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Advances in multi-elementary analysis of fluid or solid micro-crystalline inclusions (12<Z<92) by absolute PIXE, and coupled PIGE and RBS. Mineralogical and geochemical applications.

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Introduction. X-Ray-based analytical methods can be applied in an absolute fashion, provided that matrix effects are calculated and that parameters related to instrumental factors are controlled (Newbury, 1986). When EPMA (Electron Probe Micro Analysis) was conceived at the end of the 60's, this potentiality was abandoned, as the instrument works in a relative fashion, by comparison with standards. At the end of the 70's and in the 80's, PIXE (Proton Induced X-Ray Emission) by contrast was applied in a way that preserved the possibility of an absolute application: the computer programs developed to interpret PIXE spectra *calculate matrix effects and also integrate instrumental factors* (e.g., Maxwell *et al.*, 1989). In spite of this advantage, and also despite the fact that PIXE application extends to trace element analysis, the development of PIXE in the scientific community was sluggish, in deep contrast with the widespread applications of EPMA. In the field of Earth Sciences particularly, EPMA was recognized by the Mineralogical Society of America to have had 'a revolutionary, profound impact on mineralogy and petrology'. In the same time, PIXE applications remained mainly restricted to trace element analysis, and the potential accuracy of the method was never clearly realized.

A first aim of this presentation is to show that, using a simple standardization procedure, the multi-elementary absolute capability of PIXE can be revealed. This in turn changes PIXE into a tool of quantitative mineralogy and trace element geochemistry. We then show that, by coupling PIXE to PIGE (Proton Induced Gamma Ray Emission) and RBS (Rutherford Back Scattering) spectrometries, the Nuclear Microprobe becomes a tool for quantitative mineralogy *s.l.* and geochemistry, i.e., an instrument to analyze all major to trace elements from Li to U in minerals and their inclusions.

In the second part of the presentation, we illustrate the capability of µ-PIXE to analyze *in situ* individual fluid inclusions that have been carefully localized in space and time. The Hercynian French Massif Central and its sedimentary eastern margin are part of a large European Carbonic Province, which hosts numerous deep CO_2 reservoirs and carbonic springs (Blavoux, Dazy, 1990). Carbonic fluids are present at all stages of the long-lived evolution of this crustal segment, from deep metamorphic fluids involved in a thrusting event at 340 M.a to mantle-derived volcanic CO_2 related to Neogene volcanism. In order to characterize the main aquo-carbonic fluid reservoirs through time in this crustal segment, we present preliminary data on the trace element content of aquo-carbonic inclusions trapped in the schists at peak and retrograde metamorphic conditions, and compare them to contemporaneous granite-related fluid inclusions.

Multi-elementary absolute PIXE : basic concepts. <u>Principles.</u> The general formula that relates I_z, the intensity of X-Ray emission of a given element Z, to its concentration C_Z in a target irradiated by electrons or protons is as follows (Newbury, 1986):

$$I_z = f(C_z, M, I)$$

where **M** represents matrix effects and **I** stands for instrumental factors.
The derivation of absolute concentrations from a PIXE spectrum requires precise knowledge of all three factors I_z, **M and I.** Common computer programs derive I_z from the PIXE spectrum and calculate *matrix effects* with a precision of ± 5% (e.g., Campbell *et al.*, 1990). *Instrumental factors* are therefore the key accuracy-controlling parameters. This includes the detector physics (ε), the

charge on the target (Q), the detection solid angle (Ω) and transmission (T), a function that takes into account the attenuation of X-Rays by filters along the target-to-detector path. Gama *et al.* (2001) showed that, ε and Q being fixed independently, T and Ω are the accuracy-controlling parameters which, being highly changeable, need to be optimized for each experiment. We propose a single-standard procedure which allows T and Ω to be optimized on line. Let N_i be the number of certified elements from a geochemical standard analyzed by PIXE and p_j be the nominal detection geometry parameters controlling T and Ω ($N_i \gg p_j$). A fitted set of parameters p^*_j is obtained by a least-square procedure using the N_i certified concentrations of the PIXE spectrum.

Absolute multi-elementary PIXE using 'funny filters'. One way to analyze by PIXE all detectable elements in a mineral is to place 'funny filters' (filters with a hole drilled at their centre) in front of the detector, in order to avoid 'pile up' peaks (Gama *et al.*, 2001). The complex transmission function of such an analytical set up is easily optimized using the above mentioned procedure. The conditions are thereafter fulfilled to analyze in an absolute fashion any individual mineral or phase assemblage. A consequence of this is the possibility of calculation of structural formulae from PIXE analyses of minerals (Fig. 1; Table 1), in addition to trace element characterization (Table 2) or derivation from PIXE spectra of modal proportions of phases with identified stoichiometries (Table 3). The invisible elements in PIXE (O, C, H, possibly Na and Mg depending on the detector) can be reconstructed quantitatively taking into account the following conditions: (1) in the PIXE program, the matrix composition entered as an input to calculate the spectrum must be equal to the composition output; (2) the addition of invisible elements must respect mineral stoichiometry; (3) the total of analyzed plus invisible elements must be 100.
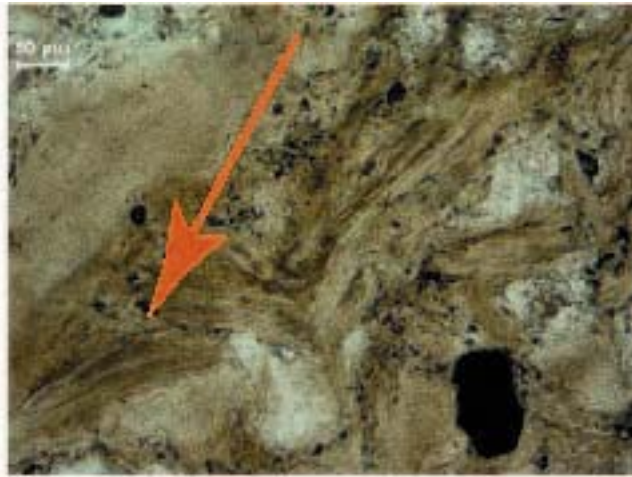

Fig. 1: Photomicrograph of illite in the basement below a natural CO2 reservoir (Montmiral borehole, Southeast Basin, France; Rubert, unpubl. (natural light).

