

and compare with equation (3), we see that they are not equal and cannot be made equal by any rearrangement of the factors. The exact equation (3), in fact, is proportional to the cube root of the mole fraction, whereas "Vegard's Law," equation (4), is proportional to the mole fraction itself.

This problem can be formulated in a slightly different way. Writing  $\alpha = (R_1/R_2)^3 - 1$  in equation (3) and expanding the cube root in a series, we get

$$R = R_2(1 + \frac{1}{3}\alpha N - \frac{1}{3}\alpha^2 N^2 + \dots) \quad (5)$$

Comparing with (4), we see that  $\beta = \frac{1}{3}\alpha$ , and the two expressions can be reconciled only when terms higher than the first power in  $\alpha$  are negligible, i.e., if

$$\left(\frac{V_1}{V_2} - 1\right) \ll 1,$$

which means that the pure end-members do not have very different molar volumes. This fact is intuitively obvious, but equation (5) expresses it analytically and gives a precise relation between allowable difference in end-member volumes and any desired degree of approximation to linearity for the solution (when the other conditions are also satisfied).

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#### THE CURVED-CRYSTAL X-RAY SPECTROMETER, A MINERALOGICAL TOOL\*

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Birks and Brooks (1955) have recently described the application of a curved-crystal, reflection-type, focusing x-ray spectrometer, using fluorescent x-rays, to the determination of microgram quantities of a number of elements. They have reported that the intensities, resolution and line-background ratios for small samples of the order of 1 mg. are comparable to those obtained from a 10-g. sample on a commercial flat-crystal spectrometer.

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The ability of this type of instrumentation to handle minute samples nondestructively and rapidly makes its application to geochemical and mineralogical problems a natural extension of the method. The technique has been successfully applied in the U. S. Geological Survey to the elemental analysis of  $x$ -ray diffraction spindles, minute single crystals, and mineral grains in polished ore sections.

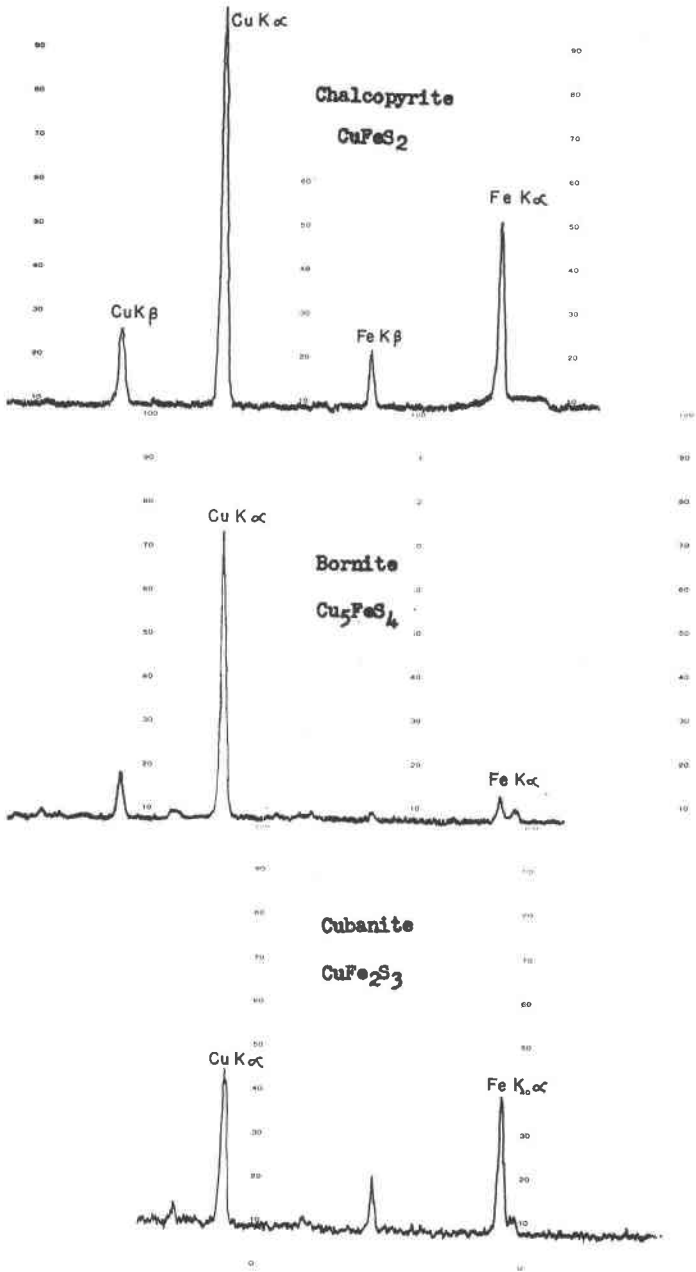
Curved-crystal spectrographs have been described by Birks and Brooks (1953) in some detail. The instrument in use in the Geological Survey is also a scanning type spectrograph similar to theirs in principle. A sample holder has been designed which is capable of taking either fibers and single crystals or sections, both thin and polished. The sample holder, which is a modified microscope mechanical stage, permits motion in two directions and makes possible the careful positioning of the sample in the stopped-down  $x$ -ray beam. For examining  $x$ -ray diffraction spindles, a narrow slit, approximately 0.5 mm. wide and 5 mm. long, is placed over the  $x$ -ray tube window. For single crystals or small areas on polished sections the  $x$ -rays emerge from a pin hole and irradiate approximately 3 square mm. of sample. The area examined may be further reduced by the use of a pin hole in a small section of lead foil which is placed directly on the polished section, with the pin hole directly over the grain to be analyzed.

