

Spectrographic and X-ray data on some fluorites from the Transvaal, South Africa.

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I. INTRODUCTION.

THE fluorites of the Transvaal occur in different rock-types,² viz. in the dolomite of the Transvaal System, in acidic rocks (red granite and granophyre of the Bushveld igneous complex and Rooiberg felsites), and in alkalic rocks. The purpose of this study was to determine:

- (1) What minor elements are present in selected fluorites.
- (2) What the effect of these elements is on the respective cube-edges.
- (3) Whether these elements have any geological significance.

Fluorite displays a wide range of colour; both colourless and distinctly coloured specimens were examined. Differently coloured varieties could in some instances be taken from the same sample. The choice of coloured varieties in the different rock-types was nevertheless limited. Only light-coloured fluorites occur in the dolomite, whereas the alkalic rocks yielded only very dark purple specimens.

II. SPECTROGRAPHIC EXAMINATION.

A large Hilger Littrow type of spectrograph with a setting 2750–4700 Å. was generally used; only for Ge, Si, Te, P, and B was the setting changed to the range 2260–3000 Å. The material was arced between copper electrodes for 20 seconds at 5 amps; carbon electrodes were used for determining the rare-earths and copper.

Table I lists the analyses and other data. As the spectrographic sensitivities of the elements differ greatly, the intensities should be used only comparatively for each separate element. No element is reported unless its presence was definitely established; conversely, failure to report an element means that it was not present in a quantity above the limit of detection for the particular method used.

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² L. E. Kent, H. D. Russell, and D. P. van Rooyen, Fluorspar in the Union of South Africa and South West Africa. Bull. Geol. Surv. S. Africa, 1943, no. 14. [M.A. 9-28.]

The common minor elements are: Fe, Mg, Sr, Cu, Al, Mn, Si, Sb, and some of the rare-earths. Be, Pb, Na, P, and Ba are rare; the last was found only in a single specimen. The elements that could not be detected in any of the samples are: Mo, In, Ga, Cd, Li, K, Rb, Cs, Bi, Hg, V, Zn, Co, Ni, Cr, Ti, As, Zr, Nb, Pt, Os, U, W, Th, Ge, Te, B, Pr, Er, Sm, and Sn.

TABLE I. Spectrographic analysis of fluorites.
Estimated intensities using an arbitrary scale 0-10.

Sample no.	Fe.	Mg.	Be.	Sr.	Ba.	Al.	Pb.	Mn.	Na.	Cu.	Sb.	P.	Si.	Ce.	La.	Yt.	α at 25° C.
1	3	4	3	4	—	2	—	1	—	1	—	—	1	—	—	—	5-4625 Å.
2	—	3	—	—	—	—	—	3	—	2	—	—	—	—	—	—	5-4627
3	3	3	—	1	—	3	—	1	—	2	1	—	1	—	—	—	—
4	5	4	—	10	—	6	—	3	—	3	—	—	4	—	1	2	5-4686
5	7	3	—	10	—	4	—	6	1	—	—	2	6	1	1	1	5-4684
6	3	2	4	3	—	3	—	2	2	—	1	—	5	1	2	—	5-4626
7	1	2	—	1	—	1	1	1	—	—	—	—	—	—	—	—	5-4631
8	1	2	—	7	—	3	—	3	—	—	—	—	5	—	—	—	5-6434
9	1	3	—	—	—	2	—	—	—	—	1	—	—	—	1	—	5-4632
10	8	3	—	10	—	4	—	4	—	3	1	—	3	—	—	—	5-4682
11	—	4	—	5	10	1	—	—	—	—	2	—	2	—	—	—	5-4635
12	1	1	—	—	—	1	—	1	—	—	2	—	1	1	—	—	5-4631
13	2	1	—	—	—	2	—	—	—	—	3	—	—	—	—	—	—
14	—	3	—	—	—	2	—	—	—	4	—	—	—	1	—	—	—
15	3	3	—	2	—	2	5	3	—	1	2	—	2	—	—	—	—
16	5	1	—	—	—	3	6	—	—	3	—	—	2	—	—	—	5-4628
17	4	2	2	3	—	2	—	1	—	—	2	—	—	—	—	—	5-4632
18	3	2	—	4	—	2	—	2	2	4	2	—	—	1	—	—	—
19	1	5	1	5	—	4	1	—	—	—	—	—	7	—	—	—	5-4627
20	2	1	—	—	—	—	—	1	—	10	?	—	—	—	—	—	—

