigitic gneisses at the base of the crust. The Finero complex is strongly metasomatized by a crust-derived "Magic Fluid". Sm–Nd mineral ages from the internal gabbro yielded ages between 230 and 210 Ma, either dating this metasomatic event and/or a regional thermal heating (LU et al., 1997). A similar age was also reported by VON QUADT et al. (1993) for zircons of a chromitite layer in the peridotite. Further U–Pb zircon and monazite data at around 210 to 220 Ma are scattered over the Ivrea zone and argue for a crustal heating event in the Latest Triassic (VAVRA et al., 1996, 1997).

Occurrence of plagioclasites: In the gabbros around the Finero ultramafic body we can recognize strongly cataclastic pegmatoid rocks, occurring as lenses or leucocratic layers within gabbroic host rocks or possibly as dykes. They are composed mostly of oligoclase and accessory minerals such as zircon, biotite, chlorite, corundum and zoisite. One of the plagioclasite dykes was dated at 225 ± 13 Ma by STÄHLE et al. (1990). Similar pegmatoid plagioclasite rocks have been described near Vercelli and in the Val Sesia (BERTOLANI, 1957; LOSCHI GHITTONI, 1969; ROSSI, 1968; STÄHLE et al., 1986).

U–Pb dating of zircons: The studied zircons were sampled from a plagioclasite lense within a layered gabbro near the Finero ultramafic body. The prismatic pink crystals have a length of some millimeters and are strongly fragmented, some cracks being cemented by zoisite. Completely transparent fragments were selected for U–Pb analysis, abraded and analysed for their U and Pb isotopic composition. U and radiogenic Pb concentrations were around 30 and 1.1 ppm, respectively. A mean $^{206}Pb/^{238}U$ age of 212.5 ± 0.5 Ma resulted from 4 analyses.

Interpretation of the data: The new data, together with a relatively large number of recent U–Pb ages from a variety of rocks, argue for a thermal/hydrothermal activity at around 210 Ma, disturbing high-grade metamorphic and mafic igneous lithologies of the Ivrea Zone. This event caused zircon growth in plagioclasites and almost complete lead loss in zircon and monazite from kinzigites (VAVRA et al., 1996; VAVRA and SCHALTEGGER, 1999), as well as resetting of Sm–Nd mineral isochrons in the Finero peridotite. A temperature in excess of 600 °C may therefore be anticipated locally for this fluid activity. The participation of mantle material (melts and fluids) is evidenced by the geochemistry of the pegmatoid dyke dated by STÄHLE et al. (1990). The data support previous results that suggest the presence of another short episode of mantle upwelling and advection of heat and fluids into lower and middle crustal levels after the well-known magmatic pulses in Late Permian and Middle Triassic.

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M. Passeraub, L. Holzer, K. Kreissig, J.D. Kramers, I.M. Villa (Bern):

Metamorphic history of the Archean Kaapvaal-Limpopo Belt suture.

The metamorphic evolution of the Archean suture between the Kaapvaal Craton and the Limpopo Belt has been studied on rocks from the Rhenosterkoppjes Greenstone Belt (RGB), one of the northernmost units of the craton. We applied multiple chronometry to microstructurally and petrologically characterized mineral generations.

(1) The age of the protolith. Zircons have a multi-stage overgrowth history; U/Pb TIMS analyses indicate that zircon cores are > 2.9 Ga. Zircons are very U-poor. We also calculated Sm/Nd model ages for three whole rocks, which range between 2.95 and 3.1 Ga and substantiate the zircon result.

(2) The main deformational event, the amphibolite-facies D2, was dated by PbSL of titanite in equilibrium with oriented hornblende, at 2729 ± 29 Ma. A more precise lower age limit is provided by post-tectonic, retrogressive epidote + titanite and titanite, giving 2743 ± 21 and 2754 ± 2 Ma, respectively. This shows that retrogression immediately followed the peak.

(3) $^{39}Ar/^{40}Ar$ dating of three D2 amphiboles revealed unexpected complexities. The K contents < 1000 ppm reduced the analytical resolution of our analyses. Age spectra are irregular and apparently suggest a c. 2.5 Ga age. However, we identify this value as a mixed age, basing on three arguments: (a) if it were a "cooling age", one would have to assume an unrealistically slow cooling. Peak temperature conditions of D2 hardly if ever exceeded the "closure temperature" of amphibole, so that the age difference of 250 Ma between amphiboles and titanite would require "cooling rates" < 0.2 °C/Ma. (b) The chemical correlation diagram, Ca/K vs Cl/K (based on Ar isotopes), in all three cases shows a good anticorrelation, evidence of a binary mixing of heterochemical phases. (c) Electron microprobe traverses with a 2 µm spatial resolution show the same pattern of correlated variation of Ca/K and Ca/Al ratios; the spread in K concentration exceeds the analytical reproducibility and supports the identification of two distinct amphibole generations. In conclusion, we identify an Archean amphibole ($t > 2.6$ Ga, $Ca/K > 50$) and a small but detectable Proterozoic intergrowth ($t \approx 2.0$ Ga, $Ca/K = 25$).

(4) The post-D2 hydrothermal overprint was dated by PbSL on a fuchsite + kyanite assemblage. The kyanite gave 2634 ± 49 Ma.

(5) Pegmatites crosscutting greenschist-facies retrogression were dated by Rb/Sr, PbSL and Sm/Nd. A garnet-feldspar pair in an undeformed pegmatite yielded a Sm/Nd age of 2.79 Ga; Sm and Nd concentrations were extremely low, and the garnet gave the most radiogenic Nd ever measured ($^{143}Nd/^{144}Nd = 0.69$). Muscovite Rb/Sr ages vary within the same hand specimen; they range from 2.68 to 2.45 Ga. Their interpretation is probably a mixing of Archean and Proterozoic generations, similarly to the amphibole pattern (3). PbSL on another garnet shows a very high scatter both in ages and Th/U ratios. No age is defined by more than two leach fractions, implying that alteration must have played a dominant role.

The deformation history in the RGB started at an ill-defined time after 2.9 Ga and was essentially finished around 2.75 Ga. This age is substantially older than crustal thickening in the Limpopo Belt, 2.69 Ga. This discourages the interpretation that the granulite event in the Limpopo is due to the postulated N-vergent thrusting in the Kaapvaal Craton. Archean tectonometamorphism in the Limpopo Belt is not coupled to tectonics in the Kaapvaal Craton as proposed by De Wit et al. (1992).

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R. Schönberg, F.J. Kruger and J.D. Kramers (Bern, Johannesburg):

The origin of the PGE enriched chromitite layers in the bushveld complex: a combined Re–Os and Rb–Sr study.

The Critical Zone of the Bushveld Complex (South Africa) is famous for its repeated crystallization series (Cyclic Units), each comprising a basal chromitite layer associated with platinum-group-element (PGE) mineralizations. Of economic interest are mainly the uppermost chromitite layer of the Critical Zone and the Merensky Reef – the basal layer of the overlying Transition Zone – containing together more than 70% of the world's mined platinum reserves.

