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Analysis of fluid inclusions using a pulsed laser microprobe

THE object of this investigation was to assess the potential of the laser microprobe to obtain qualitative analyses of individual fluid inclusions in minerals. Samples were selected from tin deposits in Bolivia, Cornwall, and Nigeria, and from the Panguna porphyry copper deposit, New Guinea.

Since the optical maser or laser was first built by Maiman (1960), there has been a rapid expansion in laser research. Mineralogists quickly recognized that lasers could be used to vapourize microscopic amounts of material for spectrographic analysis and rapid ore mineral identification (Maxwell, 1963). The first detailed mineral analysis by laser microprobe demonstrated the reproducibility and low detection limits that could be obtained (Snetsinger and Keil, 1967). Subsequently, mineral zoning and trace element variations across single crystals have been successfully investigated by laser microprobe (Blackburn *et al.*, 1968; Blackburn, 1969; Eremin, 1975; Blackburn and Schwendeman, 1977). Previous attempts at fluid inclusion analysis by this method were described by Tsui *et al.* (1975), and Tsui and Holland (1979), who used standard fluids recessed into fused silica-glass plates to calibrate the instrument for semi-quantitative analysis. They reported very low detection limits, for example about 3×10^{-10} g for Cu, Mn, Ca, and Mg.

Method. The instrument used in these experiments was a Carl Zeiss LMA-1, in which a pulsed (or Q-switched) ruby laser is used as a source of energy. When focused through the microscope on to a specimen, the laser pulse vapourizes a very small volume of sample material, which rises as a plasma between two charged electrodes held at just below their breakdown potential. The resultant spark excites the sample plasma still further and the emission spectrum is analysed in an optical spectrograph (fig. 1).

In the case of qualitative analyses of opaque materials sample preparation is unnecessary, but in order to focus beneath the surface of transparent specimens it is essential that the surface should be flat. For fluid inclusion analysis the most convenient method is to use polished sections, or doubly polished plates of about 0.5 mm thickness (i.e. the same type of specimen used for microthermometry).

All inclusions analysed in the experiments described here were contained in quartz. In the early stages great difficulty was experienced in obtaining a plasma, since quartz is highly transparent to wavelengths in the visible region and therefore did not absorb sufficient energy. The optical density of quartz at 694.3 nm (ruby laser light) is very low, and within the range of visible wavelengths could only be increased significantly if a laser operating at 450 nm were used (Cohen, 1956). It is possible, however, that for a material of a less refractory nature but similar optical density to quartz (e.g. fluorite or topaz), the heating effect of the laser pulse would be sufficient to burst an inclusion.

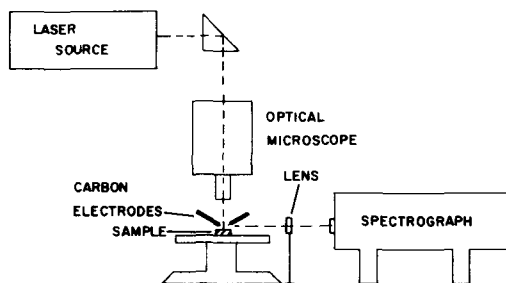


FIG. 1. Schematic diagram of laser microprobe.

For the quartz samples studied, it was necessary to select large near-surface inclusions and use close to the maximum flashtube power available (2 kV). The best results were obtained with inclusions containing daughter minerals where good absorption of the laser energy occurred and deep conical craters resulted. The best crater diameter to depth ratios obtained were about 3:1; this is not as good as results obtained from metals, where ratios of 1:2 or 1:3 have been reported (Morton *et al.*, 1973; Moenke-Blackenburg and Moenke, 1973). In quartz, much of the cratering effect appears to be the product of mechanical fracturing, producing large irregular craters (fig. 2). These do have, however, a narrow 'burn hole' in the centre. In view of the conchoidal fracturing commonly encountered, the majority of the shallow part of the crater was presumably formed by the ejection

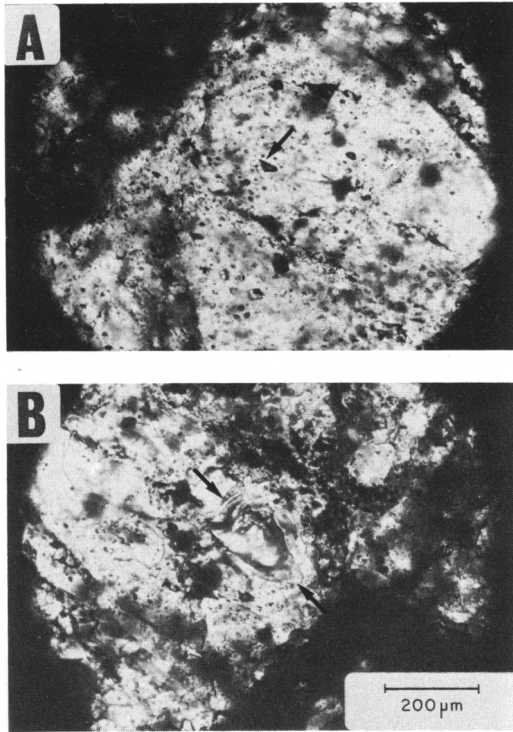


FIG. 2. View down optical path of laser microanalyser. A. Before firing, target (arrowed) is a fluid inclusion in quartz, containing daughter minerals. B. After firing, showing magnitude of resulting crater (ends arrowed).

of solid fragments and was probably not included in the plasma plume.