Successful analyses have been performed with a pin hole approximately 0.5 mm. in diameter.

The area or grain to be investigated is easily located in the  $x$ -ray beam by the following technique: a small fragment of Patterson screen embedded on a small strip of scotch tape is placed over the grain and the polished section is manipulated by means of the mechanical stage until the fragment of Patterson screen fluoresces brightly. The scotch tape is then peeled off leaving the desired grain in the  $x$ -ray beam.

Some semiquantitative results obtained on mounted polished sections are illustrated below. Three small areas—chalcopyrite  $\text{CuFeS}_2$ , bornite  $\text{Cu}_5\text{FeS}_4$ , and cubanite  $\text{CuFe}_2\text{S}_3$ —were run consecutively. The chalcopyrite was taken as a standard and the iron-copper ratios in the other two calculated. The results of the analysis, all obtained in less than one hour, are shown in the following table.

Mineral	Formula	Ratio of peak intensities CuK:FeK	Calculated atomic ratios
Chalcopyrite	$\text{CuFeS}_2$	2:1	Standard (1:1)
Bornite	$\text{Cu}_5\text{FeS}_4$	10:1	5:1
Cubanite	$\text{CuFe}_2\text{S}_3$	1:1	1:2



The curved, reflection-type  $x$ -ray spectrograph is a promising tool in mineralogical research where rapid qualitative or semiquantitative analysis of  $x$ -ray diffraction spindles, minute grains, or crystals is needed. The nondestructive character of the method makes it of special value. The present instrument is limited to elements of atomic number greater than 23.

We wish to express our appreciation to Charles Milton of the U. S. Geological Survey for the polished sections and mineralogical data. We also wish to thank L. S. Birks and E. J. Brooks for their help and advice in assembling the spectrometer.

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#### INCORPORATION OF IMPURITIES IN SYNTHETIC QUARTZ CRYSTALS

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Controlled amounts of selected impurities were incorporated in synthetic quartz crystals during growth to determine their effect on the growth rate, quality and properties of synthetic quartz.

The impurity experiments were carried out under conditions generally used for the growth of quartz from sodium carbonate solutions. The concentration of the solutions was 0.5N and the degree of fill was 70%. The average temperature measured at the top and bottom of the autoclave was 350° C. Temperature gradients between the top and bottom of the autoclaves varied from 20° C. in some runs to 50° C. in others. Observed pressures were 5000-6000 *p.s.i.* The capacity of the autoclaves ranged from 250 cc.-500 cc. The quartz seeds for this work were mostly *AT*-cuts. Growth runs lasted from 8 to 15 days. Resonator plates for evaluation could be cut from the growth obtained in that period of time.

Selection of impurities for addition to solutions for quartz growth was confined to those elements which were believed to be structurally compatible in the quartz lattice with respect to ionic radius and valence. Elements used as additives in these experiments are listed in Table 1 in accordance with their grouping in the periodic table.

Group IV elements were added as oxides; the Group III elements, aluminum and boron as sodium metaborate and sodium aluminate; calcium, the only element tried in Group II, and silver, the only element tried in Group I were added as carbonates. The use of sodium carbonate