

Laser ablation sulphur isotope analysis at the University of Tasmania — preliminary results from a new technique with research and exploration applications

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INTRODUCTION

Over the past five to ten years, lasers have been used to sample geological materials at microscopic scales for isotopic and compositional analysis. Development of laser sampling techniques has proceeded in parallel with advances in instrumentation which allow the analysis of much smaller amounts of material. In particular, the development of micro-inlets on stable isotope mass spectrometers has decreased the sample size required for analysis by several orders of magnitude. Isotope labs at the University of Wisconsin (Crowe *et al.*, 1990) and the Scottish Universities Research and Reactor Centre (Kelley and Fallick, 1990; Fallick *et al.*, 1992) have demonstrated the application of laser ablation microprobes to sulphur isotope analysis. Spatial resolution of 100–200 μm with a precision (0.15–0.43 ‰) comparable to conventional analyses has been demonstrated by Crowe *et al.* (1990). Smalley *et al.* (1989; 1992) demonstrated an analogous method for carbon-oxygen isotope analysis of carbonate minerals at the Institute for Energy Technology in Norway.

In June 1991 a Nd:YAG laser and ancillary facilities (fig. 1) for laser ablation extraction of SO_2 gas from sulphide minerals was installed in the Central Science Laboratory at the University of Tasmania. After initial experiments off-line, the laser ablation facility was connected on-line to a VG SIRA Series II mass spectrometer to analyse the SO_2 gas. A VG Isogas automatic clean-up system attached to the mass spectrometer has been used for sample purification; in mid-May 1992 SO clean-up and analysis was automated. This contribution reports the design of this system and some preliminary calibrations of fractionation factors involved in the analysis.

SYSTEM DESIGN AND ANALYTICAL PROCEDURES

Figure 1 illustrates the University of Tasmania laser ablation system. The system consists of four components:

- (1) an 18 watt Quantronix model 117 Nd:YAG laser and Geolase designed beam delivery system;
- (2) an optical viewing system including an Olympus SMC zoom microscope, video camera and monitor;
- (3) a heated sample chamber with facilities to introduce O_2 gas and for evacuation; and

- (4) the automatic clean-up system and mass spectrometer.

Sample chips 150 μm thick, which were polished on one side, were cleaned in acetone and dried overnight at 110°C before being placed on a glass pedestal in the sample chamber. Prior to analysis of the first spot on each sample, the sample chamber was evacuated for at least 30 minutes. This extended evacuation was not required for subsequent spots on the same sample chip. For each analysis 10–50 torr of O_2 were introduced into the sample chamber to facilitate the oxidation of sulphide minerals to form SO_2 .

The chosen spot on the sample chip was then ablated for 1–3 seconds using a laser power level such that an even burn was just initiated. The produced SO_2 and any excess O_2 were then let into the automatic clean-up system where the water and SO_2 were frozen down in traps at -100°C and -190°C, respectively, for 7.5 minutes. After the freeze-down period, O_2 and other non-condensibles were pumped away above the traps. SO_2 was then transferred cryogenically to the cold finger in the mass spectrometer from whence it was analysed. The trapping and analysis of the gaseous samples was carried out automatically. The entire process, from ablation to analysis, requires 30–40 minutes, of which the operator only has to be present for the first five minutes.

RESULTS

Ablation of the samples resulted in holes which penetrated through the chip and which varied in diameter from 70 to 500 μm . Holes in chalcopyrite and sphalerite tended to have a relatively constant size of 150–250 μm , whereas hole sizes in pyrite, pyrrhotite and galena tend to be more variable. Ablation of sphalerite and galena produced white (ZnO) and brown (PbO ?) powders which coated the sample chip. The power required for ablation varied with mineral, as follows: pyrite > sphalerite > pyrrhotite > chalcopyrite > galena. The power required also varied with the quality of the polish, with polished surfaces requiring higher power for ablation than rough surfaces.

