

# Dufrenite in iron-formation on the Kangnas farm, Aggeneys district, Bushmanland, South Africa

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## Abstract

An occurrence of yellowish green to green dufrenite in iron-formation from Proterozoic metamorphites on Kangnas farm near Aggeneys, Bushmanland, South Africa is described. The mineral formed by reaction between iron oxides and hydroxides and a phosphate, probably apatite. It was identified by its characteristic X-ray diffraction pattern, but microprobe analyses presented here indicate that the chemical compositions are extremely variable.

**KEYWORDS:** dufrenite, EMP analyses, Proterozoic metamorphites, iron-formation.

## Introduction

DUFRENITE is an iron phosphate with an ideal formula of  $\text{CaFe}_6(\text{PO}_4)_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$  (Moore, 1970). The pure mineral is scarce in nature and, although first described in 1833 (Nriagu, 1984), it occurs at only a few localities. In the literature it is described as a secondary phosphate at Rock Run, Cherokee County, Alabama; at Wheal Phoenix, Cornwall, England; and at deposits in Saxony, Hesse, Westphalia and Thuringia, Germany (Nriagu, 1984).

The occurrence of dufrenite at Kangnas was first mentioned by Van der Westhuizen *et al.* (1986). This paper reports results of the first investigation of this rare mineral at the former locality and presents data on its range of chemical composition, as well as its mineralogy.

## Occurrence and geological setting

Dufrenite occurs as a secondary iron phosphate in iron-formation on Kangnas farm, which is situated approximately 60 km east of the town of Springbok in Bushmanland (Fig. 1).

The Kangnas, K'oumoesk'naap (Fig. 2) and Ou-Eendop Formation (not shown in Fig. 2) form part of the Khurisberg Subgroup (SACS, 1980) which in turn is part of the Bushmanland Group (Strydom *et al.*, 1987). The Kangnas Formation represents the structurally lowermost unit and

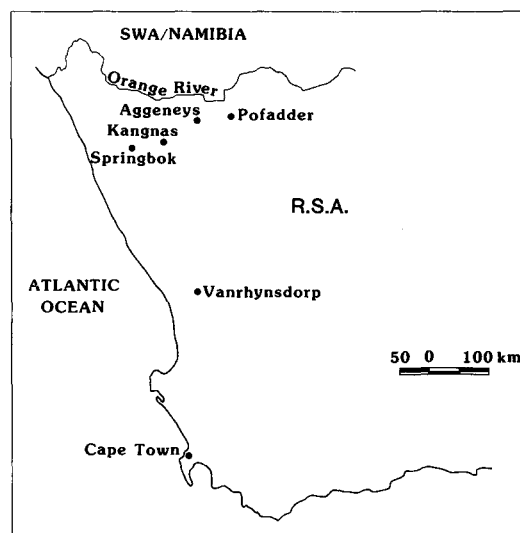


Fig. 1. Locality map of the Kangnas area in the north western Cape Province, South Africa.

overlies refoliated augen gneiss. The latter probably belongs to the Klein Namaqualand Suite (Strydom, 1985). The Kangnas Formation is approximately 70–180 m thick and can be subdivided into a basal brown quartzite unit (70–100 m thick), consisting of several second-order upward

