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CHEMICAL COMPOSITIONS OF FLUORITES FROM JAPAN.

(Studies on the Fluorites from Japan. I)

By

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Introduction

Fluorites has been investigated from its peculiar properties. But we have heard scarce about its impurity. I studied fluorites from 20 different localities by chemical and spectrographic analyses to ascertain the relations between its impurities and crystallization. I wish to express my sincere thanks to Prof. Z. HARADA for his kind guidances throughout this work, and thanks I. KAYAMA for his helps in spectrographic analyses and thanks to S. HASHIMOTO for his advices in chemical analyses.

Locality, Occurrence and Parageneses

Specimens were collected from 7 localities in Japan, adding 7 localities in Korea and 3 localities in China. Fluorites of those localities have been found in hydrothermal or contact ore deposits, and they are in different colours and forms. Their crystal forms, occurrences and paragenesis are shown in Table I.

Methods of Analyses.

a) Chemical analysis

Crystalline or massive part were picked out from specimens and crushed into 2—5 mm. in diameter. And pure fluorites fragments are

TABLE I. Form, Occurrence, Parageneses and Colour, fluorites of 20 different localities.

Nos.	Locality	Form	Occurrence	Paragenesis	Colour
1	Hayakawa Mine Hokkaido	a (100) ~massive	fluorite vein	pyrite quartz kaolin	blue
2	Omoya Niigata Pref.	„	gangue[1]	pyrite quartz	light green
3	Ishigure Mie Pref.	„	fluorite vein	quartz kaolin	greenish blue
4	Kiura Mine Oita Pref.	„	gangue[1]	sulphides	colourless
5	Akenobe Mine Hyogo Pref.	massive	fluorite vein[1]	„	light blue
6	Obira Oita Pref.	a (100) ~o (111)	contact deposit	axinite hedenbergite quartz calcite sulphides	colourless
7	„	o (111)	„	„	„
8	„	o (111) massive	„	„	„
9a	Kano mine Fukushima Pref.	a (100) ~massive	fluorite vein	calcite gypsum	pale purple
9b	„	o (111) ~massive	„	„	dark green
10	Korea	massive	fluorite vein	quartz sulphides	white apacity
11	„	„	„	„	„
12	Obira Oita Pref.	a (100) ~o (111)	contact dep[1]	axinite quartz sulphides	light pink
13	Korea	massive	fluorite-quartz vein[3]	sulphides	dark purple
14	„	„	„	„	colourless
15	Ryuka Mine Manchuria	a (100)	fluorite vein[2]	quartz calcite	light blue green
16	China	o (111)	pegmatite ?	single cry.	dark green
17	Gojyotin China	a (100)	fluorite vein[2]	sulphides	pale purple
18	Korea	„	fluorite vein[3]	sulphides calcite	colourless
19	Kinka mine Korea	„	„	„	pale purple
20	Fuso mine Korea	„	„	quartz	dark green

1) T. ITO & K. SAKURAI : WADA's minerals of Japan. III Ed. Tokyo. (1947), 142.
2) S. MONDEN : Fluorite and Fluorite deposits. Tokyo. (1943).
3) T. MIYAZAWA : J. Mining Inst. Korea. (1941), 21.

picked out from those crushed pieces. (for example, green pieces are selected from green fluorite only). Those selected pieces are ground into powder. The powder is fused with anhydrous sodium carbonate, and fluorine-base is changed to sodium fluoride. Then it is separated into residue and solution. The residue are treated with HCl ; SiO_2, Fe_2O_3, Al_2O_3, CaO and MgO etc are treated in usual course of common rock analysis. On the other hand, Calcium salt solution is added into sodium fluoride solution and there fluorine-base is precipitated as CaF_2 and then the base is measured, but this method show low value. Following treatment of acetic acid (10%) about another powdered specimens have been done.[4),5)] In this treatment $CaCO_3$, CaO are solved and then they are measured as CaO, and Ca in pure fluorite is determined by the difference of the quantity of Ca in both cases.

b) Spectrographic analysis

The selection of spectrographic specimens has been in the same way of chemical analysis. Spectral lines were photographed for one minute in exposure by arc method, using carbon electrode and direct current. By those spectral lines, presence of minor elements were determined.

