



Measuring Fluid Inclusions in Geochemical Samples

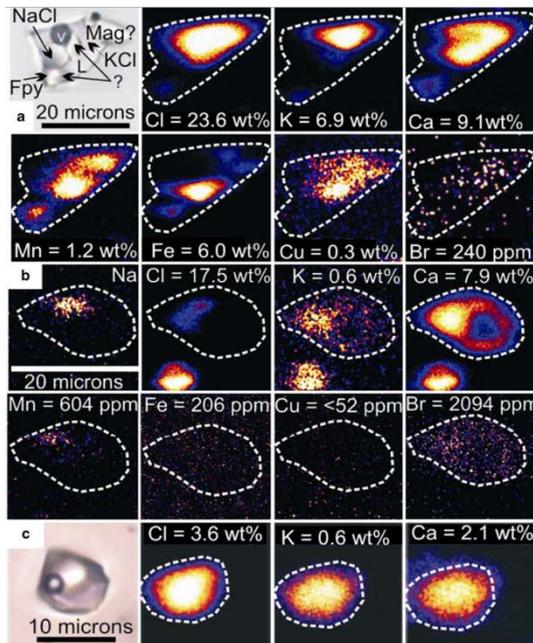


Figure 1: Buried fluid inclusion analysis by PIXE

3 MeV protons focussed to nearly 1 μm . Doubly polished mineral sections of iron-oxide/copper/gold (IOCG) deposits from the Cloncurry district of northwest Queensland, with inclusions within about 10 μm of the surface.

- a) Complex multi-solid inclusion rich in copper. Solid halite (NaCl), sylvite (KCl), ferropyrosmalite (Fpy), and possibly magnetite particles are identified.
- b) Three-phase halite-bearing inclusion poor in Cu
- c) Two-phase aqueous inclusion

Figure 4 of Baker et al, *Mineralia Deposita* 2008

“Fluids play a key [geochemical] role in crustal evolution, the transport of metals and the formation of ore deposits. Understanding these processes requires knowledge of fluid and metal sources, phase separation and the mechanisms or triggers for ore deposition. Small samples of fluids, trapped and preserved as fluid inclusions in minerals, provide unique windows on these processes containing snapshots of elemental composition and clues to prevailing temperature and pressure. Inclusions of melt can be trapped in growing minerals in a magma chamber to preserve samples of the evolving magma or along healed fractures to sample infiltrating melts responsible for alteration or metasomatic change in rocks. Some types of melt inclusions are extremely rare, which argues against destructive analysis.” (Ryan, *NIMB* 2004 [1]).

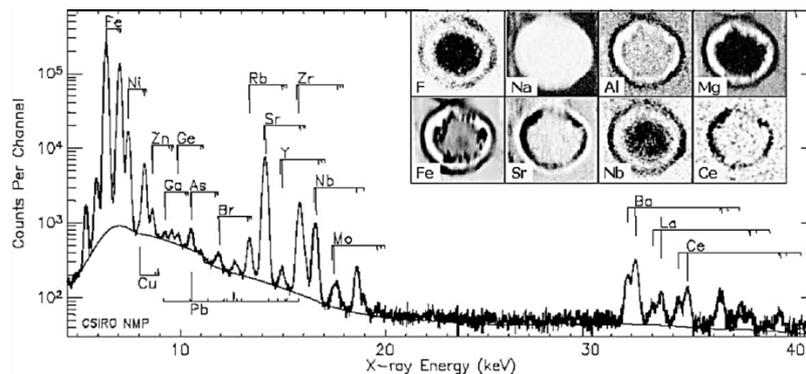


Figure 2: Characteristic X-ray spectrum for buried inclusion

3 MeV protons. PIXE spectrum extracted from the entire melt inclusion region of a silicate-carbonate melt inclusion in clinopyroxene from the Slave craton, Canada. Inset are PIGE (F, Na, Al, Mg) and PIXE (Fe, Sr, Nb, Ce) elemental images (image area 190×190 μm^2)

Figure 3 of Ryan et al, *NIMB* 2004

Figure 1 ([Baker et al, *Mineralia Deposita* 2008](#) [2]) shows how the geochemists use particle-induced X-ray emission (PIXE) to non-destructively analyse the material in fluid inclusions in their rock samples. This paper reports quantitative analysis of over 130 separate inclusions. The immediate purpose in this case was to understand more of the geology of the Cloncurry district, which is the site of one of the world's richest copper mines:

"[It] contains major deposits of copper, lead, zinc and silver, and significant deposits of gold, uranium and cobalt; it has also produced minor amounts of manganese, cadmium, bismuth, tungsten, beryl, and mica." ([Blake, *Bureau of Mineral Resources Bulletin* 225, 1987](#))

Figure 2 [1] shows a characteristic total PIXE spectrum from an inclusion, together with PIXE images of elemental distributions. PIXE is blind to low-Z elements (see [Figure 3](#) [3]) so simultaneous particle-induced gamma emission (PIGE) can be used to give equivalent maps of the light elements. In Figure 2, all the elements except Mg were detected with sensitivities below 10 mg/kg levels.

What the geochemists do for this sort of analysis is to cut a sample of the rock and polish a thin section ($\sim 30 \mu\text{m}$) both sides to allow optical microscopy (petrography in both reflection and transmission). Inclusions can be identified and characterised in both shape and position, including the depth in the sample (using the small depth of field given by a large numerical aperture). It is critical to know the depth of the inclusion since that dramatically affects both the intensity for a given concentration and the ratios of the characteristic lines in the X-ray spectrum (see [Figure 3](#)).

