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Combined SEM and Raman spectroscopy
A new analytical tool for geology and mineralogy
- analysis of cement clinker and a meteorite

Introduction

The Renishaw structural and chemical analyser (SCA) allows geologists and mineralogists to benefit from the imaging and analytical capabilities of scanning electron microscopes (SEMs) whilst combining the chemical and structural characterisation provided by Raman spectroscopy. The SEM-Raman system is unique, allowing both rapid observation and elemental analysis at macro and micro scale. An overview and detailed classification of the sample is now available in a single instrument.

The SEM-SCA at McCrone Associates Inc – Westmont, IL

Raman spectroscopy measures the vibrational frequencies of molecular bonds in the material being analysed. The resultant Raman spectrum is not only unique for a given compound, but is also sensitive to the local environment. This means the spectra can also reveal structural data. More information about the SCA, and the general theory of Raman and optical spectroscopy, are available in product note SPD/PN/096 (www.renishaw.com/spectroscopy)

Raman spectroscopy uses a focused laser spot as the excitation source; the analysis is unaffected by the vacuum condition and is non-destructive. The laser spot size is in the order of one micrometre, giving a spatial resolution comparable to that of EDS (energy-dispersive x-ray analysis).

SEM-Raman investigation of OPC (ordinary Portland cement) clinker

Cement is a very important structural material, and although its manufacture is on an industrial scale, understanding the basic chemistry helps to predict its behavior and properties.

Roasting clay and limestone at approximately 1400ºC in rotary kilns produces "clinker" nodules that are then ground to a powder – cement. Cement comprises four principal components - these affect the hydration of the cement (how quickly it "sets") and its strength.

C_3S (alite)	50% to 75%	rapid hydrating, high strength
C_2S (belite)	15% to 30%	slow hydrating, high strength
C_3A	5% to10%	rapid hydrating, low strength
C_4AF	5% to15%	slow hydrating, low strength

$C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$

Raman analysis of cement powder is normally prevented by fluorescence[1, 2], but clinker does not fluoresce, so the components within it may be identified.

Observations using SEM, x-ray analysis, and Raman spectroscopy were carried out on a polished nodule of Rugby OPC (ordinary Portland cement) clinker. The sample is non-conductive so the SEM was used in low vacuum (LV) mode to avoid charging artefacts. (In LV-SEM collecting backscattered electrons emitted from the surface forms the image. The number of incident electrons backscattered from the surface depends on the mean atomic number of the sample – brighter areas are denser than light ones).

Figure 1 shows an LV-SEM image with a region (boxed) where dark globular inclusions exist in a light matrix. Raman spectra (Figure 2) were collected from a dark region (in blue), and from a light one (in red).
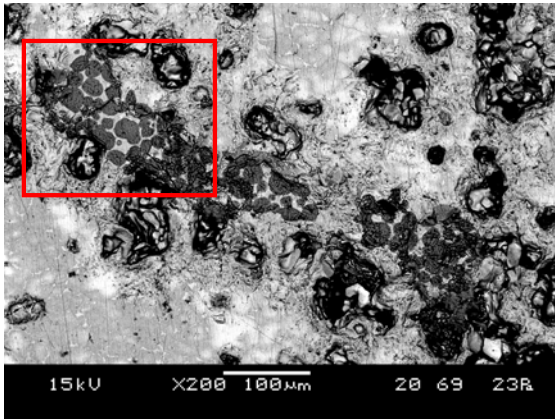

Figure 1
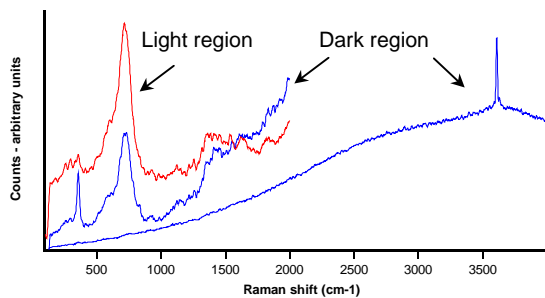**LV-SEM image showing region from which Raman spectra were collected**

Figure 2
Raman spectra from dark (in blue) and light (in red) areas shown in Figure 1

The broad band in the spectrum from the light region is normally attributed to small amounts of iron-bearing interstitial phases (although not haematite or magnetite – Fe_2O_3, Fe_3O_4) - but the phase could not be identified unambiguously

The spectra from the dark region also contain the interstitial iron band, but the other bands are characteristic of **portlandite** - $Ca(OH)_2$. This is an unexpected finding since hydrated phases would not be expected in clinker, but Taylor[3] reports that this is most likely due to hydration of free lime (CaO) during sample preparation.