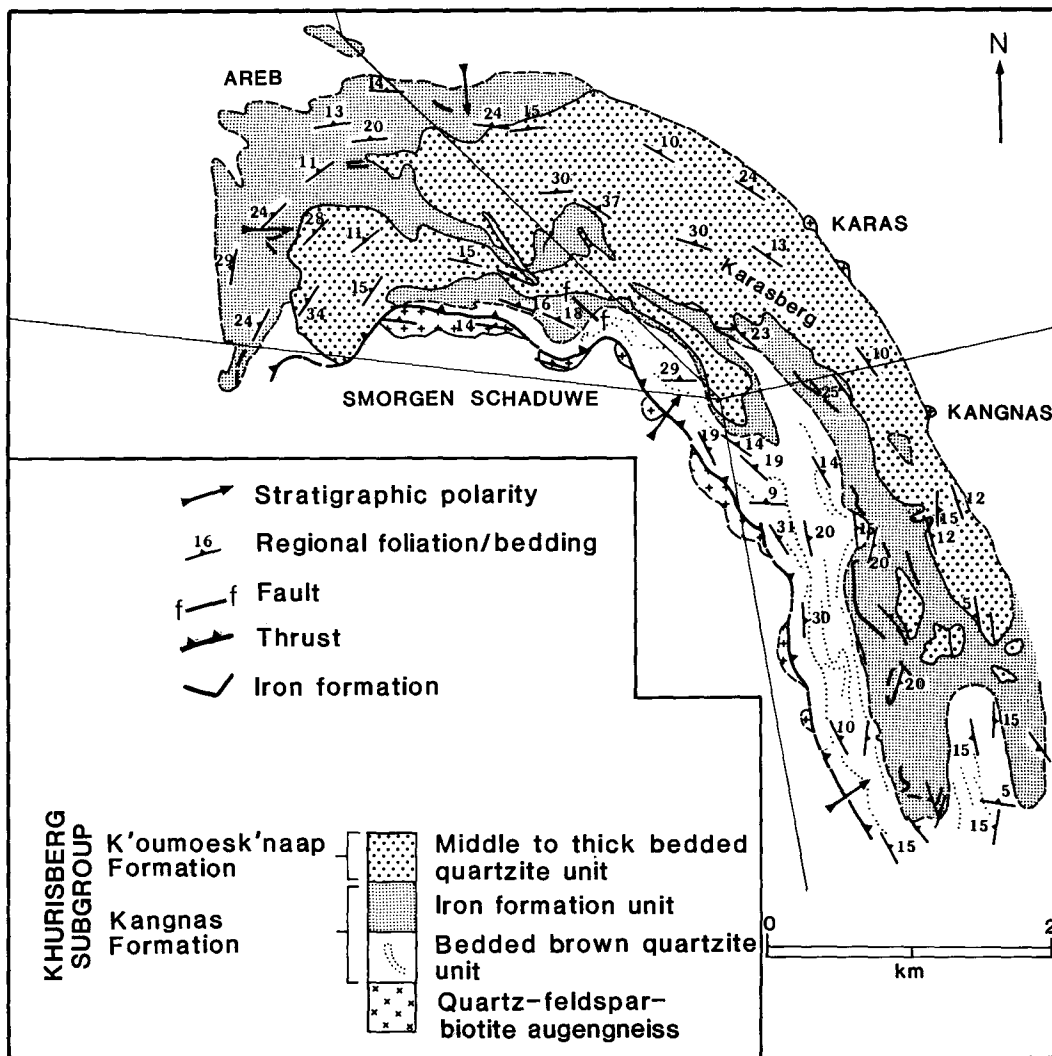


FIG. 2. Geological map of Kangnas and environs.

coarsening cycles which are composed of quartz-sillimanite-biotite schist, and thin quartzite with interbedded schist layers. The upper iron-formation unit of the Kangnas Formation consists of quartz-sillimanite-biotite schist with interbedded white to brown quartzites and iron-formation beds and lenses. The quartzites have a massive appearance, but are laminated near the contact with the overlying K'oumoesk'naap Formation. The contact between the Kangnas and K'oumoesk'naap Formations is gradational from the laminated quartzites of the former to the medium to thickly bedded quartzites of the latter.

The Khurisberg Subgroup was subjected to several episodes of complex and intense deformation, resulting in isoclinal folds. This produced a duplication of the stratigraphy at some localities (Strydom, 1985).