1. Witkop 288, Marico district, Transvaal. Colourless. Dolomite.
2. Malmani Oog 101, Marico district. Colourless. Dolomite.
3. Malmani Oog 101, Marico district. Light purple. Dolomite.
4. Seekoeigat 287, Pretoria district. Very dark purple. Alkalic rock.
5. Leeuwfontein 320, Pretoria district. Very dark purple. Alkalic rock.
6. Cyferfontein 57, Warmbad district. Yellowish. Granite.
7. Groblershoek 785, Potgietersrust district. White. Granite.
8. Groblershoek 785, Potgietersrust district. Bluish-green. Granite.
9. Ruigtepoort 1373, Warmbad district. Colourless. Granite.
10. Houtenbek 392, Groblersdal district. Very dark purple. Granite.
11. Valsfontein 432, Groblersdal district. Green. Granite.
12. Zaaiplaats tin-mine, Potgietersrust district. Colourless. Granite.
13. Zaaiplaats tin-mine, Potgietersrust district. Greenish. Granite.
14. Zaaiplaats tin-mine, Potgietersrust district. Purple. Granite.
15. Mutue Fides tin-mine, Potgietersrust district. Light purple. Granite.
16. Stavoren tin-mine, Potgietersrust district. Purple. Granophyre.
17. Stavoren tin-mine, Potgietersrust district. Colourless. Granophyre.
18. Stavoren tin-mine, Potgietersrust district. Yellowish. Granophyre.
19. Synthetic fluorite.
20. Blank copper electrodes.

III. X-RAY EXAMINATION.

The X-ray work was carried out on a Seifert X-ray unit with unfiltered copper radiation. A Debye-Scherrer type of camera was employed. The exposures were about $2\frac{1}{4}$ hours at 35 kV. and 20 mA. The variation in temperature never exceeded 1° C. after certain precautionary measures. The films were measured in triplicate after drying for a week; the cube-edge was calculated after 2θ had been corrected for film

shrinkage. The parameters tabulated in table II were derived by the extrapolation method of Bradley and Jay.¹ The following values, expressed in terms of (*hkl*), were used in constructing the graphs: (444), (533), (620), (531), (440), (511) $K\alpha_1$; (642) $K\beta$.

The exposures were all made within a temperature range 22°–27° C., and the results corrected to correspond to a mean temperature of 25° C. Taking the thermal expansion of fluorite as 0.16 % at 20–100° C. (Dana, 7th edit., 1951, p. 32), the expansion correction for the fluorite parameter is therefore 0.00012 Å. per degree centigrade. The accuracy of the apparatus and the technique has been indicated by Wasserstein² of this laboratory. The results listed in table II, subject to a limit of error of 0.0005 Å., can therefore be regarded as precision measurements.

Synthetic fluorite was prepared by precipitating CaF_2 from CaCO_3 with hydrofluoric acid. This material yielded a very weak back-reflection pattern. After heating the precipitate in a crucible to a high temperature a perfect pattern was obtained; a 5.4627 Å.

TABLE II. X-ray data for fluorite from the Marico district, Transvaal.

No.	<i>hkl</i> .	Wave-length.	Int.	$d\text{Å. (meas.)}$	$d\text{Å. (calc.)}$
1	(111)	$K\beta$	5	3.149	3.154
2	(111)	$K\alpha_1$	10	3.150	3.154
3	(220)	$K\beta$	6	1.928	1.932
4	(220)	$K\alpha_1$	10	1.927	1.932
5	(311)	$K\beta$	2	1.646	1.647
6	(311)	$K\alpha_1$	9	1.642	1.647
7	(400)	$K\alpha_1$	4	1.364	1.366
8	(331)	$K\alpha_1$	5	1.251	1.253
9	(422)	$K\alpha_1$	8	—	1.115
10	(511)	$K\alpha_1$	3	1.050	1.050
11	(440)	$K\alpha_1$	3	0.964	0.966
12	(531)	$K\alpha_1$	4	0.922	0.923
13	(620)	$K\alpha_1$	6	0.864	0.864
14	(533)	$K\alpha_1$	4	0.834	0.833
15	(642)	$K\beta$	3	0.730	0.730
16	(444)	$K\alpha_1$	5	0.788	0.788
17	?	?	5		

No indices or spacing have been given to reflection no. 17. This highest back-reflection angle, with intensity the same as the (444) $K\alpha_1$ line, is most probably caused by interference of the (444) $K\alpha_2$ and (731) $K\beta$ lines. It gives a relatively high value for the cube-edge if taken as (444) $K\alpha_2$ and a relatively low value if taken as (731) $K\beta$.

¹ A. J. Bradley and A. H. Jay, Proc. Physical Soc. London, 1932, vol. 14, p. 563. [M.A. 5-305.]

² B. Wasserstein, Amer. Min., 1951, vol. 37, p. 102. [M.A. 11-316.]

The purest fluorites encountered in this study are those from the dolomite in the Marico district (samples 1 and 2); their parameter is $a\ 5.4626 \pm 0.0005\ \text{\AA}$., at $25^\circ\ \text{C}$. The averages of their spacings are listed in table II.

IV. DISCUSSION.

Although a large range of minor elements was detected spectrographically, substitutions likely to affect the cube-edge, after allowing for errors, were encountered in only three samples. The ionic radii of some of the minor elements and that of Ca are: Mn^{''} 0.91, Na['] 0.98, Ce^{'''} 1.18 (1.02), La^{''} 1.22 (1.04), Yt^{'''} 1.06, Ca^{''} 1.06, Sr^{''} 1.27, Ba^{''} 1.43 kX. Due to similarity in size, replacements of Ca^{''} may occur in the fluorite structure without affecting the cube-edge to any measurable extent.