Figure 3 shows an LV SEM image from another region - the atomic number contrast clearly identifies a grain boundary precipitate, and compositional variations within the grains themselves - these variations are not visible in the white-light image.
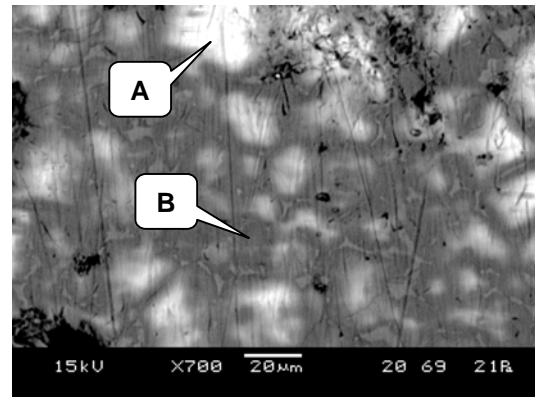

Figure 3
LV-SEM image showing light and dark regions in the clinker matrix, and the presence of grain boundary precipitates. Raman spectra were collected from points A and B

X-ray mapping (see Figure 4) shows that calcium and oxygen are everywhere, but the aluminium is confined to the grain boundaries, and the silicon to the grains. Iron is also present in the grain boundaries, but not continuously.
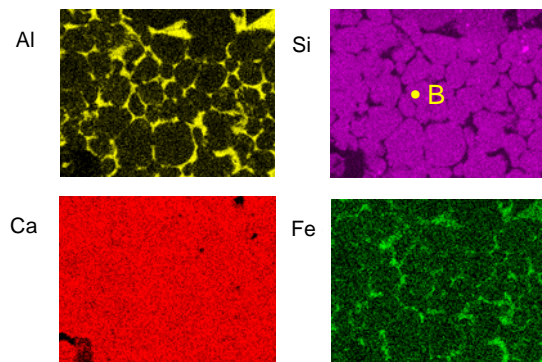

Figure 4
X-ray maps from the region shown in figure 3

X-ray analysis from the brighter region A (in Figure 3) showed the matrix comprised predominantly calcium, silicon, and oxygen - the Raman spectrum collected from point A (Figure 5 red spectrum) correlated well with a monoclinic C_3S standard (in blue). The bright regions are therefore identified as **alite** - $(CaO)_3.SiO_2$

Figure 5
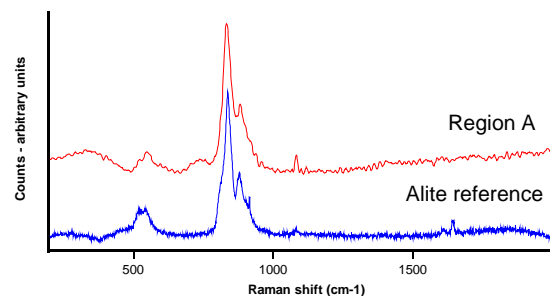**Raman spectrum collected from point A (Figure 3) in red, with alite reference - $(CaO)_3.SiO_2$ – in blue**

X-ray analysis showed the darker areas (region B) also comprised calcium, silicon, and oxygen but more calcium compared to the bright regions. The Raman spectrum collected from point B (Figure 6) shown in red correlated well with a C_2S standard shown in blue. The darker regions are therefore identified as **belite** - $(CaO)_2.SiO_2$
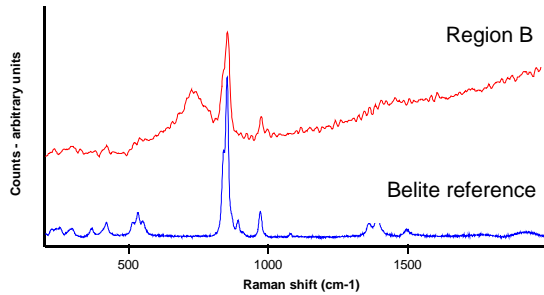

Figure 6

Raman spectrum collected from point B (Figure 3) in red, with belite **reference - $(CaO)_2.SiO_2$ – in blue**

Backscattered electron imaging in the SEM image shows the subtle variations in composition of the sample - these changes are not visible using optical microscopy. Furthermore, unlike optical microscopy, SEM imaging is insensitive to surface roughness and flatness due to imperfect sample preparation making visualisation simpler.

X-ray mapping confirms the spatial relationships of the sample components - the C_3A and C_4AF phases appear to be present as intergranular precipitates - image analysis of the x-ray maps allows the relative concentrations of these components to be estimated.