Injections of new melt and magma mixing are widely accepted to be responsible for bringing chromite onto the liquidus (Irvine, 1977) and thus for the accumulation of the chromitite layers. However, the composition of the magmas involved and the origin of the "crustal" signatures, observed in different isotope systems, are still much debated. At stratigraphic levels where new melt injections are predicted, geochemical indicators, such as magnesian numbers (M') or Ni/Ti ratios, suggest that the new influxing magma is primititve in composition (Eales et al., 1990), whereas increasing initial $^{87}Sr/^{86}Sr$ ratios point to the opposite (Kruger, 1994). Further, PGE mineralization in the chromitite layers and the Merensky Reef is ascribed variously to scavenging by an immiscible sulfide melt (CAMPBELL et al., 1983), hydrothermal fluid flow (BALLHAUS and STUMPFL, 1986) or chromitite control (SCOON and TEIGLER, 1994). We adressed these problems by carrying out Os and Sr isotope analysis on Critical Zone chromitites and whole rock feldspathic pyroxenites of the Merensky Cyclic Unit.

Initial $^{187}Os/^{188}Os$ ratios of the lowest chromitites (lower group = LG) are only slightly above the value of the contemporaneous chondritic mantle (~ 0.120 versus 0.113, respectively), but become more radiogenic in the overlying middle group chromitites (~ 0.137). The upper group (UG) initially shows a decrease of the initial Os signature to 0.126 for the UG1 chromite, followed by a major increase to 0.145 for the UG2 chromite, culminating in the value of 0.177 for the interstitial phases of the Merensky Reef (HART and KINLOCH, 1989; these authors also found erlichmanite grains with the value of the contemporaneous chondritic mantle). Os concentrations of gangue phases of the upper Critical Zone (i.e. MG and UG) exceed those of their associated chromite samples by up to 30 fold, demonstrating the presence of platinum group minerals and/or PGE-bearing sulfides as interstitial phases. Although initial $^{187}Os/^{188}Os$ ratios of gangue phases of upper Critical Zone chromitite layers are somewhat more radiogenic than those of their respective chromite separates, chromite and associated gangue both broadly express the same $^{187}Os/^{188}Os$ trends with stratigraphic height. Four pyroxenitic whole rock samples of the Merensky Cyclic Unit define a Re–Os isochron yielding a new independent age of 2043 ± 11 Ma and an initial $^{187}Os/^{188}Os$ ratio of 0.151. Initial $^{87}Sr/^{86}Sr$ values of interstitial gangue phases are more radiogenic than those of enclosing silicate rocks (i.e. 0.7045–0.7065; KRUGER, 1994) with "spikes" of up to 0.721 (LG3).

Offsets in initial $^{187}Os/^{188}Os$ ratios between chromite and interstitial gangue separates support the magma mixing concept. Merensky Reef erlichmanites with chondritic mantle Os signature reveal the presence of a primitive subreservoir within the magma chamber, indicating that the new injections must be primitive in composition, whereas the "radiogenic" isotope signatures originate from the residual magma. The "spikes" in initial $^{87}Sr/^{86}Sr$ ratios of the gangues are most probably the effect of entrainment of granophyric roof melt, pointing to fountain-type injections (CAMPBELL and TURNER, 1989). Os isotopic trends show an association in the formation between chromite and interstitial PGE phases, and the lack of correlation in the initial $^{187}Os/^{188}Os$ vs 1/Os space, which would be expected for a Os introduction by hydrothermal fluid flow, gives further evidence for a magmatic enrichment of PGE in the chromitite layers and the Merensky Reef.

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T.M. Seward (Zürich):

Experimental Hydrothermal Geochemistry.

Aqueous fluids occur throughout the earth's crust and upper mantle at elevated temperatures and pressures. These hydrothermal solutions are involved in magmatic processes, metamorphism and metamorphic reactions, tectonics and fault movement and the formation of ore deposits. They are responsible for the redistribution of enormous amounts of material throughout the crust and facilitate the transport of many chemical components to the earth's surface via hydrothermal fluids which discharge both subaerially and onto the seafloor. As such, they have contributed to the chemistry of the Earth's oceans and atmosphere in a fundamental way (WOLERY and SLEEP, 1976; VAN DAMM et al., 1985, SEWARD and KERRICK, 1996) throughout geological time. In addition, about 20% of the earth's current heat loss is effected by surface discharging hydrothermal fluids (RONA, 1988). An understanding of how these major processes operate is thus intimately involved with insight into the chemistry and physics of aqueous solutions in the earth's crust over a wide range of temperatures and pressures.

We are carrying out experiments on hydrothermal solutions over a range of temperatures and pressures. Ultraviolet and visible spectroscopic studies of ionisation and metal complex equilibria are being measured up to 450 °C and 1500 bar. These data are required to understand geochemical processes occuring in the earth's crust. Data on the first ionisation constant of hydrogen sulphide up to near the critical point of water has recently been obtained and these measurements will be extended to higher pressures. Studies of chloride complexing with manganese(II) and tin(II) are also in process. X-ray absorption (EXAFS) spectroscopic studies of high temperature aqueous solutions are also underway and have yielded information on the solvation of ions and ion pairing in hydrothermal fluids. Oxygen and hydrogen isotope fraction between hydration shell water and bulk solvent are also being measured in electrolyte solutions at high temperatures and pressures. These experiments are being complemented by molecular dynamics simulations and ab initio calculations.

The solubility of sparingly soluble compounds in aqueous solutions up to 500 °C and 1500 bar are being measured in large volume autoclaves containing flexible gold cells. The aim is to obtain information on the stability of certain complex ions under extreme conditions. For example, data on the stability of hydrosulphido-complexes of gold(I) and copper(I) are being obtained. These results provide information about the mechanisms of transport and deposition of transition metals by fluids in the crust. In addition, there are applications to the storage and isolation of toxic metal and radioactive waste as well as to hydrothermal corrosion in energy systems and hydrometallurgical processing. The solubilities of uncharged molecular species in supercritical carbon dioxide are also being measured with potential applications not only to geochemistry but also to chemical processing.

VAN DAMM, K.L., EDMOND, J.M., GRANT, B., MEASURES, C.I., WALDEN, B. and WEISS, R.F. (1985): Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. Geochim. Cosmochim. Acta 49, 2197–2220.

WOLERY, T.J. and SLEEP, N.H. (1976): Hydrothermal circulation and geochemical flux at mid-ocean ridges. J. Geol. 84, 249–275.

RONA, P.A. (1988): Hydrothermal mineralisation at oceanic ridges. Canadian Mineralogist 26, 431–465.