#### Petrographical relations

Dufrenite is a secondary mineral which predominantly occurs as small isolated, rounded grains in cracks in garnet, juxtaposed to garnet or adjacent to goethite in iron-formation (Fig. 3). Most of these grains display botryoidal features with

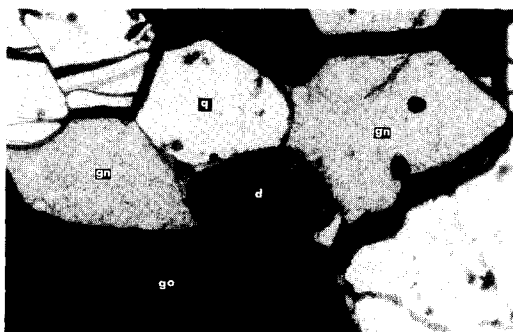


FIG. 3. Photomicrograph of dufrenite-bearing sample from Kangnas: Dufrenite (d) adjacent to garnet (gn), goethite (go), and quartz (q).

a radial fibrous structure. The grains range from 0.01 to 0.25 mm in diameter with a mean of 0.10 mm. Stringers of dufrenite also exist, but are less common than the isolated grains. This highly pleochroic mineral is green, bluish-green to yellowish-green in colour, but the variation in colour is heterogeneous.

The iron-formation in which the dufrenite occurs consists of garnet-hematite quartzite. The garnet varies in composition from predominantly spessartine to spessartine-rich almandine. Goethite is omnipresent and results from the breakdown of hematite.

#### Mineral chemistry

Electron microprobe analyses of dufrenite and associated minerals were carried out with a CAMECA CAMEBAX electron microprobe using a 15 kV accelerating voltage, 40 nA beam current and 1  $\mu$ m beam diameter. Mineral standards were used in conjunction with ZAF-correction techniques.

Due to the inability of the electron microprobe to analyse for H<sub>2</sub>O and the non-availability of sufficient amounts of material for a modified Penfield determination (Kolthoff *et al.*, 1969), the (F,OH) was accepted to be 8 and the crystal water calculated accordingly to sum to 100% total. All analyses were recalculated using the above norms and are presented in Table 1. Structural formulae were computed on the basis of 24(O,OH,F) and the charge balances calculated. All data from literature were recalculated on the basis of 24(O,OH,F) to conform with the data from Kangnas.

From Tables 1 and 2 it is evident that there is a large variation in the chemical composition of the dufrenite from Kangnas, especially in the

Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> concentrations. Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and F are prominent constituents in the samples from Kangnas, while data from the literature show that Fe<sub>2</sub>O<sub>3</sub>, MnO and CaO are more abundant elsewhere, and with the exception of a small number of samples, they are almost devoid of Al<sub>2</sub>O<sub>3</sub>. It is clear that both Al<sub>2</sub>O<sub>3</sub> and F may not always have been analysed for (see Table 1).

The correlation matrix (Table 3) which was generated from the data contained in Table 1 shows that Fe<sub>2</sub>O<sub>3</sub> has a good correlation with both P<sub>2</sub>O<sub>5</sub> and Al<sub>2</sub>O<sub>3</sub>. As both these values are negative, it may be attributed to the breakdown of goethite by Al- and phosphatic solutions and the consequent formation of dufrenite. The relationship between these elements is also illustrated by Fig. 4a where Al, P, and Fe replace one another in the structure. The replacement of Fe<sup>2+</sup> by Mn and of Fe<sup>3+</sup> by Al is also depicted in Fig. 4b. The amount of replacement of Fe<sup>2+</sup> by Mn is very small in the case of the Kangnas samples, whereas the replacement of Fe<sup>3+</sup> by Al is very low for samples from literature. When the minerals associated with dufrenite from Kangnas are considered, it is evident that the hematite contains negligible amounts of MnO, whereas the garnet is MnO-rich. End-member compositions of the garnet were calculated by the method of Rickwood (1966), while those of hematite were calculated by the method of Carmichael (1967).