Table 1 summarises the results of experiments undertaken from 13 May 1992, when automatic sample purification and analysis was initiated, to 8 July 1992. During this period over 180 analyses were undertaken to establish correction factors and uncertainties associated with ablation. Experiments were undertaken on monomineralic chips that were inferred to be homogeneous from conventional analyses. From these and earlier experiments the following observations were made:

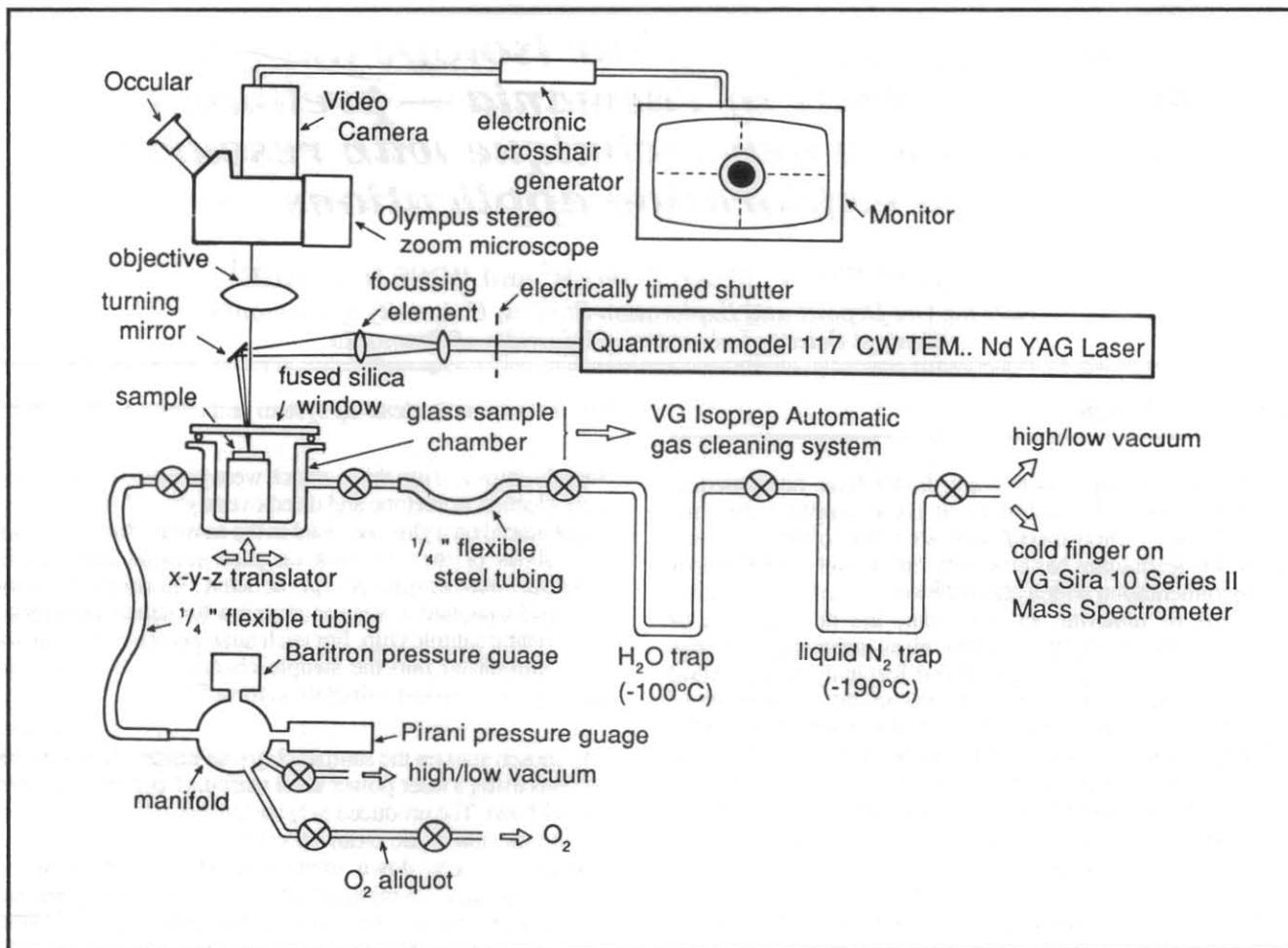


Figure 1

- (1) Heating of the sample chamber and transfer lines is required to facilitate sample transfer.
- (2) Varying the O₂ pressure between 10 and 50 torr did not effect the ablation or fractionation factors significantly.
- (3) Varying the ablation time from 1 to 3 seconds also had no significant effect.
- (4) The present method of SO₂ collection only retains 60% of the SO₂ produced. Use of lower O₂ pressures (<10 torr) improves SO₂ collection. Increasing the collection time also improves SO₂ collection. Improved SO collection decreases fractionation factors.
- (5) Ablation of rough surfaces resulted in larger fractionation factors than ablation of polished surfaces.
- (6) Analyses of larger holes (>250 μm) yielded larger fractionation factors and poorer precisions than analyses of smaller holes (150–250 μm).
- (7) One 150–250 μm hole provide sufficient SO₂ gas for analysis for pyrite, sphalerite, pyrrhotite and chalcopyrite. Two or three holes are required for galena analysis, as galena contains proportionately less sulphur.

If an O₂ pressure of 25 torr is used with a 2 second ablation time on polished surfaces, the one sigma precision for 150–250 μm holes is generally between 0.3 and 0.4 ‰. For

pyrite a precision of 0.15 ‰ was obtained, but the lack of a large number of analyses suggests that this may be an underestimate. This precision compares with precisions reported by Crowe *et al.* (1990) and Kelley and Fallick (1990) based on substantially fewer analyses. The precision of laser ablation is roughly twice that of conventional sulphur isotope analysis (0.2 ‰ at the University of Tasmania), but it is two to three times better than that of the SHRIMP ion microprobe at the Australian National University (C. S. Eldridge, pers. comm., 1992), which has a better spatial resolution.