Two types of 'blank' were run at the beginning of each spectral plate: a spark produced by the electrodes alone, and one where comparatively inclusion-free quartz was vapourized. Any faint lines that resulted from these blanks, apart from cyanogen bands and silicon lines, were ignored if they also occurred in the samples.

Good results were also obtained in experimental tests on subsurface microscopic grains of opaque minerals (fig. 3).

Spectral analysis. A Zeiss Q-24 quartz prism spectrograph was used. Because this spectrograph operates in the ultraviolet (200–550 nm) range, only a limited number of elements could be detected, principally the alkaline earth and heavier metals. The results of numerous individual analyses are summarized in Table I. The data show a significant iron concentration in some inclusions, particularly those from the tiny veins of the Chorolque deposit, Bolivia, in which an Fe-chloride daughter mineral has been identified by other methods (Grant, 1979).

TABLE I. *Laser microprobe qualitative results*

Element	Spectral line (Å)	1	2	3	4
Fe	Many	XXX	XX	XX	
Mn	2949	XX	XX	XX	
	2939	XX	XX	XX	
	2933	XX	XX	XX	
B	2496.7	XX	XX		
	2497.7	XX	XX		
Al	3082	XX		XX	XX
	3092	XX		XX	XX
Ca	3158.9			XX	XX
	3179.3	XX		XX	XX
Ti	3190	XX	XX	XX	
	3249.4	XX	XX	XX	
	3337	X			
Cu	3247.5	XX	XX	XX	XX
	3272.9	XX			
W†	2444	XX	XX	XX	XX
	2452	XX	XX	XX	XX
	2533.6	XX	XX	XX	XX
K‡	3446	X	X	X	X
Sn	2840	X			
	3262	X			

1. Chorolque, Bolivia.
2. Bostraze, Cornwall.
3. Panguna, New Guinea.
4. Liruei, Nigeria.

XXX. Strong response. XX. Weak response. X. Tentative response. † Probably due to contamination by solid inclusions. ‡ Beyond optimum range of spectrograph.

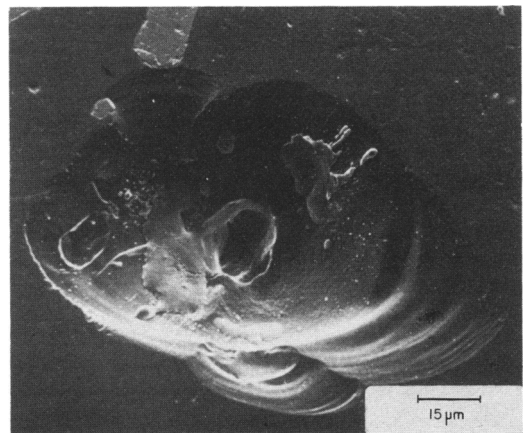


FIG. 3. SEM image of crater produced by laser firing at subsurface microinclusion of pyrite in quartz. Splashed material on crater sides is iron from incompletely vapourized pyrite grain. Note 'burn hole' in centre of crater. Most of the crater was clearly produced by mechanical fracturing.

Several elements not detected by other methods were found, the most important being the tentative identification of tin in the Chorolque fluid, and the presence of boron in the samples from both the Chorolque and Bostraze tin deposits.

In comparison with the data of Tsui and Holland (1979), the relatively strong response for Cu is notable. They studied material from a variety of moderate temperature vein ores and found extremely low Cu concentrations in the inclusion fluids (< 100 ppm). Some of the quartz sample material used in the study reported here contains solid microinclusions in addition to fluid inclusions, so some degree of contamination is possible. The strong Cu response in our Liruei and Bostraze samples could be partly a result of contamination; however, the other deposits belong to the porphyry class and the fluids had very high temperatures and salinities when trapped. They would have been capable of carrying high Cu concentrations. In the case of the Panguna deposit, Cu values exceeding 2000 ppm have been independently determined in fluid inclusions (Eastoe, 1979), which tends to support the validity of the strong response for Cu observed in the laser experiments.

Conclusions. Qualitative laser microprobe analysis is a rapid and simple technique. In fluid inclusion analysis, however, there are several problems, including poor absorption of ruby laser light by transparent host minerals, dilute inclusions, and vapourization of solid microinclusions. In the experiments described here, the best results were obtained on inclusions containing daughter salts.

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Additional data on sugilite

SUGILITE, a member of the milarite group, was described by Murakami *et al.* (1976) from the Iwagi Islet, Ehime Pref., south-west Japan where it occurs as aggregates of small crystals in an aegirine-syenite associated with pectolite, albite, and aegirine. The violet mineral from the Wessels mine, South Africa, recorded as sogdianite (another member of the milarite group) by Bank *et al.* (1978) and Dillmann (1978), has been shown by Dunn *et al.* (1980) to be a manganoan sugilite. This note records a third

occurrence of this mineral, rather richer in manganese than the material from the Wessels mine with which it is compared. Chemical and X-ray data for both occurrences are presented.

Some years ago Mr E. H. Shackleton, of the former United Steel Companies Ltd., sent a number of manganese mineral specimens to the British Museum (Natural History) for identification. He had picked them out from shipments made to the ore processing plant at Workington in Cumbria,