Chemical compositions of fluorites and minor components in fluorites.

a) Chemical compositions of fluorites

From foregoing methods, following results were obtained as shown in Table II. Also pure compositions* and a sum of impurities, being recalculated in 100%, are shown in Figure 1. From this figure, it is obvious that there is differences between two occurrences, crystalline and massive form. Massive specimens contain always over 2.5% of impurities. (Nos. 3, 5, 9a, 10, 11, 13 and 14). In other words, fluorite in crystal form, contains less impurities than massive one. But these facts are very common, but it will be considerable to make any suggestions on a crystallization of fluorites by following relations between impurities. In Fig. 2, comparion of weight % of impurities

* Here pure composition means CaF_2 in fluorites, and impurities indicate SiO_2, Fe_2O_3, Al_2O_3, CaO and MgO etc. But in fact it is uncertain whether those impurities are single oxides or minerals of other form.

4) S. Harada : Method of mineral analysis. Tokyo. (1941), 512.

5) J. W. Meller & H. V. Thomson : A treatise on quantitative in organic analysis. London. (1938), 721.

TABLE II. Chemical compositions in 20 fluorites.

Sample No.	Ig. loss.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	CaF_2	Total
1	0.16	tr.	0.91	0.17	tr.	0.71	97.83	99.78
2	0.62	tr.	0.08	0.32	tr.	1.02	98.42	100.46
3	0.23	tr.	1.35	0.48	non.	0.57	98.07	100.70
4	0.43	tr.	0.15	0.20	non.	1.26	97.84	99.88
5	0.22	tr.	1.53	0.57	tr.	1.20	96.98	100.50
6	0.23	tr.	0.75	0.16	non.	0.89	98.79	100.82
7	0.06	tr.	1.01	0.32	tr.	1.04	98.07	100.50
8	0.29	tr.	0.51	0.29	non.	0.75	98.59	100.43
9a	0.28	non.	0.99	0.13	non.	1.47	98.03	100.90
9b	0.27	non.	0.32	0.31	tr.	0.95	98.85	100.75
10	0.16	tr.	1.52	0.54	tr.	1.05	97.25	100.52
11	0.05	0.31	0.36	0.15	tr.	1.72	97.62	100.21
12	0.19	tr.	0.48	0.41	tr.	1.13	98.30	100.51
13	0.46	non.	1.06	0.81	tr.	1.56	96.01	99.90
14	0.35	non.	0.34	0.25	tr.	1.51	97.25	99.70
15	0.38	tr.	0.73	0.24	tr.	0.71	98.75	100.81
16	0.14	0.06	0.13	0.67	non.	0.39	99.04	100.43
17	0.03	tr.	0.45	0.16	non.	0.98	98.90	100.52
18	0.45	tr.	0.85	0.24	tr.	0.79	98.65	101.06
19	0.11	tr.	0.53	0.15	non.	0.95	98.94	100.68
20	0.08	tr.	0.92	0.10	non.	0.74	99.10	100.94

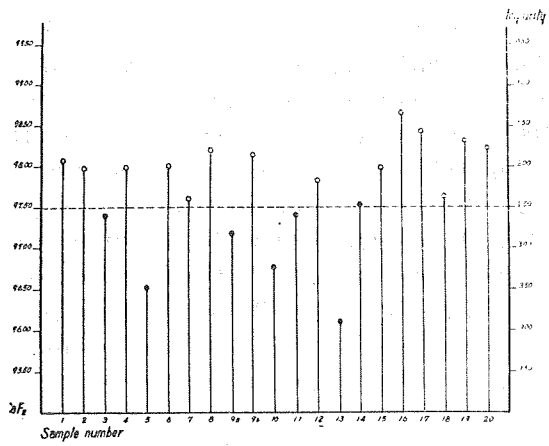

Fig. 1. CaF_2 and a sum of impurities that were recalculated in 100%.

○ : well formed crystals.
● : massive specimens.

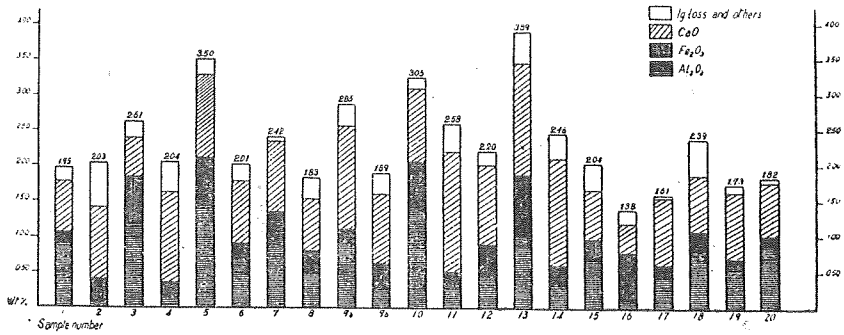

Fig. 2. Weight % of impurities in fluorites from 20 different localities.