SEWARD, T.M. and KERRICK, D.M. (1996): Hydrothermal. CO_2 emission from the Taupo Volcanic Zone, New Zealand. Earth and Planetary Sci. Lett. 139, 105–113.

K. Valenza, R. Moritz et A. Mouttaqi (Genève, Marrakech):

Minéralisations de barytine dans le Massif des Jebilet occidentales, Maroc: Géochimie isotopique (Sr, S) et microthermométrie des inclusions fluides.

L'étude en cours porte sur les minéralisations filoniennes et karstiques de barytine dans le Massif des Jebilet occidentales, au Maroc. Ce massif est constitué de calcaires du Cambrien inférieur, surmontés par des séries schisto-gréseuses épaisses du Cambrien moyen, qui encaissent la plupart des filons de barytine. Ces roches du socle acadien sont recouvertes par des séries évaporitiques triasiques, encaissées dans des semi-grabens, puis par des conglomérats du Jurassique supérieur transgressif, qui marquent une discordance angulaire avec les lithologies sous-jacentes.

Les minéralisations étudiées, d'âge tardi-triasique, se sont vraisemblablement mises en place dans un contexte tectonique d'extension, lié à l'ouverture de l'Océan Atlantique. Elles se répartissent sur un district de 200 km^2 et plusieurs familles de barytine ont pu être distinguées en fonction: du mode de gisement de la barytine (remplissage karstique à Irhoud, stockwerk ou filon), de l'orientation EW ou NS et de l'encaissant du filon, de la texture et de la couleur de la barytine, qui définissent en partie le caractère précoce ou tardif du minéral, et finalement de la paragenèse à laquelle s'associe la barytine. Les analyses isotopiques et la microthermométrie des inclusions fluides ont pour but de caractériser la source et la nature du ou des fluide(s) minéralisateur(s), de différencier géochimiquement les familles de barytine et d'en tirer un scénario de mise en place des minéralisations.

Les compositions isotopiques du S ont été mesurées sur 46 barytines au laboratoire des isotopes à Lausanne. Les valeur $\delta^{34}S$ varient d'une façon générale entre 8,9 et 14,7‰, avec une majorité des valeurs entre 9 et 10‰. Ces $\delta^{34}S$ correspondent à la signature isotopique de l'eau de mer triasique, dont les valeurs varient entre 10 et 15‰. Ce sont donc les évaporites du Trias qui auraient fourni le S nécessaire à la mise en place de la barytine.

L'étude isotopique du Sr sur la barytine a fourni des valeurs comprises entre 0,70973 et 0,71365, sans distinction notable entre les échantillons en provenance des filons EW ou NS et ceux du massif karstique d'Irhoud. Si les rapports isotopiques les plus hauts semblent refléter l'influence d'une source radiogénique, vraisemblablement composée des séries schisto-gréseuses appartenant au socle, on remarquera que les rapports les plus bas tendent vers des valeurs proches de l'eau de mer triasique ou des calcaires cambriens, qui vont de 0,707 à 0,709. Comme le confirme l'étude isotopique du S, ceci indique qu'une partie des fluides minéralisateurs a migré à travers une source moins radiogénique, constituée des évaporites triasiques et, plus localement, des calcaires du massif karstique d'Irhoud. La complexité du système devient cependant plus grande si l'on considère le diagramme de corrélation 1/Sr vs $^{87}Sr/^{86}Sr$. Les tendances évolutives des échantillons indiquent en effet qu'outre un fluide non radiogénique et riche en Sr, issu du Trias évaporitique, et un fluide plus radiogénique et dilué, influencé par les séries schisto-gréseuses, un troisième fluide, radiogénique et riche en Sr, est intervenu dans l'épisode minéralisateur.

L'étude microthermométrique des inclusions fluides a porté sur la barytine, le quartz et la calcite des divers sites minéralisés. Malgré les nombreux problèmes liés à la fragilité des minéraux, qui ont souvent rendu inutilisables les températures d'homogénéisation, certains échantillons ont permis de déceler l'existence d'au moins deux types de fluides; certaines inclusions aqueuses à H_2O–NaCl sont de faible salinité, tandis que d'autres inclusions fluides à H_2O–NaCl–$CaCl_2$ montrent des salinités élevées (Tm ice comprises entre –10 °C et –20 °C). L'échelonnage quasi systématique des salinités pour un type donné d'inclusions fluides indique qu'il y eu mélange d'au moins deux fluides et/ou rééquilibrage des inclusions fluides précoces par un ou plusieurs fluides plus tardifs. Il n'a cependant pas été possible d'établir une chronologie des fluides.

La relative constance des compositions isotopiques en S et en Sr, ainsi que l'ubiquité des deux fluides observés dans les inclusions fluides pour les différentes familles de barytine indiquent que l'ensemble des minéralisations correspond à un seul événement minéralisateur. En effet, les caractéristiques géochimiques et microthermométriques restent grossièrement les mêmes pour la barytine des filons d'orientation NS et EW et les remplissages karstiques pour l'ensemble du massif. Ainsi, les fluides minéralisateurs sont assez homogènes à l'échelle des Jebilet occidentales.

ORE DEPOSITS

S. Beuchat, R. Moritz et D. Gasquet (Genève, Vandœuvre-lès-Nancy):

Le gisement de Fe – Cu – (Pb – Ag – Ba) de St-Georges d'Hurtières (Massif de Belledonne, Savoie, France): contexte structural, géochimie isotopique (Sr, S) et inclusions fluides.

Le gisement étudié se trouve à St-Georges d'Hurtières dans le massif de Belledonne (Massifs cristallins externes) à une vingtaine de kilomètres à l'est de Chambéry (Savoie, France). La mine a été exploitée depuis le Moyen Age jusqu'au début de ce siècle principalement pour son fer et son cuivre. L'exploitation du minerai s'est faite par un réseau de plus de 20 km de galeries sur plus de 500 m de dénivelé dont les trois quarts restent accessibles.

La minéralisation étudiée se trouve dans le rameau externe du massif de Belledonne au NE du synclinal médian. L'unité encaissante est la Série satinée dont l'âge est indéterminé (Protérozoïque à Carbonifère selon les auteurs). Cette série est composée de schistes séricitеux et localement graphiteux. Elle a au moins subi les orogenèses varisque et alpine, l'orogenèse hercynienne l'ayant plus fortement marquée par un métamorphisme de faciès schiste vert et des déformations ductiles, alors que l'alpin se limite à des déformations cassantes. Les minéralisations de St-Georges font partie d'un chapelet de minéralisations Fe – Cu qui existent dans le rameau externe de Belledonne.

Les buts de l'étude sont de comprendre le contexte structural, de caractériser la source des éléments et des fluides, le mécanisme et les conditions P-T de mise en place, de définir le moment de mise en place (hercynien ou alpin) et de savoir si le gisement que l'on observe aujourd'hui est le résultat d'un seul événement minéralisateur ou d'un téléscopage de plusieurs événements hydrothermaux.