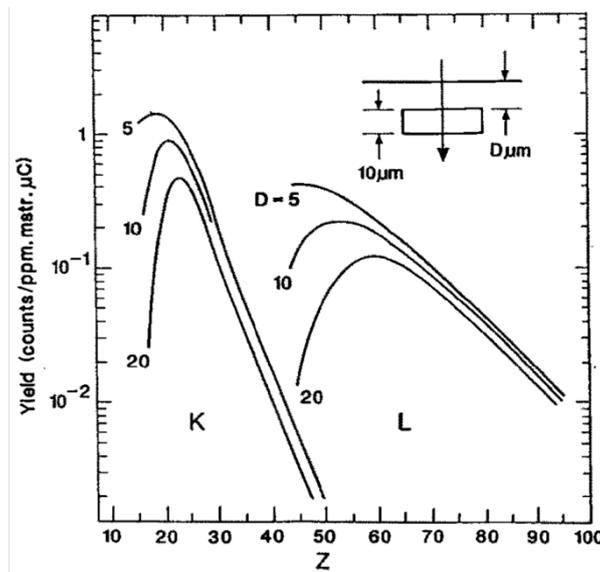


Figure 3: Calculated X-ray yield for buried 10 μm inclusion
3 MeV protons, 135° detector. Ordinate is per-unit elemental concentration in the inclusion, in counts/(msr. μC)/(mg/kg), for various inclusion depths.
Figure 3 of Ryan et al, *NIMB* 1991

It is extraordinary that this sort of analysis is even possible. Of course, it depends on the systematic preparation of high quality samples by the standard methods of mineralogy, and then standard characterisation by optical microscopy. It also depends, crucially for the reliable interpretation of the samples by the geologists, on using sophisticated computational methods, both for the accurate unfolding of the X-ray spectra themselves, and also for untangling spectral overlaps that may give rise to misleading artefacts in the elemental images.

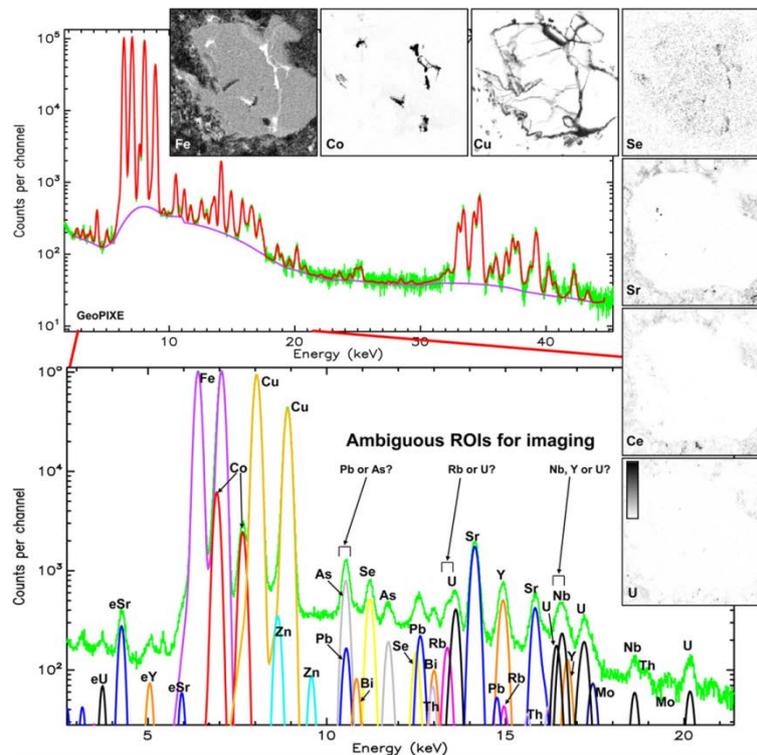


Figure 4: Elemental mapping of large samples by PIXE

3 MeV protons, 1×1 mm² image (512×512 pixels). **Above:** Full spectrum (green data) fitted with GeoPIXE (red line). Background is shown in purple. **Below:** Expanded region with systematic elemental overlaps shown.

Elemental distribution images: obtained with “dynamic analysis” (see text)

Figure 3 of Ryan et al, *NIMB* 2011

[Figure 4](#) [4] shows (again) the complex PIXE spectra usual for mineral samples: any particular region of interest of the spectrum is likely to be ambiguous. In particular, small quantities of cobalt are mapped in the presence of the major elements Fe and Cu, and trace U is mapped in the presence of the minor element Sr. This (amazingly) can be done in real time using matrix methods (*dynamic analysis*: see the review by [Ryan, 2011](#) [4]) on the incoming data stream.

When it is realised that even large areas (as in Figure 4) can be scanned rapidly (typically with electrostatic scanning units), taking only a few seconds per frame and avoiding misleading artefacts in the real-time elemental maps due to line overlaps in the spectra, it can be seen how quickly the geologists can search a sample for interesting features, and home in on small areas (like a fluid inclusion). It is almost always the details that interest the geologists!

Quantitative PIXE is very important in this field, with significant contributions including :- the origin of South African gold and uranium ores ([Fuchs et al, *Ore Geology Reviews*, 2016](#) [5]); the geochemistry of Mars ([Gellert et al, *Elements*, 2015](#) [6]); the coupled geochemistry of Au and As in pyrites from hydrothermal ore deposits ([Deditius et al, *Geochimical & Cosmochimica Acta*, 2014](#) [7]); the mineralogy and geochemistry of platinum-group elements in an Iberian deposit ([Pina et al, *Mineralogy & Petrology*, 2008](#) [8]); and the evolution and source of ore fluids in the Hellyer deposit, Tasmania ([Zaw et al, *Ore Geology Reviews*, 1996](#) [9]).



Cited Literature

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