apparent, therefore, that any specimen suspected of containing vanadinite should be heavily diluted with powdered gum tragacanth, or some other inert material which does not itself give rise to powder diffraction lines, before an *x*-ray diffraction powder photograph is taken for identification purposes.

Indexed *x*-ray diffraction powder data for vanadinite, when absorption is negligible, are presented in Table 2. Values of *d*(calc.) were calculated for both sets of unit cell data (Trotter & Barnes, 1958, and the present note) by an IBM 650 computer with a programme written by Dr. F. R. Ahmed.

Grateful acknowledgment is made to Mr. Howard Clark for taking the powder photographs and assisting with their measurement, and to Mrs. M. E. Pippy for carrying out the computer calculations.

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X-RAY METHOD FOR RAPID DETERMINATION OF SULFUR AND COBALT IN LOELLINGITE

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One of the common constituents in arsenide-type ores is a loellingite-safflorite [(Fe,Co)As_2] solid solution which often contains 1 or 2 per cent sulfur. In other occurrences, such as in pegmatites, the loellingite may be the pure iron end member, or more often contains some sulfur with very little cobalt. The composition of loellingite may be obtained by chemical analysis only when the sample is mineralogically pure. The normal association is with other arsenide minerals from which complete mechanical separation is usually impossible. The *x*-ray diffraction method presented here, although not highly precise, will give the sulfur and cobalt contents of loellingite within ±0.2 and ±0.5 weight per cent, respectively. This is a non-destructive process which requires only a few milligrams of loellingite and can be performed rapidly without especial pains for purification. This method may find application at least (1) for routine mineralogical investigation of loellingite compositions, (2) as a quick check on results obtained by other analytical procedures, and (3) to facilitate collection of physical-chemical data on the environment of loellingite deposition.

In regards to the third point, I have, without much success, attempted to determine the sulfur-rich loellingite solvus curve (*i.e.* in the loellingite-arsenopyrite join of the Fe-As-S system) because preliminary data indicate it will be useful as a geothermometer. Unfortunately, reaction rates below about 630° C are so slow that the solvus determination is impossible employing current synthesis techniques. Runs heated 756 days at 600° C were far from equilibrium. Points along the solvus curve of approximate equilibrium composition are, in weight per cent sulfur: 630° C, 2.9; 660° C, 3.0_5; 690° C, 3.2_5; and 702° C, 3.4. The sulfur solubility in loellingite is a maximum at 702° C at which temperature arsenopyrite melts (Clark, 1960). In any event, application as a geothermometer would require determination of the sulfur content in loellingite and demonstration that the cobalt content was low.

Nickel substitution for iron in loellingite has a slightly more pronounced effect than cobalt on the interplanar spacings (Roseboom, 1958). However, according to Holmes (1947), the nickel content of natural loellingites is usually much less than cobalt. The following analytical procedure probably should not be employed if the nickel content exceeds 1 per cent.

Nine loellingites were synthesized in which 0 to 3.1 weight per cent sulfur was substituted for arsenic in the structure. Syntheses were performed in sealed, evacuated, silica glass capsules employing previously described (Clark, 1960) materials and procedures. The resultant shifts in *x*-ray spacings of four reflections (120, 101, 210, and 111)[1] are illustrated in Fig. 1. These curves will give the sulfur content of an otherwise pure loellingite when the *x*-ray powder diffraction measurements are performed with a quartz internal standard employing diffractometer settings and measurement techniques similar to those described by Clark (1960).

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[1] Indexing is that employed by Roseboom (1958) in the setting suggested by Buerger (1937).