Les relations observées dans la mine mettent en évidence plusieurs stades de minéralisations. En première phase, un filon de sidérite et de quartz est sécant à la schistosité de la Série satinée avec une orientation générale NE–SW avec un pendage de 20° à 40° vers le sud. Un réseau de faille le découpe en panneau. La sidérite est riche en Mn (jusqu'à 10% poids) et partiellement oxydée. Les mâcles en courbes observées indiquent qu'elle s'est déposée lors d'un métamorphisme schiste vert. La deuxième phase est mise en évidence par plusieurs générations de filons de quartz recoupant le filon de sidérite, ils ont des orientations variables et peuvent être riche en sulfures (pyrite, chalcopyrite, galène, sphalérite, tétrahédrite). Les fluides associés à ces filons tardifs ont transformé par endroit la sidérite en ankérite. Des filons de barytine recoupent également la sidérite dans la partie supérieure du gisement. En outre on observe des minéralisations de galène et de barytine dans les lentilles de Trias surmontant la Série satinee

L'étude isotopique du Sr sur les sidérites, ankérites et barytines a fourni des rapports compris entre 0.71695 et 0.72787. Ces valeurs élevées laissent supposer un fluide provenant d'une roche fortement radiogénique puisque la teneur en Rb des carbonates et de la barytine sont négligeables. Les ankérites présentent des rapports isotopiques plus élevés que les sidérites. Le graphique 1/Sr vs $^{87}Sr/^{86}Sr$ met en évidence trois groupes parmi les carbonates, ce qui laisse supposer une minéralisation en plusieurs étapes.

Les compositions isotopiques du soufre ont été mesurées à l'Université de Lausanne sur les chalcopyrites, les galènes et les barytines. Les chalcopyrites montrent une large palette de valeurs $\delta^{34}S$ allant de 5 à 14‰, les galènes de 14 à 15‰ et les barytines de 19 à 29‰. La grande disparité des valeurs pour une même espèce minérale n'est pas entièrement comprise, mais elle pourrait être due à un mélange de fluides ou à des variations de la fugacité de l'oxygène. Une partie du soufre provient probablement des évaporites du Trias.

L'étude préliminaire des inclusions fluides du quartz de deuxième génération a mis en évidence des fluides $H_2O - CO_2 - NaCl$. La température de fusion du CO_2 indique que celui-ci est pur. La température de fonte du clathrate donne une salinité moyenne de 10,7% poids NaCl équivalent et les températures d'homogénisation totale en phase liquide sont comprises entre 270 et 320 °C.

Y. Haeberlin, R. Moritz, M. Cosca, M. Chiaradia, J. Spangenberg and L. Fontboté (Genève, Lausanne):

The Pataz gold province of Peru: a regional scale homogeneous mineralizing event along brittle-ductile shear zones at 315 Ma.

The Pataz gold district is situated in the eastern Andean Cordillera along the east flank of the Marañón Valley. It provides about 15% of the gold production of Peru with Au grades from 7 to 15 g/t. The gold is in quartz-sulfide veins at the edge of a 70 km long granodioritic batholith, dated by U/Pb at 329 ± 1 Ma (VIDAL et al., 1995), close to the contact with the low-grade metamorphic Precambrian and Lower Paleozoic series (Marañón Complex and Contaya Formation). The study is focused on three main veins in the northern part of the province, namely La Lima, Mercedes and Consuelo, and includes a regional comparison with the Picaflor vein at Culebrillas, 35 km to the southeast.

The gold-bearing veins occur mainly as N–S oriented metric to decametric structures with a moderate dip to the east and as undulating subhorizontal structures. Their anatomy is generally asymmetric with a hydraulic breccia along the footwall and a shear zone at the hangingwall. The veins show banded textures and contain various rock slivers. Some veins have different orientations and are emplaced along lithologic discontinuities, such as aplitic dykes, or are parallel to the bedding of the Contaya slates. The entire vein system was probably formed during a roughly E–W compression. These structures were overprinted by block tectonics in the Permian, followed by two phases of reverse movements and a phase of normal faulting during the Tertiary orogeny. The reverse movements indicate a first NE–SW compression followed by a weaker NW–SE compression, and are consistent with the Miocene folding phases of the Eastern Cordillera; the normal faulting is related to the Pliocene E–W extension tectonics which affected the Central Andes.

The parageneses of the mineralized veins consist of two stages with a first generation of pyrite and arsenopyrite followed by fracturation and filling with galena, sphalerite, chalcopyrite, electrum and gold. Electrum is mainly in sphalerite or fractured pyrite; pure gold precipitated later with galena, generally at the boundary with arsenopyrite. A decimetric to metric pervasive hydrothermal alteration, mainly composed of quartz, sericite, ankerite and coarse pyrite, surrounds the gold-bearing quartz veins. The intrusive textures are replaced by recrystallized quartz surrounded by an intergrowth of fine white mica, later crosscut by calcite veinlets. Fuchsite is locally present as alteration of dioritic rocks as at the Consuelo vein and argillic alteration is widespread at the Picaflor vein at Culebrillas.

$^{40}Ar/^{39}Ar$ age determinations on the mineralization were undertaken at the University of Lausanne. Five sericites from different veins including Picaflor, give a similar plateau age for the ore-forming event between 312 and 314 Ma. These ages are clearly younger than the ages of the Pataz Batholith and exclude a genetic link with the former magmatism. The initial staircase shape of the $^{40}Ar/^{39}Ar$ spectrum points out to a partial rejuvenation of the micas during the Jurassic, probably due to the emplacement of small porphyric stocks in the Eastern Cordillera.

Sulfur isotope analyses were carried out at the University of Lausanne. $\delta^{34}S$ values are clustered between 0.4 and 3.7‰ for sphalerite and between –2.1 and 1.9‰ for galena. The galena-sphalerite sulfur exchange geothermometer yields an equilibrium temperature for gold deposition between 300 and 370 °C for most veins and around 250 °C for the Culebrillas veins. This difference could be explained by the emplacement of veins at different depths. Lead isotopic analyses on galenas were carried out at the University of Geneva. $^{206}Pb/^{204}Pb$ ratios range between 18.35 and 18.46, $^{207}Pb/^{204}Pb$ between 15.62 and 15.69 and $^{208}Pb/^{204}Pb$ between 38.26 and 38.50. The isotopic signatures of galenas are homogeneous for the province and suggest a common lead origin from the batholith for all gold veins with some contamination from the Marañón basement. A microthermometric fluid inclusion study evidences a large NaCl–H_2O group with calculated salinities between 8 and 15 wt% NaCl equivalent, a NaCl–CO_2–H_2O system, evidenced by clathrate, and some $CaCl_2$–NaCl–H_2O inclusions with ice freezing temperatures below –25 °C.