Although a number of the analysed samples (Table 1 no. 6 and 13) show very high Al<sub>2</sub>O<sub>3</sub> values there is, however, a wide variation in the Al<sub>2</sub>O<sub>3</sub> content of the samples from Kangnas, ranging from 3.98 to 12.10 wt.% Al<sub>2</sub>O<sub>3</sub> (Table 2). However, only two dufrenite samples from literature contain in excess of 1 wt.% Al<sub>2</sub>O<sub>3</sub> (nos. 26 and 34). The presence of the high Al<sub>2</sub>O<sub>3</sub> in some samples makes it possible to refer to these as aluminian dufrenite. This is, as far as known, the highest concentration of Al<sub>2</sub>O<sub>3</sub> ever recorded for dufrenite; Hey (1955) reported that dufrenite sometimes contains appreciable aluminium, although he omitted any values. According to Moore (1984) replacement of Ca by Na is possible. This can also be observed in the samples from Kangnas (Table 1).

According to Frondel (1949), several basic iron phosphates have been confused with dufrenite and he redefined dufrenite as a monoclinic basic phosphate of ferric and ferrous iron (Fe<sup>2+</sup>Fe<sup>3+</sup><sub>4</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>5</sub>·2H<sub>2</sub>O). Palache *et al.* (1951), however, found that small amounts of Ca can substitute for Fe in the structure and the formula would then change and so becomes CaFe<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>5</sub>·2H<sub>2</sub>O. Moore (1970) regards

the formula for dufrenite to be  $\text{CaFe}_2\text{Fe}_{10}(\text{OH})_{12}(\text{H}_2\text{O})_4(\text{PO}_4)_8$  while Nriagu (1984) presents it as  $\text{CaFe}_6(\text{PO}_4)_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ .

### X-ray data

All the samples from Kangnas were subjected to close scrutiny by X-ray diffraction using Debye-Scherrer cameras (114.6 mm. diameter with Ni-filtered  $\text{Cu-K}\alpha$  radiation). The samples were prepared using the small-sample method of Hiemstra (1956). The  $d$ -values were measured and then compared with the data generated from the atomic coordinates of Moore (1970) by the Lazy Pul-

verix computer programme (Yvon *et al.*, 1977). These  $d$ -values also compare favourably with the data in literature (Table 4). The  $d$ -values from the Kangnas samples were subjected to the least-squares refinement programme of Appleman *et al.* (1972) for determination of cell parameters accepting a  $C2/c$  space group. These are also presented in Table 4 and clearly reflect the different phosphatic phases.

### Conclusion

Dufrenite represents a secondary phosphatic alteration product of iron oxides and hydroxides.