is shown, and Figs. 3, 4 and 5 are shown on Al_2O_3-Fe_2O_3, Al_2O_3-CaO and CaO-Fe_2O_3 in weight % relations respectively, the weight % relations of Al_2O_3, Fe_2O_3 and CaO is illustrated in Fig. 6, which are recalculated in 100%.* But as it is shown in Fig. 3, 4, 5 and 6, points which indicate well formed crystals group in oval region, (oblique striated), and points which point out massive specimens (Nos. 3, 5, 9a, 10, 11, 13 and 14) scatter outside of the oval region. Even, in those relations, there are some exceptions. They are specimens of Nos. 2, 4 and 16. But specimens of Nos. 2 and 4 is a mixture of cubic crystals and massive parts respectively. But No. 16 specimen shows remarkable exception in each figures, and it is dark greenish single octahedral crystal. (an edge 15 cm). Moreover, well formed crystal has following characters in Al_2O_3-Fe_2O_3-CaO relation. Quantities of Fe_2O_3 and CaO fluctuate in small scale with increase of Al_2O_3-content. Al_2O_3-impurity varies remarkably with increase of Fe_2O_3-content, while CaO-content varies slightly. Also Al_2O_3-content shows marked fluctuation with increase of CaO-content, while Fe_2O_3-impurity shows slight variation. The crystal contains Al_2O_3 and CaO impurities in almost same quantity and less Fe_2O_3. But above relations are not seen in massive specimens. But it is still uncertain about the origin and mechanism of above relations that exist in three impurities.

b) Minor components in fluorites.

From results of spectrographic analyses, minor components in fluorites are indicated in Table III.** But only 2—3 elements are

* Al_2O_3, Fe_2O_3 and CaO are contained in fluorite as dominant impurities, so that I have inquired into relations of these compositions.

** Moreover, from the cathods-luminescence spectral lines, it had been reported that Sm, Eu, Dy, Tb, Pr, Er, Nd and Gd etc were contained in fluorites.[9]

9) J. Yoshimura : Sc. Pap. I. P. C. R. 23 (1934), 224.

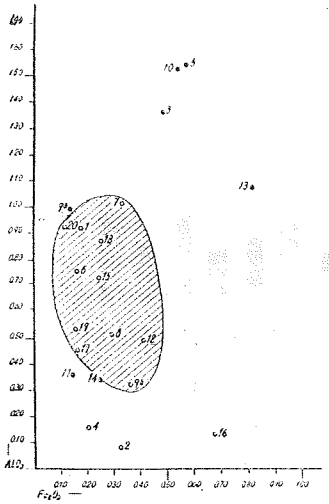

Fig. 3. Relation of Al_2O_3-Fe_2O_3 each weight %.

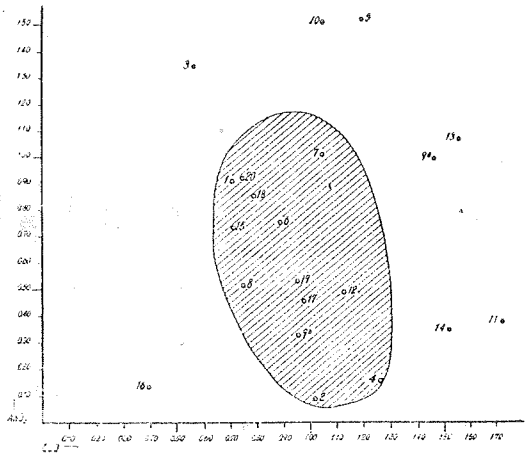

Fig. 4. Relation of Al_2O_3-CaO each weight %.

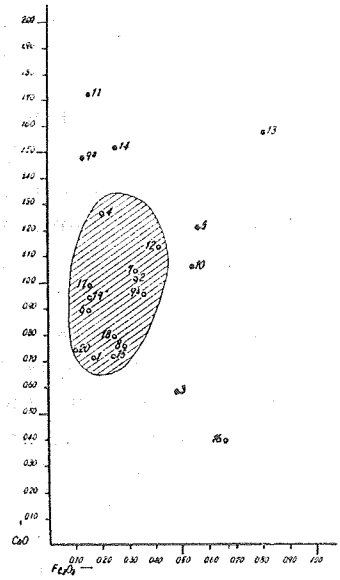

Fig. 5. Relation of CaO-Fe_2O_3 each weight %.