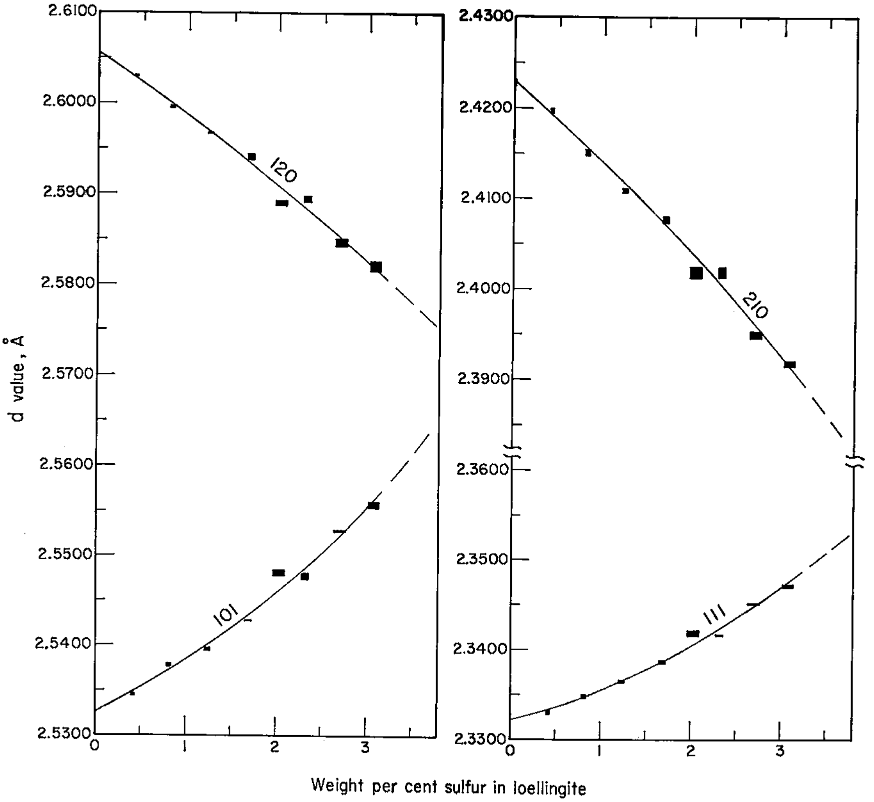

FIG. 1. Variations of four interplanar spacings in loellingite ($FeAs_2$) as a function of sulfur substitution for arsenic.

Similar curves were prepared for seven loellingite-safflorite compositions in the range 0 to 13.5 weight per cent cobalt. These measurements were performed previously by Roseboom (1958) and were repeated merely to maintain internal consistency in this investigation.

Upon addition of either sulfur or cobalt to the loellingite structure the two pairs of x-ray reflections converge but at different rates. Since the shifts in peak locations caused by substitutions of sulfur and of cobalt are somewhat different it is theoretically possible to plot the d value of a reflection as a simultaneous function of both composition variables in a three-dimensional model. Alternative to using such a model we may plot the two independent variables in two dimensions and project the dependent variable, d, onto this plane, with variations in d shown as contours. Fig. 2 was drawn in this manner employing the data from Fig. 1 for the

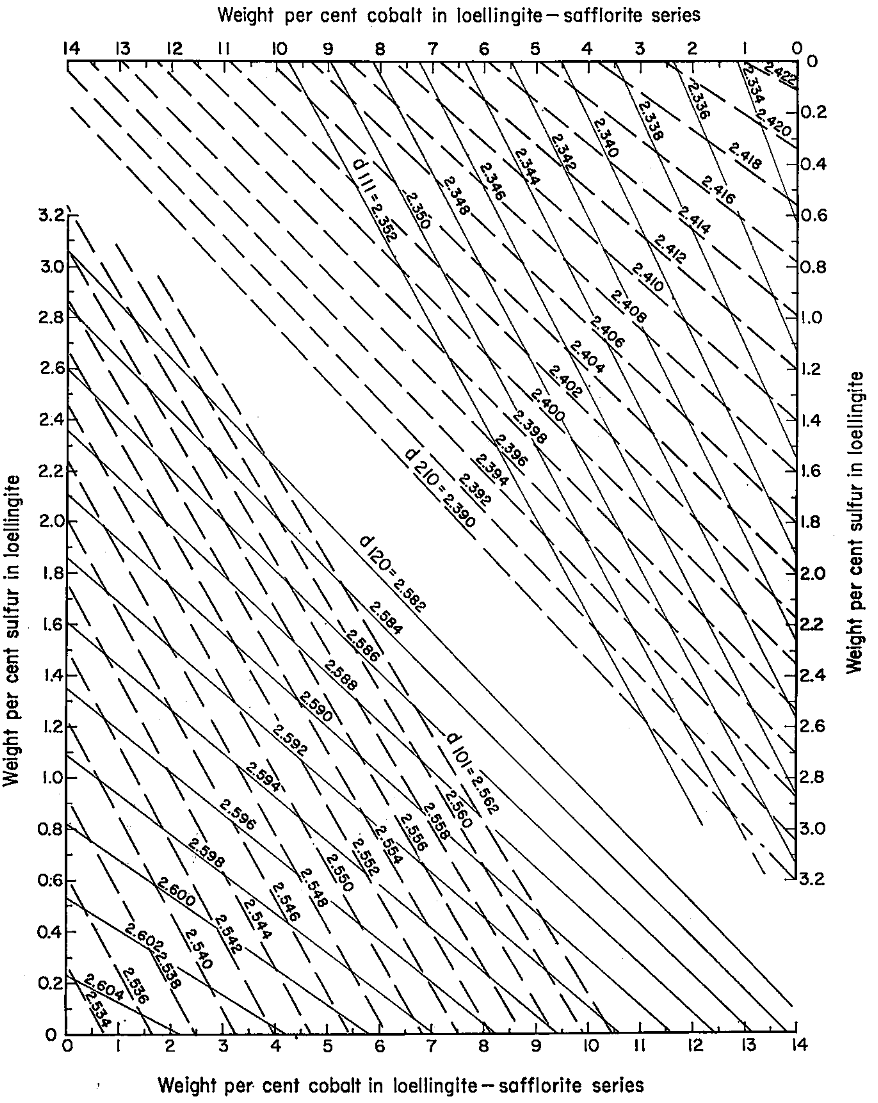

Fig. 2. Loellingite interplanar spacings vary as functions of both sulfur and cobalt content. These are related here so that measurements of either the 210 and 111 or the 120 and 101 reflections give the sulfur and cobalt contents of a loellingite specimen. The *d* values are in Ångström units.

sulfur variable, and the previously mentioned data for the cobalt variable. It was assumed that the variations of each of the *d* values were linear with respect to the composition variables.