TABLE 1 CHEMICAL ANALYSES OF DUFRENITE AND OTHER PHOSPHATES

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
SiO2	00.30	00.70	00.34	00.25	01.19	00.82	00.40	01.16	00.34	01.69	00.32	00.40	00.16	00.33	00.00	00.00	00.00	00.00
Al2O3	04.21	05.02	05.13	04.46	04.63	12.10	07.81	09.07	08.27	03.98	08.55	07.45	11.99	07.40	00.00	00.00	00.87	00.00
Fe2O3*	49.23	54.84	48.43	48.52	65.86	39.01	42.22	42.80	44.01	48.09	42.35	43.39	38.55	43.74	56.20	63.45	53.15	55.63
MnO	00.21	00.44	00.40	00.62	00.72	00.84	00.10	00.26	00.31	00.00	00.25	00.27	00.50	00.35	06.76	00.00	00.00	00.00
CaO	00.24	00.29	00.33	00.34	00.23	01.50	00.44	00.26	00.33	00.46	00.25	00.24	00.04	00.23	00.00	00.00	01.68	01.50
Na2O	01.38	01.41	00.95	01.24	00.42	01.56	00.35	01.37	01.07	02.30	01.02	01.01	00.00	01.93	00.00	00.00	00.00	00.00
K2O	00.02	00.02	00.02	00.02	00.01	00.40	00.39	00.07	00.35	00.11	00.02	00.03	00.02	00.06	00.00	00.00	00.00	00.00
P2O5	31.87	23.66	30.81	32.28	13.09	32.64	33.18	32.16	31.52	32.90	32.50	32.67	32.78	32.27	27.84	27.72	31.10	30.26
F	02.54	02.05	01.19	02.78	00.92	02.71	01.68	02.64	03.51	00.00	03.32	02.88	03.22	02.40	00.00	00.00	00.00	00.00
H2O+	11.07	12.43	12.48	10.66	13.32	09.56	14.14	11.32	11.77	10.47	12.82	12.87	14.10	12.30	09.20	08.83	13.20	12.61
Total	101.07	100.86	100.80	101.17	100.39	101.14	100.71	101.11	101.48	100.00	101.40	101.21	101.36	101.01	100.00	100.00	100.00	100.00
F=O	-01.07	-00.86	-00.80	-01.17	-00.39	-01.14	-00.71	-01.11	-01.48	-00.00	-01.40	-01.21	-01.36	-01.01	-00.00	-00.00	-00.00	-00.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
STRUCTURAL FORMULAE TO THE BASIS OF 22(O,OH,F)																		
Si	00.05	00.11	00.05	00.04	00.21	00.12	00.06	00.17	00.05	00.25	00.05	00.06	00.02	00.05	00.00	00.00	00.00	00.00
Al	00.75	00.95	00.92	00.79	00.96	02.03	01.38	01.57	01.46	00.68	01.51	01.31	02.10	01.30	00.00	00.00	00.16	00.00
Fe3+	05.58	06.64	05.55	05.47	08.70	04.19	04.75	04.72	04.96	05.28	04.76	04.89	04.30	04.92	06.60	07.33	06.19	06.52
Mn	00.03	00.06	00.05	00.08	00.11	00.10	00.01	00.03	00.04	00.00	00.03	00.03	00.06	00.04	00.89	00.00	00.00	00.00
Ca	00.04	00.05	00.05	00.05	00.04	00.23	00.07	00.04	00.05	00.07	00.04	00.04	00.01	00.04	00.00	00.00	00.28	00.25
Na	00.04	00.44	00.28	00.36	00.14	00.43	00.10	00.39	00.31	00.65	00.30	00.29	00.00	00.56	00.00	00.00	00.00	00.00
K	00.00	00.00	00.00	00.00	00.00	00.07	00.07	00.01	00.07	00.02	00.00	00.01	00.00	00.01	00.00	00.00	00.00	00.00
P	04.06	03.22	03.97	04.09	01.95	03.94	04.20	03.99	04.00	04.06	04.11	04.14	04.11	04.08	03.68	03.60	04.08	03.99
F	01.66	01.43	01.27	01.81	00.70	01.68	01.09	01.68	02.29	00.00	02.16	01.88	02.08	01.56	00.00	00.00	00.00	00.00
OH	06.34	06.57	06.73	06.19	07.30	06.32	06.91	06.32	05.71	08.00	05.84	06.12	05.92	06.44	08.00	08.00	08.00	08.00
SUM	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00
H2O	02.39	03.39	02.98	02.23	04.15	01.39	03.60	02.37	03.02	01.09	03.47	03.37	04.01	02.91	00.79	00.52	02.82	02.55
n	20.00	06.00	03.00	08.00	03.00	07.00	10.00	10.00	10.00	13.00	10.00	05.00	05.00	05.00				
STRUCTURAL FORMULAE TO THE BASIS OF 22(O,OH,F)																		
SAMPLE No.	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	
SiO2	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	02.64	
Al2O3	00.00	00.00	00.21	00.29	00.00	00.00	00.00	04.44	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	01.75	
Fe2O3*	58.30	61.55	57.67	57.62	56.94	57.97	54.74	49.42	64.74	47.53	62.02	59.14	80.03	66.49	79.86	73.58	52.73	
MnO	00.00	00.00	00.40	00.24	02.24	02.84	05.51	00.20	00.00	00.45	00.00	02.09	00.00	00.00	00.00	00.00	02.61	
CaO	00.00	00.00	01.12	00.00	00.00	00.00	00.99	00.64	00.00	05.71	00.00	00.00	00.00	00.00	00.00	00.55	02.84	
Na2O	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	
K2O	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	
P2O5	31.80	31.82	31.76	31.66	32.86	30.43	31.87	31.26	28.39	32.40	27.71	25.20	06.25	20.11	05.66	13.69	15.90	
F	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	
H2O+	09.96	06.63	08.84	10.19	07.96	08.76	10.09	14.04	06.87	13.91	10.27	13.57	13.72	13.40	14.48	10.17	24.39	
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
F=O	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	-00.00	
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
STRUCTURAL FORMULAE TO THE BASIS OF 22(O,OH,F)																		
Si	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.51	
Al	00.00	00.00	00.04	00.05	00.00	00.00	00.00	00.80	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.36	00.00	
Fe3+	06.59	06.77	06.47	06.53	06.31	06.60	05.91	05.69	07.32	05.56	07.26	07.30	10.47	08.51	11.77	09.55	07.72	
Mn	00.00	00.00	00.05	00.03	00.28	00.36	00.71	00.03	00.00	00.06	00.00	00.29	00.00	00.00	00.00	00.04	00.25	
Ca	00.00	00.00	00.18	00.00	00.00	00.00	00.16	00.10	00.00	00.95	00.00	00.00	00.00	00.00	00.00	00.10	00.59	
Na	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	
K	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	
P	04.05	03.94	04.01	04.04	04.10	03.90	04.11	04.05	03.61	04.26	03.65	03.50	00.92	02.90	00.94	02.00	02.62	
F	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	
OH	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	
SUM	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	08.00	
H2O	00.90	00.77	00.39	01.12	00.09	00.42	01.12	03.17	-0.56	03.21	01.32	03.43	3.95	03.60	05.46	01.85	11.83	

