Micro-spectroscopy—shedding light on rock formation

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Introduction
Whilst there are many imaging techniques available to a research scientist, the information which is provided is often only of a visual/topographical nature. What they fail to provide is true compositional (chemical/elemental) analysis of the materials. However, microscopic techniques such as Raman or X-ray fluorescence (XRF) can fill this gap, allowing highly detailed images to be generated based upon the sample’s material composition.

The information the two techniques provide are quite different, but their application areas are strongly linked. Raman probes chemical bonding within a material using laser radiation, giving information on molecular functional groups, whilst XRF probes elemental composition by analysing fluorescence X-rays emitted following irradiation with a primary X-ray beam.

Raman is now routinely coupled with standard optical microscopes to yield spatial resolutions down to 1 µm, whilst the latest X-ray optical design allows ultranarrow, high intensity beams with diameters down to 10 µm to be produced for XRF.

Both micro-Raman and micro-XRF provide convenient, non-destructive, microscopic analysis. For example, their non-destructive nature allows fragile museum/archaeological objects to be investigated, and forensic scientists can obtain fast characterisation whilst ensuring the trail of evidence is preserved—from samples as varied as polymers and fibres, explosives and narcotics, glasses and even fingerprints.

For materials research, the sensitivity of Raman to very subtle effects provides valuable insight into stress/strain in semiconductors, chirality/diameter of carbon nanotubes and crystallinity of polymers. The elemental characterisation of XRF, however, is ideal for micro-electronics, including analysis of circuit boards and soldering, and compliance testing for the forthcoming European WEEE/RoHS "lead free" legislation.

Other areas of interest for micro-spectroscopy include pharmaceuticals (crystal polymorphs, tablet formulation, well plates), coatings (homogeneity, thickness) and metallurgy (alloys, plating, corrosion). New applications continue to be developed, assisted by continued advances in instrumentation: for example, inverted (Raman) microscopes and high sensitivity micro-XRF analysis at atmospheric pressure open up new possibilities in biology/medicine (disease diagnosis, medicine efficacy, bacteria etc).

Shedding light on rock formation
Investigation of mineral and rock samples can gain strongly from Raman and XRF analysis. Raman allows fast identification of mineral forms, and with microscopic spatial resolution, can be used to study heterogeneity within rocks, probe inclusions in situ, and identify minute fragments.

At the Johannes Gutenberg-Universität in Mainz, Germany, Dr Lutz Nasdala and co-workers have extensively explored the use of micro-Raman in mineralogy, including an interesting study into the metamictisation of natural zircon. Zircon (ZrSiO₄) is a common mineral in a range of rocks, and incorporates a number of trace elements, including uranium (U) and thorium (Th). These two radioactive elements cause self-radiation of the zircon, damaging its structure and lead-
ing to a “metamict” form which is amor-
phous and isotropic. Investigation into
such processes is aimed at understand-
ing the cause and effect of the degrada-
tion of chemical and physical stabilities in
zircon and other such minerals.

With micro-Raman, the extent of radia-
tion damage can be quantitatively esti-
mated—with increasing radiation damage
the Raman bands decrease in intensity,
become broader and show strong shifts
to lower wavenumbers. Figure 1(a) illus-
trates typical spectra of zircon, from well
ordered through to damaged and fully
amorphous. The 1000 cm⁻¹ SiO₄ band
provides a good indication of the level
of metamictisation and can be used to
generate highly resolved mapped images
[Figure 1(C)].

As with Raman, the application of
micro-XRF has been used to more fully
understand rock structure and distribu-
tion of specific minerals. Dr Nicholas
Arndt of the Université Joseph Fourier,
Grenoble, France has reported many
studies on kimberlite, the type of rock
that is mined for diamond. Recent work
used micro-XRF to produce high spatial
resolution elemental images of kimber-
lite sections. These contain abundant
crystals of olivine (Mg,Fe,Ni)₂SiO₄ and
one zoned, partially altered crystal of
garnet. In the resulting elemental images
(Figure 2), the garnet crystal is immedi-
ately identified by its alteration rim, which
is rich in K-rich mica. High K content also
identifies mica crystals within the matrix.
The olivine crystals are black in the K
and Ca images but have various shades
in the Fe and Ni images. These variations
indicate the remarkable extent to which
the compositions of these elements vary
from crystal to crystal. In the Fe image,
the olivine grains are seen to have thin
Fe-rich rims. Notice also the addi-
tional information on physical structure
provided by the transmission X-ray imag-
ing.

Material phase analysis using principal
components enables regions of similar
elemental composition within the map to
be grouped and imaged as one (Figure
3). In this manner, it is possible to visu-
aise quickly where specific minerals
and phases are located, and thus, oliv-
ine crystals (red/pink–varying composi-
tion), garnet with its outer mica region
(blue/green), and titanium rich ilmenite
(yellow) can be quickly identified.

These images provide valuable infor-
mation about the origin of the olivine
crystals and thus about the processes
that formed this diamond-bearing rock.

Conclusion

The high information content of
spectroscopic techniques such as X-
ray fluorescence and Raman has been
coupled with analysis on the micron
scale to provide imaging techniques for
scientists from many varied research
fields. Micro-spectroscopy is leading the
way in many novel applications, provid-
ing far more detail and contrast than is
possible through more traditional tech-
niques.

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