To justify these assumptions and to indicate whether this approach might have application as an analytical procedure, eight loellingites were synthesized, each containing the known contents of sulfur and cobalt indicated in Table 1. Powder patterns of the products were obtained with the *x*-ray diffractometer employing Cu radiation. Measurements were performed on each of four separate traces using as internal standard the 110 and 102 reflections of Lake Toxaway quartz. Measurement of each of the four loellingite reflections under consideration permits the derivation from Fig. 2 of two separate values for both the sulfur and cobalt contents. In Table 1 the absolute errors of these measurements are shown relative to the weighed compositions. The random errors justify the straight line contours in Fig. 2. The determination using the 210 and 111 reflections is somewhat more reliable than that obtained with the 120 and 101 reflections. However, if arsenopyrite is present in the sample, it may not be possible to measure the 210 reflection since it coincides with one of the strongest arsenopyrite reflections. Determinations involving the 120 reflection are a little less reliable because it contains a small contribution from the very weak and seldom resolved 011 reflection. As a consequence, determinations involving only the 120 and 101 reflections may not always be within the stated limits of error.

TABLE 1. ABSOLUTE ERRORS IN SULFUR AND COBALT DETERMINATIONS ON PURE, SYNTHETIC LOELLINGITES OF KNOWN COMPOSITIONS

Temp. (°C)	Time (days)	Composition of loellingite, (weight per cent)		Determination error employing 210 and 111 reflections		Determination error employing 120 and 101 reflections	
		S	Co	S	Co	S	Co
700	253	0.2_3	11.3_2	−0.1	0.0	−0.2	+0.2
700	253	1.0_3	4.2_3	+0.1	−0.3	+0.4	−1.6
700	253	1.0_4	1.4_1	−0.2	$+0.3_5$	−0.1	$+0.0_5$
700	253	2.2_5	1.3_9	0.0	-0.4_5	0.0	−0.6
800	14	0.6_7	6.8_5	−0.1	+0.1	−0.2	$+0.5_5$
800	14	0.3_1	8.9_1	−0.2	+0.5	0.0	−0.1
800	14	0.5_0	4.2_5	−0.1	$+0.3_5$	−0.1	$+0.2_5$
800	14	1.5_6	1.4_0	−0.2	+0.5	-0.0_5	−0.2

Natural loellingites from Drag, Norway, and Kuortane, Finland, were obtained through the kind co-operation of Dr. H. Neumann, Mineralogisk-Geologisk Museum, Oslo, Norway. In the Drag material the sulfur and cobalt contents were given as 2.77 and 1.29 weight per cent, respectively, by Neumann, Heier & Hartley (1955). They report that the loellingite occurs with abundant quartz, minor arsenopyrite, and rare molybdenite. There is no statement regarding the mineralogical purity of the analyzed sample. Using the present *x*-ray method, the sulfur and cobalt contents were estimated as 2.5_5 and 0.9 weight per cent, respectively. Analysis of the Kuortane loellingite, performed by P. Kivalo (in Pehrman, 1950), indicated 1.34 weight per cent sulfur and no Co, Ni, Bi, or Sb. The present *x*-ray method indicates 0.9 weight per cent sulfur and $\leqslant 0.1$ per cent cobalt.

The correlation between results obtained by the two analytical procedures, wet chemistry and *x*-ray diffraction, is not excellent. However, the differences may in part be due to (1) errors in the wet chemical analyses since determinations of sulfur, and perhaps also of cobalt, are difficult to perform; and (2) admixed phases in the chemically analyzed samples.

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ON KOLOVRATITE[1]

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Kolovratite, a vanadate of uncertain composition, is reported to be widely distributed as yellow to greenish yellow incrustations and botryoidal crusts in quartz schists and carbonaceous slates at Ferghana, Russian Turkestan (Palache, Berman & Frondel, 1951). Partial analyses of ore samples by Preobrazhensky (in Chirvinsky, 1925) gave 6.50 to 12.22 per cent NiO, and 5.94 to 11.55 per cent V_2O_5. The lack of descriptive data has long resulted in the mineral being regarded as a doubtful species (Foshag, 1926).

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