1-14, dufrenite from Kangnas; 15-20, dufrenite, Table 3, Frondel, 1949; 21-24, rockbridgeite, Table 9, *ibid.*; 25-28, unidentified dufrenite-like minerals, Table 11, *ibid.*; 29-35, altered dufrenite and rockbridgeite, Table 12, *ibid.* FeO from literature converted to Fe<sub>2</sub>O<sub>3</sub> to correspond to format of kangnas samples from present study.

Table 2. Statistical parameters of the chemistry of dufrenite and related phosphates.

Data from Kangnas				
VARIABLE No.	Name	MEAN	STANDARD DEVIATION	SMALLEST VALUE
1	Si	.6000	.4541	.1600
2	Al	7.1479	2.7219	3.9800
3	Fe3	46.5029	7.0937	38.5500
4	Mn	.3764	.2327	.0000
5	Ca	.3700	.3407	.0400
6	Na	1.1436	.6110	.0000
7	K	.1100	.1492	.0100
8	P	30.3093	5.4974	13.0900
9	F	2.3257	.9629	.0000
Largest Value				
1	Si	.6000	.4541	.1600
2	Al	7.1479	2.7219	3.9800
3	Fe3	46.5029	7.0937	38.5500
4	Mn	.3764	.2327	.0000
5	Ca	.3700	.3407	.0400
6	Na	1.1436	.6110	.0000
7	K	.1100	.1492	.0100
8	P	30.3093	5.4974	13.0900
9	F	2.3257	.9629	.0000
Literature				
1	Si	.1257	.5761	.0000
2	Al	.3600	1.0232	.0000
3	Fe3	60.2648	8.8376	47.5300
4	Mn	1.0710	1.9000	.0000
5	Ca	.7157	1.3772	.0000
6	Na	.0000	.0000	.0000
7	K	.0000	.0000	.0000
8	P	25.9852	8.5273	5.6600
9	F	.0000	.0000	.0000

Table 3. Comparison of correlation matrices of kangnas dufrenite with data from literature.

	Kangnas	Literature
SiO2 - F	- 0.7438	0.0000
Al2O3 - Fe2O3	- 0.7356	- 0.1789
Fe2O3 - P2O5	- 0.9006	- 0.8051

TABLE 4. D-VALUES AND UNIT CELL PARAMETERS OF DUFRENITE FROM VARIOUS LOCALITIES.