The auriferous lodes of the Pataz province denote a regional homogeneity in their structural setting, parageneses and isotopic signatures along at least the 70 km long belt. The differences between the alterations, generally sericitic, but argillic at Culebrillas suggest a vertical structuration of the deposit. The Pataz gold veins, rich in sulfides and with medium saline, CO_2-poor fluids, can be classified as mesothermal brittle-ductile shear zone gold deposits, similar to the European Hercynides shear zone gold deposits (BOUCHOT et al., 1997).

BOUCHOT, V., MILESI, J.-P., LESCUYER, J.-L. and LEDRU, P. (1997): Les minéralisations aurifères de la France dans leur cadre géologique autour de 300 Ma. Chron. Rech. Min. 528, 13–62.

VIDAL, C.E., PAREDES, J., MACFARLANE, A.W. and TOSDAL, R.M. (1995): Geología y metalogenia del distrito minero Parcoy, provincia aurífera de Pataz, La Libertad. Sociedad geológica del Perú, Volumen jubilar A. Benavides, 351–377.

APPLIED MINERALOGY AND PETROLOGY

F. Girod, M.-H. Derron, M. Jaboyedoff, A. Meunier, S. Petit and Ph. Thélin (Lausanne, Poitiers):

Water-rock interactions and clay mineral neoformation within fractures of the Randa augengneiss (Mattervalley, Wallis, Switzerland).

As part of the study of orthogneiss weathering associated with the Randa rockfall (see GIROD and THÉLIN, 1998), some new results about the mineralogy of fault gouges and the geochemistry of percolation waters in the gneiss are presented.

The clay fraction (< 2 μm) of fault gouges located within the Randa augengneiss (RA) contains smectite alongside with quartz, feldspar, albite and mica grains. The separation of the rock fraction less than 0.1 μm by ultracentrifugation did no allow significant concentration of smectite due to the very small size of the quartz, feldspar, albite and mica grains. Nevertheless, analyses of the layer charge distribution of smectite was carried out using infrared spectroscopy (FTIR). This method is based on the integrated intensitiy measurement of the band assigned to the ammonium fundamental v4 mode of NH_4^+ – exchanged clays before and after lithium fixation (PETIT et al., 1998). It revealed that smectite is a pure montmorillonite (octahedral position of the charge).

No transformation of a particular mineral phase of the gouge into smectite could be observed by scanning electron microscopy (SEM) or detected by X-ray diffraction (XRD). A honeycomb texture of the clay and its montmorillonitic nature indicate that it might be precipitated from a solution (authigenesis) rather than resulting from mineral transformation.

Precipitation of montmorillonite is to be found only within the gouge-rich fractures where the activity of Si must be high as a result of a low percolation rate of waters and a high reactivity of the fine grained minerals.

Waters coming from several fractures in a galery crossing the RA show a good correlation between the thickness of the overlying rock and their cation (Si, Na and Mg) enrichment. This cation enrichment is due to advance of water rock interaction; i.e. dissolution of the most soluble minerals of the RA (chlorite, albite and K-feldspar) as reaction time progress. Consequently, gouge-rich fractures with low permeability may lead to a strong dissolution (especially feldspars) and precipitation of montmorillonite. The nature of the fractures and their permeability control the percolation mode of the water and hence the dissolution rate of the minerals.

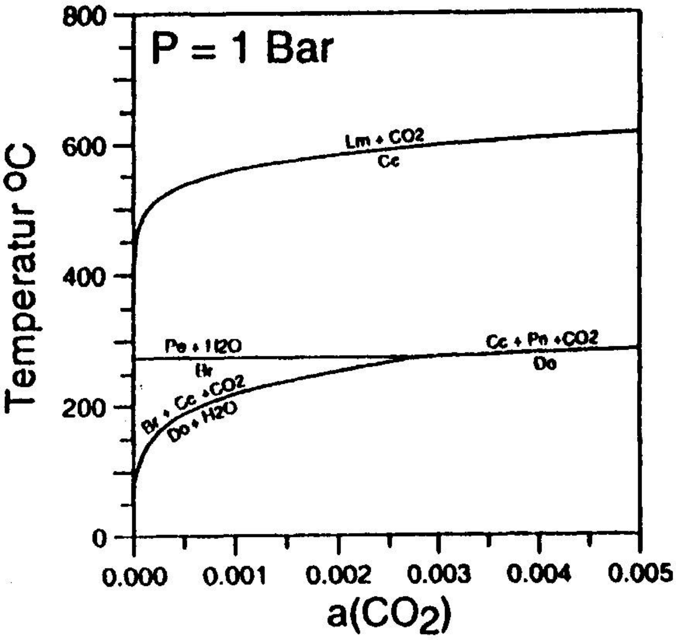
GIROD, F. and THÉLIN, P. (1998): Weathering of granitic rocks in the Alps: preliminary results from orthogneiss associated with the Randa rockfall (Matter Valley, Valais, Switzerland). Schweiz. Mineral. Petrogr. Mitt. 78, 179–184.

PETIT, S., RIGHI, D., MADEJOVA, J. and DECARREAU, A. (1998): Layer Charge Estimation of Smectites Using Infrared Spectroscopy. Clay Miner. (in press).

St. Graeser (Basel):

Dolomit-Brennerei – Probleme und neue Erkenntnisse.

Das Brennen von Kalk-Gesteinen zur Herstellung von Kalk-Mörtel ist in unseren Breiten seit knapp 1000 Jahren in Gebrauch gewesen. Im Jura, Mittelland, in den Voralpen und stellenweise in den Alpen stand i.a. genügend geeignetes Rohmaterial für die Kalkbrennerei zur Verfügung – im Gegensatz zu grossen Bereichen vor allem in den Penninischen Alpen (Wallis, Tessin, Graubün-



den), wo Kalke nicht oder nicht in genügender Reinheit vorkommen. Es konnte nicht in Erfahrung gebracht werden, seit wann in diesen Regionen anstelle des fehlenden Kalkes das Ca-Mg-Karbonat-Gestein Dolomit zur Verwendung gelangte.

Untersuchungen an Mörtel von Häusern aus dem 17. Jahrhundert im Binntal/VS zeigten, dass der aus Dolomit gebrannte Mörtel zwar aus Mg-haltigem Calcit besteht, dass aber trotzdem – gegenüber dem Ausgangsmaterial – ein beachtliches Defizit an Mg existiert. Eine klare Beschreibung des Dolomit-Brennverfahrens, ausser einigen wagen Erinnerungen, war leider nicht erhältlich. Die von uns zunächst rein empirisch geäusserte Vermutung, dass der durch Dolomit-Brennerei hergestellte Mörtel resistenter sei als reiner Kalkmörtel, scheint durch neuere Untersuchungen an historischen Mörteln bestätigt zu werden.