Samples 4, 5, and 10 show an increase in the cube-edge of at least 0.0055 \AA . as compared with pure CaF₂. *These three are all very dark purple in colour and contain an appreciable amount of strontium.* The large amount of strontium present in these fluorites was the most significant result of the spectrographic analyses. Chemical analyses confirm these findings (table III). The highest cube-edge sample, viz. 5, contains over 1 % strontium, whereas the other samples, with normal cube-edges, contain virtually no strontium. The Sr^{''} ion is larger than the Ca^{''} ion. Furthermore, SrF₂ has a greater cube-edge ($a\ 5.86\ \text{\AA}$.) than CaF₂. The results therefore prove that the replacement of Ca^{''} by Sr^{''} in fluorite causes an appreciable enlargement in the size of the fluorite cell.

TABLE III. Chemical analyses of fluorites. (Numbers as in table I.)

			5.	1.	6.
CaO	71.66	71.55	69.62
SrO	1.34	0.05	trace
MgO	0.008	0.012	0.008
MnO	0.005	—	—
Na ₂ O	0.02	—	0.02
FeO	0.04	0.04	0.03
SiO ₂	0.03	—	0.28

Analyst: C. van Rooyen. High CaO in no. 5 due to presence of apatite.

The presence of contaminating minerals in fine cracks in the fluorite host (fig. 1) or as inclusions (fig. 2) has an influence on the minor element content of fluorite; lead was found, for example, in samples 15 and 16, which are accompanied by galena; phosphorus was encountered only in the Leeuwfontein fluorite (no. 5), which occurs with apatite.

The large amount of barium found in sample 11 is due to the contamination of baryte, a mineral accompanying this fluorite. If Ba⁺⁺ had replaced Ca⁺⁺, the larger ionic size of the former would have caused a remarkable increase in the cube-edge of this particular fluorite. Because of the difference of 0.37 kX in their ionic size it is also unlikely that Ba⁺⁺ would ever replace Ca⁺⁺: 'Generally speaking, it may be stated that the ion (*A*) may replace the ion (*B*) diadochically if the difference in size of their radii does not exceed about 15 % of the radius of (*B*).'¹ In this example the difference is about 35 %.

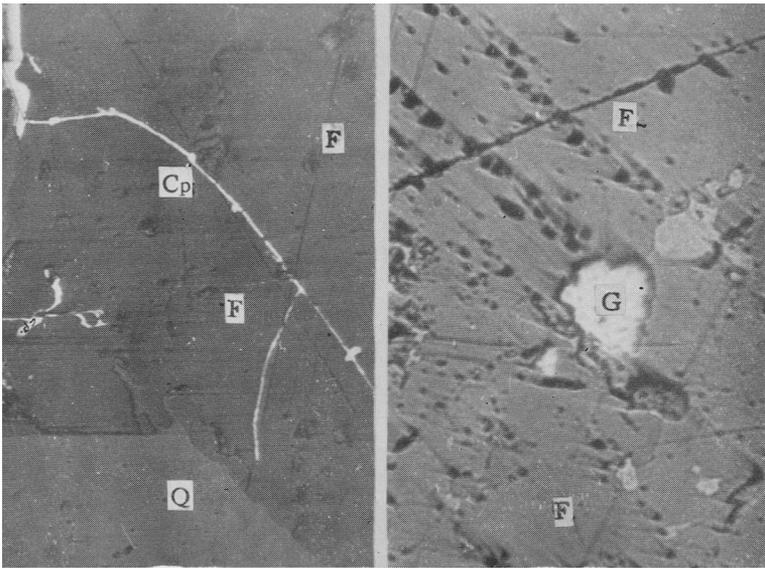


FIG. 1.

FIG. 2.

FIG. 1. Photomicrograph showing chalcopyrite (Cp) along a microscopically fine fracture in fluorite (F) with quartz (Q). Magnification $\times 160$.

FIG. 2. Photomicrograph showing inclusions of galena (G) in fluorite (F). Magnification $\times 56$.

There exists a relation between the minor elements of fluorite and the country-rock in which the mineral was deposited. The fluorites occurring in the alkalic rocks contain larger quantities of impurities, whereas those occurring in the dolomite are purer.

¹ K. Rankama and T. G. Sahama, *Geochemistry*. Chicago, 1950, p. 122. [M.A. 11-409.]

Except for the relatively large amount of strontium present only in the very dark purple fluorites, an attempt to correlate the colour of the fluorites with their minor element content was not successful.

Addendum.—The above results were obtained prior to the publication by R. D. Allen, Variations in the chemical and physical properties of fluorite. (Amer. Min., 1952, vol. 37, p. 910.) [M.A. 12, 161]. He reports: a 5.46295 ± 0.00010 Å., at 28° C. for a synthetic fluorite of optical grade. If this value is corrected to correspond to a temperature of 25° C., it becomes a 5.4626 Å., which is identical with the value found for the fluorites of the Marico district.