Calculated fractionation factors vary from 0.19 ‰ for sphalerite to 6.75 ‰ for pyrite. Ablation of rough surfaces increases these values by up to 2.58 ‰. Precision also deteriorates. Fractionation factors and precisions also deteriorate for holes larger than 250 μm.

GEOLOGICAL APPLICATIONS

Sulphur isotope analysis has been an integral part of the study of mineral deposits over the past three decades. Sulphur isotopes can provide information about the source of sulphur, the importance of redox reactions during sulphide deposition, and the temperature of mineral deposition. Conventional analysis has given a great deal of information about the former two factors, but less information about geothermometry. The difficulty of obtaining geothermometric data relates to both disequilibrium sulphur isotope fractionation during mineral precipitation and also

Table 1

Fractionation factors and precision (one sigma) for laser ablation sulphur isotope analysis at the University of Tasmania (150–250 μm holes).

	Fractionation factor (‰)	Precision (‰)	n	Fractionation factor (‰)	Precision (‰)	n
Pyrite	6.75	0.15	4			
Chalcopyrite	3.80	0.33	12	4.63	0.46	6
Sphalerite	0.19	0.41	20	2.77	0.66	12
Galena	3.90	0.40	6			
Pyrrhotite	2.92	0.38	8	4.82	0.50	7

the fine intergrowth of sulphide minerals, which makes mineral separation very difficult. Hence, one of the great promises of laser ablation sulphur isotope analysis is definitive geothermometry. Crowe and Shanks (pers. comm., 1991) have demonstrated this for volcanogenic massive sulphide mineralisation in Alaska.

Analysis of trace sulphide minerals in sedimentary, volcanic and magmatic rocks is possible using laser ablation techniques. This application has particular relevance to determining the potential sources of sulphur in ore-forming fluids. Laser ablation sulphur analysis is one technique that will be used to determine the source of metals and sulphur in Mt Read Volcanics volcanogenic massive sulphide deposits in studies currently being undertaken by Bruce Gemmill and Joe Stolz at CODES. With respect to exploration, Solomon *et al.* (1988) have suggested that sulphur isotopes may have some use in distinguishing barren from mineralised systems in the Mt Read Volcanics; barren systems tend to have sulphur isotope values lighter than those of mineralised systems. The use of laser ablation analysis may help refine these differences.

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