Die Restaurierung eines Dolomit-Brennofens nahe der bekannten Mineralfundstelle Lengenbach im Binntal lieferte neue, überraschende Erkenntnisse zu dem rätselhaften Verfahren: Überreste eines letzten, evtl. nicht vollständig durchgeführten Brandes könnten den Vorgang etwas näher erläutern. Es handelt sich um etwa kopfgrosse, harte Knollen, die beim Brennen aus dem vorwiegend in zuckerkörniger Beschaffenheit vorliegenden Dolomit entstanden sind. Der Befund, dass dieses leuchtend blaue Gestein aus einem Gemisch von Calcit und Brucit besteht, das von aussen her durch Mg-haltigen Calcit verdrängt wird, lässt vermuten, dass beim Brennen des Dolomits zunächst ein kompaktes Calcit-Brucit-Zwischenprodukt entsteht (das auch in anderen Öfen des Tales gefunden wurde), das beim weiteren Brennen in Mg-Calcit übergeht – etwa nach der Gleichung:

$CaMg(CO_3)_2 + H_2O \rightarrow$
Dolomit Wasser
$CaCO_3 + Mg(OH)_2 + CO_2 \nearrow$
Calcit Brucit

Die Tatsache, dass der lockere, zuckerkörnige Dolomit durch Erhitzen offenbar zunächst in ein kompaktes, hartes Calcit-Brucit-Gemisch übergeht, brachte uns auf die Idee, dass diese Erkenntnis eventuell auf allfällige Probleme mit zuckerkörnigem Dolomit bei der Durchtunnelung der Piora-Mulde anwendbar sei. Diesbezügliche Versuche wurden am Mineralogisch-petrographischen Institut in Bern durchgeführt.

GRAESER, S. (1994): Kalk- (resp. Dolomit-) Brennerei im Binntal – oder: wo ist das Magnesium geblieben? Minaria Helvetica 14a, 46–52.

A. Mais (Fribourg):

Provenance studies on Neolithic to Iron age pottery from the Castel Grande (Bellinzona, Ticino, Switzerland).

The pottery which was found in the Castel Grande during excavations by P. DONATI in the years 1980–1984 provides a unique possibility to look into early middle European history. A very exact typological seriation by R. CARAZZETTI showed that the ware represents a complete sequence from the early Neolithic period (~ 5300 B.C.) to the late Bronze age (~ 1400 B.C.). This suggests a permanent settlement of the area around Bellinzona for a period of about 4000 years and makes it possible to study the development of pottery technology and changes in raw materials used.

For the provenance studies two different methods have been used. The temper analysis was used to determine if the rock and mineral fragments in the sherds are of local origin. To do this, petrographical methods such as polarisation microscopy with quantitative mineral analysis have been used. The first results of these studies show a good correspondence between the rocks of the Castel Grande (gneisses, coarse amphibolites) and the materials which were found in the ware.

Chemical mineral analysis for main and trace elements of some typical minerals like amphiboles, feldspars and micas with the EMP (electron microprobe) and the SEM (scanning electron microscope) are used to verify this results. The second method was a geochemical analysis of the sherds, local clays and rocks by XRF (X-ray fluorescence analysis) which was used to compare the ware of the different periods and the supposed local raw materials. Up to now there is no certain proof for the local origin of the ware, but the data makes a local production of the pottery much more probably than an importation.

H.-R. Pfeifer (Lausanne):

Environmental risks related to natural and mined ore deposits of the Central and Western Alps.

The more than 200 mostly small ore deposits of the central and western Alps have only occasionally been subject of scientific interest in the last 30 years, and, apart from uranium in the 70s, only of very limited economic interest either. However, most of these ore deposits had been mined during several historical periods (19th century, first and second world war) but were subsequently forgotten and overgrown by vegetation. Often addits started to collapse, but in some cases, to preserve a witness of this locally important industry as well as for touristic purposes, old mines have partially been saved from complete destruction (cf. journal Minaria Helvetica of the "Schweizerische Gesellschaft für historische Bergbauforschung"). Relatively little attention has yet been payed to possible natural or anthropogenic contamination of these sites through water rock interaction and erosion of old addits and mine tailings.

As the following first synthesis of existing data on the subject will show, the environmental impact in terms of metal contamination of soils, plants or water is usually limited to the nearby neighbourhood of the ore deposits. Problems can arise when former mine tailing are used for recreational purposes (e.g. secondary residences) or if percolating waters are used as drinking water. For elements such as U, As, Ni, Cr, Pb, Zn, Cu, recent environmental data such as water, soil and plant analyses is available.

The environmental compartments touched by ore deposits are (different part of catchment): (1) the immediate neighbourhood, (2) the river area downstream from the ore deposit and (3) local or regional lakes. In each of these compartments, potentially contaminated materials are plants, soils, sediments and water. The possible environmental impact depends largely on the geomorphological situation of a mine (e.g. steep slopes enhances creep and erosion of weathering products or mine tailings), the climate (precipitation rate, vegetation cover) and the solubility of the gangue or ore minerals. Uranium is known to be very mobile under oxidizing conditions and occurs often as pitchblende veins on steep slopes. For this reason in the Martigny region (Wallis), soils containing several hundred ppm U, locally U-enriched blueberry plants and and regionally elevated U-contents in drinking water up to 80 ppb can be observed (PFEIFER et al., 1994). On the scale of the whole Rhone catchment, every year about 12 tons of dissolved uranium enters the lake of Geneva.

Several former gold mines are related to arsenopyrite-veins (PFEIFER et al., 1997) and are at the origin of considerable arsenic contamination of soils and spring water. In the Malcantone area local till deposits contain between 80 and 600 ppm As (REY, 1996; world mean 7 ppm!) and in around 15 communities of the Ticino arsenic in the drinking water exceeds the recommended treshold value of the WHO of 10 ppb, locally going up to 80 ppb (even 200 ppb in not captured surface waters; REY, 1996; MARTINI and PILLET, 1996). A similar situation can be found at Salanfe/Wallis, where arsenopyrite rich mine tailings are situated within a pasture area for cows. Locally low pH ponds exist (pH 5), but since snow melt waters are in the same range, they do not create environmental problems. Nickel and chromium are well known companions of ultramafic lithologies, which typically display a restricted vegetation cover. Locally high pH waters can occur (PFEIFER, 1977; SCHLEGEL, 1997), but are readily neutralized by CO_2 of the air. Although they exhibit high Mg, Ni and Cr contents (40 ppm, 7 ppb, 4 ppb respectively), they remain below WHO guide line maximum values (Ni 20 ppb, Cr 50 ppb). Lead related to abundant silver mining also is a relatively well studied element (WOODTLI et al., 1985). Natural enrichment in soils in the vicinity of galena-veins can reach values of several thousand ppm Pb (Astano/TI: 17'000, Goppenstein 5000 ppm), however waters show extremely small Pb contents (max. 0.1 ppb). Zink is often found together with lead and shows similar concentration levels in soils. However it is more soluble in water: local creek water near Astano show up to 15 ppb Zn, which remain largely below dangerous values for drinking water (WHO guide line maximum 3000 ppb). Only little is known yet about copper contamination. Close to calcopyrite-bearing veins natural contamination in soils can reach 400 ppm (WOODTLI et al., 1985).

