AGSO's new confocal laser Raman microprobe

Terrence P. Mernagh[1]

AGSO recently acquired a state-of-the-art laser Raman microprobe (Fig. 12), which is the first one of its kind in Australia. New features such as 3D confocal imaging and Raman mineral mapping increase the capabilities of AGSO's national Raman microprobe facility, and provide important information on a much wider range of geological materials. The Raman microprobe's three laser wavelengths, broad detector range (from the visible to the near-IR), and high confocal resolution (down to 1 µm) enhance the study of fluid inclusions (in both ore deposits and petroleum reservoirs), and the identification of individual minerals in hand specimens, drillcores, and thin sections. The line-scanning accessory facilitates the generation of Raman mineral maps of drillcore or thin sections. Both the Raman data and images of the samples can be digitally captured and stored in corporate databases.

The Dilor SuperLABRAM (Fig. 12) has two interchangeable holographic gratings and a liquid-nitrogen-cooled, 2000 x 800-pixel, charge-coupled detector to provide high sensitivity. Samples are analysed on a confocal petrological microscope equipped with oculars, a video camera, a macro device (for larger samples), and — to facilitate automated Raman mineral mapping — a confocal line scanner, motorised XY stage, and autofocus. An optical-fibre probe can be directly attached to the Raman's spectrometer to obtain spectra from remote or large objects. The samples can be probed by a range of laser wavelengths — including 514.5 nm (argon ion laser), 633 nm (HeNe laser), and 785 nm (near-IR diode laser) — which are needed for different applications (see below). The spectrometer and microscope are fully computer-controlled by Windows-compatible software which acquires the Raman data, captures the video images, and performs many arithmetic operations — including 3D manipulations of the spectra.

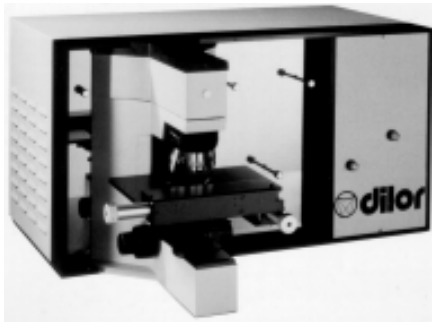

Fig. 12. AGSO's new SuperLABRAM Raman spectrometer with confocal microscope.

The Raman effect involves the interaction of light with matter, causing the emission of wavelengths of light with energies corresponding to a sample's molecular vibrations. This results in a unique Raman fingerprint for each compound. Raman spectra can be obtained from solids, liquids, and gases, and from both crystalline and amorphous compounds. This technique offers the following advantages:

- non-destructive analysis in air with little or no sample preparation,
- high spatial resolution (³1 µm), and
- sample analysis at high and low temperatures or pressures.

Fluid-inclusion studies

The laser Raman microprobe has been used to obtain important data on the composition of fluid inclusions ever since it was first invented (Rosasco et al. 1975: Science, 190, 557–560); now, fluid-inclusion studies are commonly considered incomplete if they lack these data. The Raman microprobe is particularly useful for the analysis of gases (e.g., CO_2, N_2, H_2S, CH_4, etc.) and solid phases in the inclusions (Dubessy et al. 1989: European Journal of Mineralogy, 1, 517–534). In addition, it can identify various dissolved polyatomic species, from which the data can be used to determine other thermodynamic parameters (e.g., pH, fO_2, etc.; Dubessy et al. 1992: European Journal of Mineralogy, 4, 885–894).

Until now, calculating the absolute concentration of species in fluid inclusions was difficult owing to the irregular shape of many inclusions and the associated problems of accurately determining the volume. The subtle changes in refractive index between the host rock and inclusion make it difficult to determine the volume of the inclusion because optical microscopes can focus only on the waist of the inclusion. However, equipping the spectrometer with a confocal microscope with a vertical resolution of around 1–2 µm enables the microprobe to carry out a series of depth scans, from which the spectra generated define the vertical dimensions of an inclusion (Fig. 13). A similar series of lateral scans at each depth interval completely defines the shape of an inclusion. This not only assists the Raman studies but enormously

