

the mineral shows a slightly lower birefringence than those reported by Smith *et al.* (1949) and Runnells (1964).

X-ray fluorescence examination confirmed the presence of an appreciable amount of barium in the sample.

The fact that cymrite has been recorded in rather similar geological environments in two adjacent areas in Alaska as well as in New Zealand suggests that it may well be more widespread in analogous rocks.

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Quantitative analysis by means of the laser microanalyser LMA-1

DIFFERENT methods of microanalysis have been used recently in the investigation of the chemical composition and the internal homogeneity of mineral grains in rocks and ores. These methods of analysis are popular now because they make it possible to measure the contents of almost all chemical elements in separate (individual) small grains of minerals already identified by examination in transparent or reflected light. In addition, the mineral grains are not destroyed when analysed. Electron-probe microanalysis and also emission spectral microanalysis with the laser-probe are the best-known methods in this field.

But the use of electron-probe microanalysis is limited in the investigation of trace elements in minerals because the limits of detectability for most elements in this method lie between tenths and hundredths of weight per cent. For 'laser-probe'

microanalyses these limits of detectability are higher by one or two orders of magnitude. The use of this method allows us to detect a wide range of trace elements in minerals. For example, in pyrite from Urals sulphide deposits, using electron-probe (JXA-5) we found in several cases only the three elements, copper, zinc, and lead. But when the laser-microanalyser (LMA-1) was used, we managed to find, in these same grains of pyrite, also cobalt, nickel, titanium, silver, magnesium, aluminium, silicon, often calcium, manganese, and sometimes antimony, arsenic, and bismuth.

The construction of the laser-microanalyser LMA-1 and its analytical dispersion have been described in detail by Moenke and Moenke-Blankenburg (1966). The main idea of this microanalyser is to extract a small volume of mineral material by means of a finely focused laser beam. The evaporated material enters the space between two electrodes where it is burnt away. The image of the flame is focused by the condenser lens in the collimator slit of a spectrograph with a flat diffraction grid (PGS-2), and so recorded.

At present, however, when applied to analysis of trace elements in minerals, laser microanalysis is used mostly in its qualitative and comparatively quantitative forms (i.e. 'more than . . .', 'equal to . . .', 'less than . . .').

Quantitative analysis is difficult for at least two reasons: firstly, the inadequate reproducibility of the laser-probe and, secondly, the necessity of using as standards minerals with homogeneous distribution and known contents of the minor elements to be analysed.

The inadequate reproducibility of laser-microanalysers is due, firstly to the varying amount of material that is evaporated under the laser-beam, and secondly to the varying amount of material that is burnt between the two electrodes. The problem of standards is also complicated by the necessity to use as standards the same minerals as those being analysed. This is because under some conditions of generation of the laser beam, the amount of material evaporated from different minerals is not the same.

To increase the limit of detectability and improve the reproducibility of the LMA-1 we used the following procedure: each analysis (one spectrum on the photoplate) was obtained as a result of three exposures of the laser-beam on to neighbouring points in the selected mineral grain in a polished section. When the size of the grains was too small for this, we analysed three neighbouring grains of the same mineral that were similar in form and size in reflected light. This method of analysis was described by Moenke (1966). During analysis the polished surface was arranged strictly normal to the laser beam, which in turn was passed precisely along the optical axis of the microscope.

The quality of material evaporated by the laser beam was checked by measurements of the diameter and the depth of the crater visible in reflected light after the action of the laser beam. The position of the centre of the crater in relation to the optical axis of the microscope was also checked.

Before, and just after the impact by laser beam, the homogeneity of the analysed mineral grain was checked by observation at a magnification of $\times 500$. The stability of all energy parameters was also checked throughout the generation of the laser-

beam (the voltage at the impulse tube of the laser, the voltage at the carbon electrodes, the distance between electrodes).

Spectral lines in the range from 230 to 405 nm of the optical emission spectrum were recorded on astrophysical glass photo-plates ZU-2 (ORWO, DDR), which are characterized by a very high sensitivity.

Members of the Department of Mineral Deposits in the Geological Faculty of Moscow State University under the leadership of Academician V. I. Smirnov have obtained fruitful results from the application of these methods to various questions of ore formation, for example, by using Co and Ni distributions as a key to some problems of sulphide ore genesis (Erëmin *et al.*, 1973; Smirnov *et al.*, 1972). Using this method the coefficient of variation for the spectral line Co 3453.5 measured in terms of ΔS , a logarithmic function of intensity, was up to 15 %, and the corresponding figure for the line Ni 3414.76 was about 25 % (27 analyses of sedimentary pyrite from one piece of ore gave: 0.09, 0.13, 0.07, 0.05, 0.08, 0.12, 0.11, 0.12, 0.14, 0.11, 0.13, 0.06, 0.12, 0.08, 0.11, 0.10, 0.13, 0.13, 0.09, 0.05, 0.10, 0.11, 0.10, 0.12, 0.10, 0.07, 0.09 Ni; mean 0.10, standard deviation 0.025).

That there was adequate reproducibility in such analyses was also checked by measurements of a known homogeneous distribution of iron in sphalerites. The iron contents were measured on several polished sections, both by the X-ray micro-analyser and by the laser micro-analyser; these showed a linear relation between iron content and ΔS for the line 3719.9.

The problem of standards was resolved in two ways. Firstly, there were selected from a large number of natural sulphides those that were characterized by homogeneous distribution of cobalt and nickel; this was checked by the variability of the ΔS obtained for different parts of polished sections. Secondly, similar work was done for synthetic sulphides. Specimens with homogeneous distribution of cobalt and nickel were selected as standards from both natural and synthetic groups. The contents of these metals in the standards were obtained by chemical analysis. It should be pointed out here that we tried a third way to obtain the standards by compressing a powder of appropriate composition. But the result was unsatisfactory for methodical and technical reasons.

Having the standards, we can, of course, plot a two-axis diagram in terms of ΔS against $\log C$, and so measure the contents of the trace elements in terms of percentage weight.

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