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M. Scheder, H.-R. Pfeifer, G. Beatrizzotti and G. Righetti (Cadenazzo, Lausanne, Bellinzona):

Chemical composition of shallow groundwaters from the Ticino: a synthesis about the role of the lithology and residence times.

More than 350 chemical analyses of ordinary spring waters, including conductivity, pH, temperature, SiO_2 and major ionic compounds, covering most of the area of the canton Ticino have been compiled and interpreted. Some of these springs have been monitored for more than 20 years by the water control authorities and several recent road tunnel projects have increased our knowledge on slightly deeper waters. However, the most complete data set comes from the preliminary works of the new Gotthard and Monte Ceneri railway tunnels (ALPTRANSIT) of the last few years. Over 80% of the springs have aquifers of silicate rocks (gneisses, micaschists, amphibolites of the Lepontine and Southern Alpine basement), about 10% of dolomitic-sulphatic rocks (presumably Triassic) and another 10% of the aquifers are formed by calcite-bearing rocks (marbles, calcsilicate rocks, calcschists and limestones).

As in other areas of the Alps (DERRON, 1998, SCHEDER and STREIFF, 1997; PARRIAUX et al., 1990), the aquifer lithology strongly influences the chemical composition of the waters, regardless of whether the water comes from quaternary rocks or directly from the bedrock. Waters from silicate rocks typically have conductivities between 50 and 150 µS/cm and are of $Ca\text{-}Na\text{-}HCO_3\text{-}SO_4$-type with pH values between 6.5 and 7.5. They are the result of a water-rock interaction determined by the limited solubilites of the various silicate minerals (quartz, mica, chlorite, feldspars and clay minerals such as illite and vermiculite) and pyrite. NO_3 and Cl are usually low (< 5 and 2 mg/liter respectively) and in most cases directly derive from the local rain or snow. In many cases a proportionality relationship between conductivity, pH and the size of the catchment area or circulation depth can be observed, allowing a crude estimate of the residence time in the underground. Together with time-series of the discharge and temperature variations, existing spring protection zone extensions can be checked and possibly adapted. Waters from dolomitic-sulphatic aquifers have conductivities ranging from 300 to 2500 µS/cm, are of $Ca\text{-}SO_4\text{-}HCO_3$-type with pH values between 7.5 and 8 and usually exhibit karstic hydraulics. Typical examples are the Piora-Lucomagno-, Molare-Campolungo areas in the northern Ticino. Calcite-bearing aquifers have conductivities between 300 and 500 µS/cm, are of $Ca\text{-}HCO_3$-type with pH values between 8 and 8.5 and are situated between the silicate and dolomite field in the 10*Si-2*Mg–Ca triangle of DERRON (1998). Typical examples are the Bedretto valley, Valle di Bosco (calcschists) and the Monte Generoso-Valle di Muggio area. Only few analyses of trace elements are available and most of them have been measured downstream of the springs. Several cases of natural contamination by heavy metals and metalloids such as arsenic, copper and zinc have been observed (Malcantone area, Barbengo, Tesserte, Morcote), due to presence of ore deposits or related metal enriched till material (MARTINI and PILLET, 1996; REY, 1996).

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S. Wolf (Fribourg):

The role of grain size distribution and chemical analysis for the provenance study of medieval bricks in Switzerland.

The bricks from St. Urban, a Cistercian monastery in the Canton of Lucerne became subject of archaeological and scientific enquiry because of their unusual size (45 × 30 × 25 cm) and their extraordinary decoration. From decoration themes it was assumed that apart from the manufactory at St. Urban two other production sites at Fraubrunnen and Frienisberg (Canton of Bern) existed. The present study uses X-ray fluorescence (XRF), X-ray diffraction, polarising microscopy and quantitative image analysis of bricks found at the three Cistercian monasteries to address the question of whether the bricks found in Fraubrunnen and Frienisberg were made in St. Urban, or if they had their own production sites. Element correlation suggested varying production recipes for the three sites. The existence of three individual production sites was confirmed by differing grain size distributions using quantitative image analyses. Furthermore, based on varying temper proportions it was possible to identify two different production processes within the Fraubrunnen manufactory.

R. F. Wyder and J. Mullis (Basel):

Brittle deformation and fluid impregnation of Tavetsch kakirites (Sedrun/GR, Central Swiss Alps).

Microstructural and microthermometric studies provided insights in brittle deformation mechanisms and the P-T-x-t conditions of kakiritie formation in the Tavetsch massif. Overprinted by several pre-Alpine (summarised as phase 1) and at least five Alpine to late Alpine deformation phases (II to VI), phases III to VI have been responsible for the generation of cohesionless kakirites.

In particular, deformation phase II includes an incomplete dynamic recrystallisation of quartz. At the same time feldspar and mica reacted brittle. Due to the incomplete recrystallisation of quartz, phase II is interpreted to display peak Alpine temperature conditions of the neo-Alpine metamorphism during the overthrust of the Gotthard onto the Aar massif. Approximate temperature-pressure conditions for dynamic recrystallisation of quartz are deduced to be around 435 °C and 4.5 kb at an assumed lithostatic geothermal gradient of 25 °C/km.

During phase III steepening of the overthrust plane resulted in a compressive stress regime between the Aar- and Gotthard massifs and lead to subsequent breaking and healing of quartz oblique to the main foliation. Approximate temperature-pressure conditions for the healing of broken quartz are 310 °C and 2.7 kb at an assumed lithostatic geothermal gradient of 30 °C/km.

Phase IV: Ongoing steepening and brittle deformation of quartz opened vugs and gave rise to the precipitation of fissure quartz and calcite at temperature-pressure conditions of around 275 °C and 2.3 kb and an assumed lithostatic geothermal gradient of 30 °C/km. Incomplete cementation of these vugs by fissure minerals significantly increased the total porosity of the rocks (Wyder and Rybach, 1996) and prepared them for the following loss of cohesion.

Phase V is characterized by tilting and outbreaking of fabric domains due to different exhumation rates between the Aar- and Gotthard massifs. During this process, porosity still increased, pores and vugs became interconnected and the fluid pressure dropped from lithostatic to hydrostatic conditions. Sudden precipitation of quartz (Schwammquartz) and minor calcite could not prevent the fabric collapse and the accompanying loss of cohesion. The mineralising fluid evolved to lower salinities indicating meteoric influence during hydrostatic conditions (dilution). Approximate pressure-temperature conditions for this phase are 190 °C / 0.6 kb at an assumed hydrostatic geothermal gradient of 30 °C/km.

Phase VI finally generated gouge and fault breccias due to small displacements (mm- to cm-range) along discrete faults and fractures. The precipitation of smectite and formation of gouge reduced the former high permeabilities to negligible values.