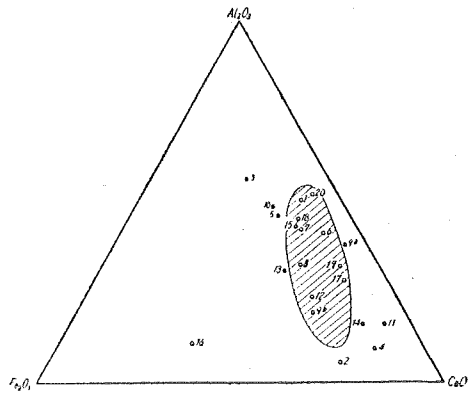

Fig. 6. Relation of Al_2O_3-Fe_2O_3-CaO impurity which are recalculated in 100%.

○ : well formed crystals.
● : massive specimens.

TABLE III. Minor components in 20 fluorites.

Sample Nos.	Contained minor elements.
1	Ni. Ru. Mn. Ti. Mg. V.
2	Ni. Ru. Mn. Ti. Mg. V.
3	Mn. Mg. V (tr).
4	Ru. Ti. V. Cd ?. Ge. Ir. Sb. Zr.
5	Ru. Mn. Ti. V. Cd ?. Ge. Ir. Sb. Zr.
6	Ti. V. Mn.
7	Ni. Ti. Mg. V. Cd ?. Ir. Sb. Co. P. Pb. Sn.
8	Ti. V. Co.
9a	Ni. Mn. Mg. V. Co. Rh (tr).
9b	Mn. Ti. Mg. Rh (tr).
10	Ni. Mn. Mg. V. Ir. Rh.
11	Mn. Ti. Mg. V. Ge. Sb ?. Zr. Mo (tr). Cu. Ba (tr).
12	Ti. Mg. V. Co. Mo. Cu. Ce.
13	Mn. Ti. Mg. V.
14	Mn. Ti. Mg. V.
15	Mn. Ti. Mg. V. Be. Ce ?.
16	Ru. Mn. V. Ge. Sb. Co. In.
17	Ni. Ru. Mn. Ti. V. Ge (tr). Ir. Sb. Zr. Co. In. P. Sn. Pb.
18	Ni. Ru. Mn. V. Ge. Sb. Co. In. P.
19	Ni. Mn. Ti. V. Co. Cu. Rh (tr). Pb.
20	Ni. Mn. Ti. V. Ge ?. Co. Cu. Rh. Pb.

possibly contained, but it is uncommon. For example, Vanadium is contained in all fluorites, and Magnesium and Manganese are found in crystallized specimens from hydrothermal ore deposits with some exceptions, and crystallized fluorites from contact ore deposits contain Antimony, Lead and Phosphorus; and Cobalt, Nickel and Indium are in coloured cubic crystals, but there are some exceptions.

Summary

On this study, chemical and spectrographic analyses of 20 different fluorites have been taken on a process to inquire the crystallization of fluorites and the relations between major and minor components, occurrences and forms etc. Many studies on chemical analyses of fluorites have been reported.[6),7),8)] But studies on relations between

chemical compositions and other properties of fluorites are few informed.[7),8),9),10)] On this study it is ascertain that there is some relations between crystallization and impurities, and well formed crystals contain less than ca 2.5% of impurities, while massive specimens more than ca 2.5%; more the major components of impurities are contained of Fe_2O_3, Al_2O_3 and CaO, fluorites in crystal forms contain a little quantity of Fe_2O_3 and nearly same amount of Al_2O_3 and CaO, and massive specimens have one or two kinds of Fe_2O_3, CaO and Al_2O_3 in large quantity. Moreover certain regularities are shown in minor elements being contained in fluorites, from crystal forms and occurrences etc, and the kinds of those elements is almost fixed. Of course there are exceptions in a few specimens.

6) C. Doelter : Handbuch der Mineralchemie. 4 (1931), 194.
7) Y. Yoshimura : J. Chem. Soc. Japan. 48 (1927), 449.
8) E. Iwase : Sci. Pap. I.P.C.R. 22 (1933), 233.
9) J. Yoshimura : loc. cit.
10) H. Haberlandt : Sitzber. Akad. W. W. M. Klasse IIa. 143 (1943), 591.