	1	2	3	4
12.30	12.00			
6.90	6.78	6.92		
6.54	6.41	6.46		6.46
6.10	5.99	6.11		
5.59		5.54		
5.05	5.00	5.06		5.00
4.84	4.80	4.85		
4.40	4.35	4.40		4.40
4.15	4.11	4.16		4.20
4.04		4.05		
3.79	3.76	3.79		3.80
3.67		3.68		
		3.63		
3.54	3.51			
3.42	3.39	3.44		3.39
3.24	3.21	3.24		3.20
3.17	3.15	3.18		3.16
3.01	2.99	3.007		2.990
2.88	2.86			2.86
2.81	2.795			
2.64	2.627			
a <sub>0</sub>	24.60	25.84	25.79	25.00
b <sub>0</sub>	5.14	5.126	4.88	5.18
c <sub>0</sub>	13.87	13.78	13.71	14.02
β	100°25'	111°12'	109°46'	111°34'

1. First 20 reflections; dufrenite from Hirschberg, Germany (JCPDS, 1980).
2. First 18 reflections; dufrenite from Cornwall, England (JCPDS, 1980).
3. Dufrenite from Kangnas (Meyer, 1986) sample LKG-009.
4. Dufrenite from Kangnas, this study, DKAG-16.

It occurs mostly as botryoidal fibres and masses, commonly associated with goethite and less often with magnetite and/or hematite. The mineral displays a large colour variation from green to yellow.

A comparison of the unit cell dimensions and consequently the cell volume indicates a large variation in these parameters. At present insufficient data are available to bring unit cell dimensions and chemistry into relation with each other.

From Table 1 it is evident that 'pure dufrenite' very seldom occurs in nature. Dufrenite could better be regarded as a general term encompassing iron phosphates displaying the characteristic dufrenite X-ray powder pattern, as the chemical composition is too variable to absolutely define its chemical ranges. From the data presented (Table 1) it seems that Ca substitution as proposed by Moore (1970) and Nriagu (1984) is minor even in samples reported as "pure dufrenite". The present authors have shown that substitution by other elements, viz. Al, Ca, Na, Si and Mn, also takes place.

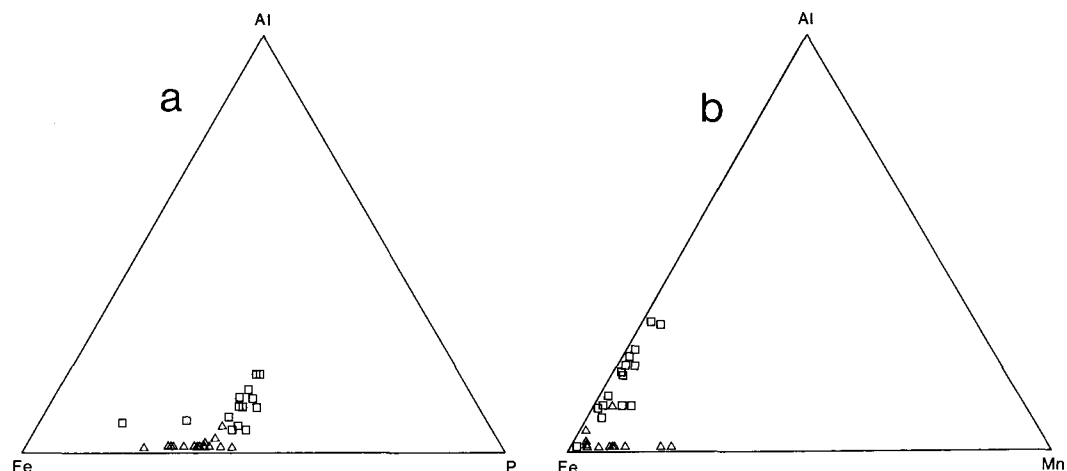


FIG. 4a. Ternary relationship between Al, Fe and P in dufrenite from Kangnas (squares) and other phosphates from literature (triangles)—Table 1. FIG. 4b. Similar diagram of Al, Fe and Mn for dufrenite from Kangnas (squares) and phosphates from literature (triangles)—Table 1.

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