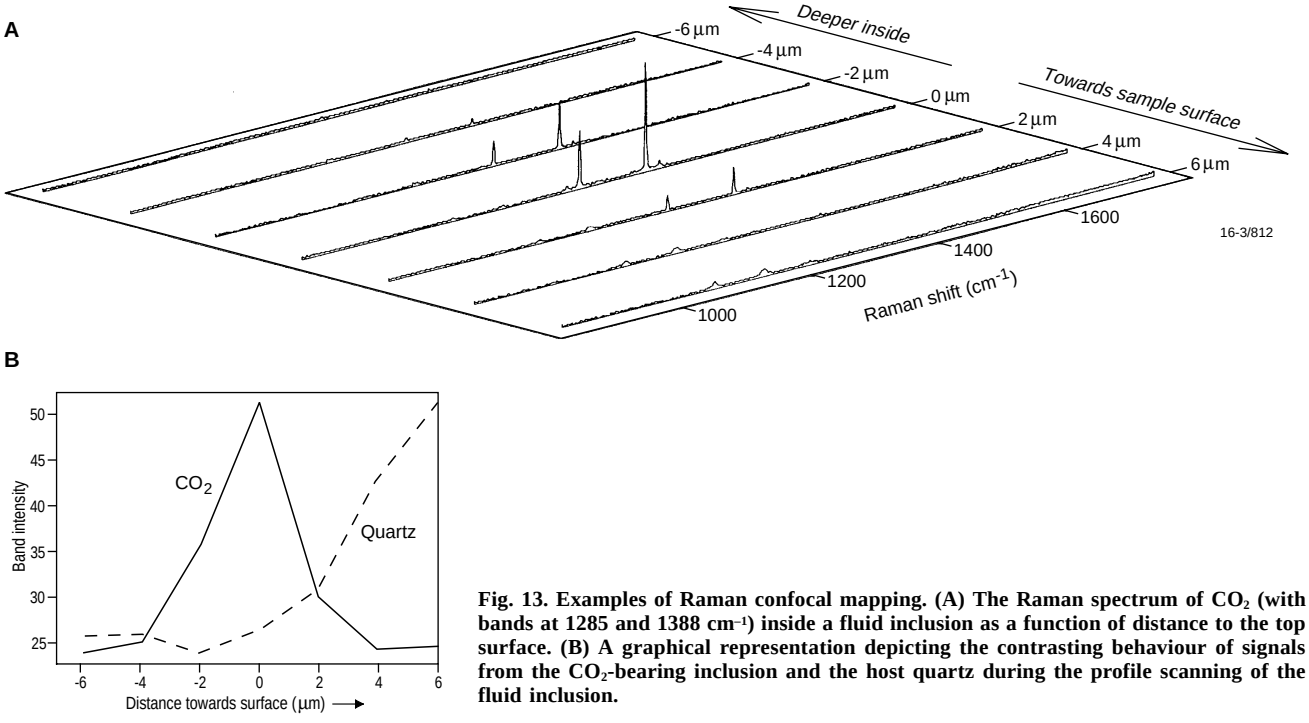

Fig. 13. Examples of Raman confocal mapping. (A) The Raman spectrum of CO_2 (with bands at 1285 and 1388 cm^{-1}) inside a fluid inclusion as a function of distance to the top surface. (B) A graphical representation depicting the contrasting behaviour of signals from the CO_2-bearing inclusion and the host quartz during the profile scanning of the fluid inclusion.

benefits other microanalytical techniques, such as PIXE, which need precise information about the shape and volume of an inclusion in order to compensate for the effects of X-ray absorption (Ryan et al. 1995: Instruments & Methods in Physics, Research Section B — Beam Interactions, Materials & Atoms, 104, 182–190).