The loss of cohesion occurred at depths between 9 and 6 km below surface at temperature-pressure conditions of approximately 275 °C, 2.3 kb and 190 °C, 0.6 kb during deformation phases IV and V and is interpreted to have occurred during a drop in fluid pressure from lithostatic to hydrostatic regime between phases IV and V.

Kakiritisation occurred as a late Alpine retrograde event (9–12 Ma, Mullis, 1996), postdating the overthrust of the Gotthard onto the Aar- and Tavetsch massifs and is related to differential exhumation rates between the Aar- and Gotthard massifs.

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A. Zanco (Fribourg):

Provenance and technology of Galloroman Terra Sigillata imitations from western Switzerland.

This paper deals with the mineralogical, chemical, petrographic and physical analysis of imperial age Galloroman terra sigillata imitations. The main aim of this study was to define the chemical mineralogical aspect and petrographic-physical characteristics of this ceramic, to obtain information concerning raw material and techniques used in the past.

Methodologies useful in this investigation are numerous and they especially concerned the ceramic paste. Thus, all samples were submitted to:

– a thin section petrographic examination to inquire relationship between matrix and tempers, their structure, texture, grain size and possibility to understand whether they were natural or artificially added;

– a mineralogical investigation by means of X-ray diffractometry to characterise mineralogical phases and define firing temperatures;

– an X-ray fluorescence analysis for chemical quantitative content of major and trace elements.

Helium and Hg-porosimeter as well as SEM and electron microprobe were performed on selected samples.

The study can be divided into two parts. The first part investigates workshop waste sherds: these are ceramic kitchenware (of proven local provenance) left at production centres by potters for whom their quality was not adequate. On this production type, coming from three different workshops of western Switzerland (Lausanne Stade, Yverdon FAUSTUS, Avenches N-E) three distinguished new reference groups were established characterised by chemical and mineralogical homogeneity and some dissident samples (probably imported) were also identified. It is worth nothing that only with the elaboration of chemical data, especially by means of statistics, it was possible to define the three new reference groups and to distinguish them from the those already established in the past.

In the second part of the thesis these homogeneous groups were used as reference to compare stamped sherds of the same ceramic category found in different parts of Switzerland: Martigny, Lausanne, Avenches, Nyon, Vindonissa, Yverdon. The aim was to identify their production places as well as the working sites of the potter who signed them on the bottom. Also in this case the analysis was mostly performed on the chemical aspects using statistic methods which permit to use several chemical elements at the same time and to compare the whole chemical composition of each stamp to the local references. Unfortunately, this study did not disclose any certain attribution of one craftsman to his respective production centre but the results can be described only in terms of probability of provenance. Only for the *FAUSTUS* production it is certain that this potter worked in the homonymous workshop, and it can also be affirmed that no potter worked in Avenches N-E. Concerning Lausanne Stade the results allow to suppose that *QUINTUS, SABINUS, ILLANUA, GENIALIS, COIUS, FLORUS, IUCUNDUS* worked there, although this is not expressed by a perfect chemical correspondence.

ANALYTICAL METHODS

R. Frischknecht, D. Günther, Ch. A. Heinrich (Zürich):

Laser Ablation-ICP-Mass Spectrometry microanalysis of single fluid inclusions from Zinggenstock (Aar Massif).

Investigations of fluid inclusions give us important information about the genesis of minerals in the Alpine fissures of the Swiss Alps and the formation of inclusions in general. Various kinds of paragenesis of minerals in Alpine fissures are known, reflecting differences in the chemical composition of the hydrothermal fluids, which are in turn determined in the past by the composition of the local host rocks.

Various analytical techniques have been applied so far to obtain more information about the fluid chemical changes during the quartz growth. These include Raman spectroscopy to get information about different kinds of gases in the inclusion, the K-Ar-method for dating and microthermometry to determine homogenisation temperature and the NaCl equivalent salinity. With the information from these methods it is possible to reconstruct pressure-temperature paths and the time scale of quartz growth during the late stages of the Alpine orogeny. However, with the techniques described above, little can be learnt about the chemical reactions of mineral precipitation.

Laser ablation ICP-MS is one analytical method for high spatial resolution analysis of trace elements in geological samples. The efficiency of this method not only for solid mineral analysis also for fluid inclusions and the measurement procedures are described elsewhere (GÜNTHER et al., 1998). The NaCl-eqivalent concentrations from microthermometry served as internal standard values for the quantification of the trace elements. Corrections for the element content of the host mineral and high salt concentrations of other cations (HEINRICH et al., 1992) in the inclusions were applied.

In this work we present concentration data for well investigated CO_2 and daughter crystal bearing fluid inclusions (MULLIS, 1995; MULLIS, 1996; MULLIS et al., 1994) in quartz from the Zinggenstock (Aar Massif) analyzed by Laser ablation ICP-mass spectrometry. Preliminary qualitative analysis were carried out to select detectable elements in inclusions of various sizes. Several trails of different generations of cogenetic inclusions were studied by microthermometry, and then analyzed quantitatively by LA-ICP-MS. Major elements like Na and K have been found in concentration ranges of 1.5 up to 4 wt% and 0.4–1.5 wt% respectively whereas elements like Li, B, Al, Fe, As, Rb, Sr and Sn have shown concentrations from 50 up to 600 ug/g. Ti, Mn, Cu, Zn, Ga, Sb, Cs, Ba, La, Ce and Pb are in a concentration range of 10 to 100 ug/g.

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A. M. Lanfranco (Fribourg):

Topographic investigation on heated (001) mica planes using the AFM.

In phyllosilicates devolatilisation promotes the change of cell parameters and chemical composition; moreover it is often connected with the growth of new phases.

In the present study the AFM-contact mode was applied as probe to look at the effect of this event on the (001) mica surfaces. The AFM data were coupled with chemical, spectroscopy and diffraction methods, which were helpful in explaining the collected images. Several biotites and muscovites, different in their origin, were chemically characterised by means of XRF for the major and trace elements; PIXE and LECO methods quantified halogens and H_2O; using XRD powder method the purity of the samples were checked as well as the presence of intergrowth and interlayered phases.

The iron oxidation was estimated by the 2,2-dipyridile method on the powders fired for 1–2 days at different temperatures; the resulting data suggested that synthesis of some oxides should start at T = 400 °C to reach a new charge equilibrium in the octahedral layers. The Mössbauer spectroscopy verified the growth of iron minerals under the detection limit of the powder diffractometer (about 2 wt%). Crystals measuring from 0,5 up to 2 cm were heated using the same conditions as for the powders before (T = 400, 600, 750 and 900 °C in atmosphere). After cleavage, their (001) surfaces were scanned in air with a Si_3N_4 tip, setting the AFM-contact mode operating condition. The surface features presented sometimes geometric shapes that imposed to orient the samples before collecting the pictures.