Raman analysis of the grains confirms they are **alite** and **belite** and similarly image analysis can reveal their relative concentrations. The SEM-Raman system therefore provides a new method for characterisation of clinker at both the *micro* and *macro* scale.

References

1   C-S. Deng, et al, J. Mater. Chem., 2002, 12, 3105.
2   S.S. Potgieter-Vermaak, et al, Cem. Conc. Res. 2006, 36, 663.
3   H.F.W.Taylor, Cement Chemistry, 2nd Ed., Thomas Telford, 1997

SEM-Raman investigation of a meteorite

Meteorites are some of the oldest objects in the solar system, they are often remnants of the original material that first allowed the sun and planets to form. The composition of meteorites therefore can yield unique insight as to the processes involved in forming planetary systems

Analysis of a meteorite from the William Mikuska collection was carried out at McCrone Associates Inc. Westmont, Illinois using their SEM-SCA.

The SEM images (Figure 7) were collected using the SEM in low-vacuum mode, so the contrast in the images comes predominantly from differences in mean atomic number. The images reveal the grain structure of the iron matrix, and identify lower atomic number inclusions within it.

Energy dispersive x-ray analysis observations (Figure 8) confirm the matrix is iron, and shows that the darker regions contain magnesium, silicon, and oxygen. Although the EDS data can be quantified, confidence in the characterisation of the inorganic phases can only be achieved if their composition is known in advance.

In-situ Raman spectroscopy (Figure 9) identifies the phases unambiguously as **enstatite** ($Mg_2Si_2O_6$) and **forsterite** (Mg_2SiO_4). The Raman spectra from the different areas are clearly very different despite the similarity in composition of the magnesium silicates.

SEM imaging and x-ray analysis make the location of areas of interest quick and easy. X-ray analysis gives an indication of the composition, and then Raman analysis can identify the phases unambiguously.
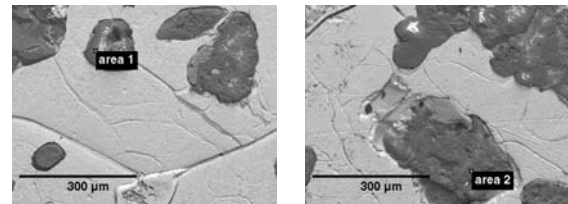

Figure 7

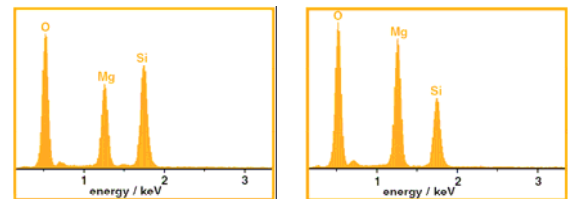**SEM images showing inorganic regions within an iron matrix, and the areas analysed by EDS and Raman spectroscopy**

Figure 8

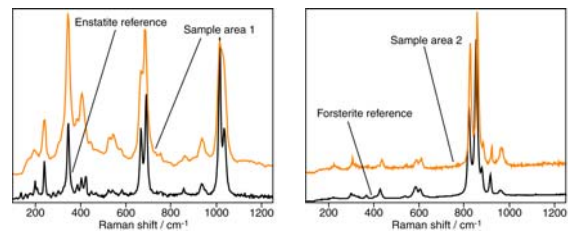**X-ray analysis from the regions indicated in Figure 7**

Figure 9

Raman analyses (in orange) from the regions indicated in Figure 7 and library reference spectra (in black)

Advantages of SEM-SCA in geology and mineralogy

- Raman determines the chemical composition whereas EDS just identifies the elements present

- Raman can distinguish between polymorphs whereas EDS cannot (e.g. rutile, crystobalite)

- Raman analysis can be carried out *in situ* so that the spatial context is maintained

- EDS analysis complements Raman spectroscopy by revealing subtle variations in concentration or the presence of trace elements

- Samples can be viewed without additional preparation permitting their re-examination using other analytical or imaging methods

- Full characterisation of minerals can be carried out quickly and easily

Why choose Renishaw?

Renishaw is an established world leader in metrology, and has been providing high performance solutions for measurement and control since 1973. In 1992, Renishaw combined several new technologies, including its metrology expertise, into its Raman microscope and rapidly became a world leader in the design and manufacture of Raman spectroscopy systems.

Renishaw has a global network of subsidiary companies, distributors, and agents, providing a level of service second to none. Its teams of highly qualified engineers and scientists can provide you with rapid and comprehensive product, technical, and application support.