Hydrocarbon fluids and gases

Economic and environmental considerations have fuelled a growing interest in the study of free-moving fluids and gases (i.e., petroleum, natural gas, and water) in sediments. Hydrocarbon-bearing inclusions are commonly identified by the fluorescence they emit when illuminated by visible or UV light. This tendency to fluoresce has previously made it difficult to obtain Raman spectra from hydrocarbon-bearing samples. Now, however, this problem can be largely overcome by using the near-IR diode laser, which emits at a wavelength of 785 nm. Thus, the SuperLABRAM can assist the study of hydrocarbon migration by rapidly identifying organic tracers trapped in rocks or fluid inclusions. The CH_3/CH_2 ratios obtained from the Raman microprobe spectra can be used as a maturation index (Pironon 1993: Comptes Rendes Academie des Sciences, 316, Serie II, 1075–1082), and organic coatings on minerals can be studied to establish the time relationships between fracture-porosity formation and oil migration.

Mineral and alteration mapping

The benefits of using the laser Raman microprobe to identify minerals in thin section, rock chips, and drillcore have been previously described in detail (Mernagh et al. 1996: AGSO Research Newsletter, 25, 14–16). The confocal imaging capabilities of the SuperLABRAM make it highly suitable for identifying very fine-grained mixtures of minerals, such as those commonly encountered in alteration zones surrounding hydrothermal mineral deposits. Note that the Raman microprobe can identify a wide range of minerals — including most silicates, carbonates, sulphates, nitrates, phosphates, hydroxides, oxides, and sulphides.

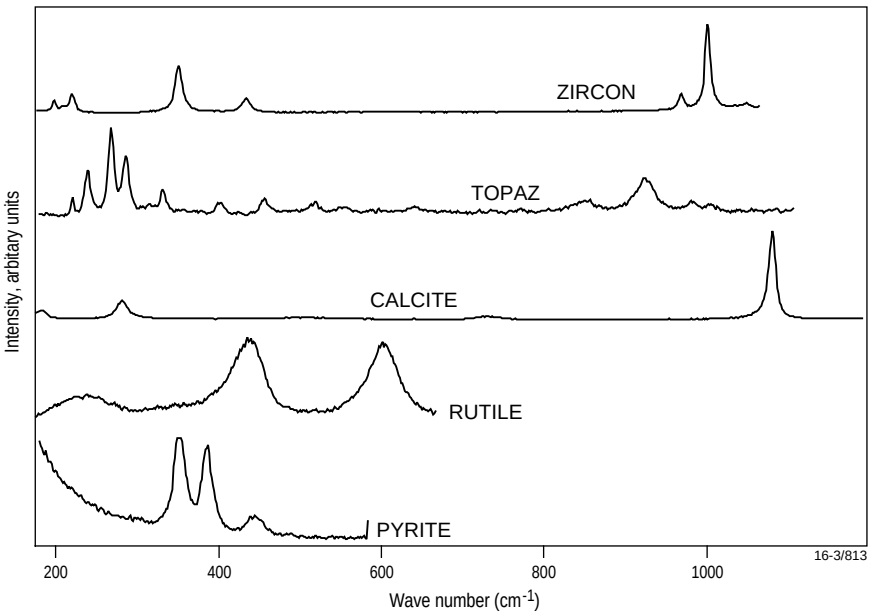

Fig. 14. Examples of Raman spectra of selected minerals.

The confocal line-scanning attachment converts the laser beam from a single point into a line that can vary in length from a few micrometres to a few millimetres. Used in conjunction with the motorised XY stage, it can scan the length of a section of drillcore or a thin section. This produces a Raman map of the sample, from which the various minerals can be identified by observing the frequencies of the bands within the spectra (Fig. 14). As the data are all digitally captured, they can be further processed to reveal the percentage abundance of each mineral, or other types of information. Furthermore, these maps and spectra can be stored in corporate databases linked with other petrological or geochemical information.

The new laser Raman microprobe will contribute important geochemical and mineralogical data to a wide range of AGSO's projects. The foregoing examples illustrate just a few of the many possible applications of the SuperLABRAM. The instrument will continue to operate as a national research facility, and researchers from industry and academia are invited to use it for collaborative studies or on a commercial basis.

Please contact the author for more information.

[1] Minerals Division, Australian Geological Survey Organisation, GPO Box 378, Canberra, ACT 2601; tel. +61 2 6249 9640; fax +61 2 6249 9983; e-mail tmernagh@agso.gov.au.