	K	Ca	Si	Al	Fe	Ti	Mg	Na	F*
(1)	0.78	0.01	3.31	2.29	0.13	0.00	0.22	0.01	
(2)	0.86	0.04	3.34	1.73	0.13	0.06	n.d.	n.d.	0.036

Table 1: Illite from Montmiral borehole basement: compared structural formulae obtained by EPMA (1) and PIXE (2); * : PIGE analysis.

Cl	420 ± 80	Ni	2 LOD (17)	As	1 LOD (8)
Br	12 ± 4	Cu	3 LOD (10)	Br	12 ± 4
V	1280 ± 100	Zn	2 LOD (10)	Rb	694 ± 18
Cr	300 ± 43	Ga	80 ± 8	Sr	29 ± 6
Mn	147 ± 34				

Table 2: Trace element content in illite from Montmiral borehole basement (PIXE, 2.5 MeV protons; charge on illite : 2 µC). Mean value $\pm$ 1 σ ; LOD = limit of detection; beam size: 50x70 µm^2).

VMO2-92	100 % Anhydrite		60% Anh- 40% Cc		50% Anh- 50% Dol (Fe$_{Dol}$=0.3 molar)	
	Input	Output	Input	Output	Input	Output
S	23.5	9	9	10	10.9	10.6
Ca	29.5	35	35	26	28.5	28.1
Fe	-	5.5	5.5	-	4.8	5.8
O	47	-	46	-	45.6	-
C	0	-	4.5	-	4.9	-
Mg	0	-	-	-	5.3	-
Total	**100**	**-**			**100**	

Table 3: Triassic from Montmiral borehole : mineralogic interpretation of a PIXE spectrum with the GUPIX program (percentages in wt.%; Anh=anhydrite; Cc=calcite; Dol= dolomite; beam size 250x250 µm^2; Y. Rubert, unpubl.). In red: invisible elements.

Quantitative analysis of intracrystalline inclusions by coupled PIXE, PIGE and RBS spectrometries. Because of the range of protons in matter ($\approx$ 40µm for 2MeV protons in muscovite), any solid or fluid inclusion placed along the beam path can be analyzed by reference to a simplified multi-layer model with infinite parallel interfaces (e.g., Ryan *et al.,* 1991). The model is all the more valid as the beam size is small compared to the inclusion size; however, it requires precise knowledge of two additional geometric parameters: the inclusion depth in the host mineral (z), and the inclusion thickness (t). Strivay *et al*. (2008) have shown that, by coupling RBS to PIXE, z and t can be measured 'on line' from a quantitative interpretation of the RBS spectrum. Finally, the light elements from Li to Mg can also be analyzed with the nuclear microprobe by adding a γ-ray detector to the experimental set up in order to quantify nuclear reactions. Light element analysis in solids by PIGE is conducted relative to standards (e.g., Volfinger, Robert, 1994). As for the characterization of light elements in intracrystalline inclusions, Volfinger (2002) proposed a simplified procedure to measure it by comparison to a homogeneous massive standard.

Fluid inclusions as samples of reservoir fluids: the trace element approach. As part of the Hercynian Belt of Europe, the French Massif Central has been the setting of repetitive circulations of aquo-carbonic fluids, from peak metamorphic conditions at 340 M.a. to the present (Arnaud, 1999; Ramboz *et al.*, 1985; Blavoux, Dazy, 1990). Aquo-carbonic fluids were particularly involved in the major W-U metallogenic event at 310 M.a. (Dubessy *et al*., 1987). However, no consensus could ever be established for a magmatic or metamorphic source of the metals, due to the contradictory arguments derived from stable isotopes, from fluid chemistry or from careful dating of the magmas and the mineralizations (Cathelineau *et al*., 1999; Bouchot *et al*., 2005). As a new approach to this old problem, we have undertaken a trace element characterization of carefully selected representative inclusions (Gama, 2000). In Central Cévennes, quartz-albite-apatite syntectonic pods are emplaced in the metamorphic schists, $\approx$10 km away from any felsic intrusion (Arnaud *et al.,* 2004). Apatite-hosted fluid inclusions have preserved the peak metamorphic fluid conditions at 500°C and 4.3 kbar (Arnaud, 1999). Their analysis by PIXE reveals the presence of trace amounts of As in the 300-910 ppm range. By contrast, the fluid inclusions in coexisting

recrystallized metamorphic quartz are essentially trace-element free. The latter are markedly distinct from the contemporaneous granite-related quartz-hosted inclusions which always show a significant base metal content (Pb Zn Fe), sometimes with associated As. These results clearly show that the fluids circulated around granite intrusions in the time range 325-310 M.a. have a non metamorphic (magmatic?) trace metal component. They also demonstrate that As, a constant pollutant in rocks and soils from this crustal segment (Barbier, 2001), was introduced early in the Cambro-Ordovician sediments, probably during exhalative sedimentary processes (Bril *et al.*1994).

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