

GEOCHEMISTRY OF SOME KYANITES FROM BRAZIL¹

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ABSTRACT

Minor elements and optical properties have been determined for seventeen kyanite samples; major elements were determined for five samples. Twelve samples are from the Quadrilátero Ferrífero of Minas Gerais, divided as follows: 4 from phyllites, 4 from veins in phyllite, and 4 from veins in low metamorphic grade quartz-rich rock. For comparison, 1 kyanite from a magnesite deposit in Bahia and 4 from high-metamorphic-grade areas in Minas Gerais were also analyzed.

Associated with the kyanite in the phyllite is quartz and muscovite, with or without chlorite, chloritoid, and pyrophyllite. Kyanite in veins is associated with quartz with or without muscovite and pyrophyllite, and may represent a "recrystallization pegmatite."

Compared to the other samples, kyanite from phyllite has a great relative abundance of minor elements including a high content (>100 ppm) of Cr, Fe, V, Mg, Ti, Zr, Na, Ca and K, which are also common in the country rock. Kyanite in veins has abundant Cr, Mg, Fe, Na and K, and some Ge which suggests pneumatolytic conditions. The sample from the magnesite deposit has the highest Be of all, 22 ppm; high Ca, Cr, Mg, V, Zr, Fe, K and Na; and some Ge. The samples from high-metamorphic-grade areas show only high V and Mg (Fe, K, Na not analyzed for).

Replacement of some kyanite by pyrophyllite took place both in veins and in the country rock. The formation of pyrophyllite must have been favored while the system cooled at the end of the cycle of intrusion and deformation.

INTRODUCTION

Evidence from field occurrences of the three Al_2SiO_5 polymorphs in metamorphic rocks indicates these relative conditions of formation: high pressure and moderate temperature for kyanite, low pressure and low temperature for andalusite, and moderate pressure and high temperature for sillimanite (Miyashiro, 1949). Probably because of the slow reaction rates, the data from laboratory experiments have indicated higher temperatures of formation than are suggested by field conditions (Clark, *et al.*, 1957; Clark, 1961).

Kyanite is a common mineral in the Quadrilátero Ferrífero area of the central part of the State of Minas Gerais, Brazil, where it is the only Al_2SiO_5 polymorph found in any great quantity and occurs in veins, phyllites, quartzites, and rock of higher metamorphic grade. The samples studied from this area are from low-grade metamorphic rocks that range from the chlorite to the biotite isograd; or the quartz-albite-epidote-biotite or the quartz-albite-epidote-almandine subfacies of the

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greenschist facies (Turner and Verhoogen, 1960, p. 537-541). The T-P conditions suggested for this facies (p. 534) are 300°-500° C. and $P_{H_2O} = 3$ to 8 kilobars, which is lower than that determined for kyanite in the experimental work, but is more reasonable for conditions of metamorphism in the Quadrilátero Ferrífero.

The authors wish to express their indebtedness to the Conselho Nacional de Pesquisas do Brasil for making the instruments available for the spectrographic work, to the various geologists named in Table 1 who collected the samples, to E-An Zen, U. S. Geological Survey, for x-ray diffractometer determination of some of the pyrophyllite, and to F. J. Turner both for many helpful discussions of the problems and for critically reading the manuscript. The study was carried out under the auspices of the Agency for International Development of the U. S. Department of State.

GEOLOGIC SETTING

The geology of the Quadrilátero Ferrífero has been described in greater detail by various authors in Departamento Nacional da Produção Mineral, 1959, and the descriptions below are from that publication. Chemical analyses of low grade pelitic rocks from this area have also been published (Herz, 1962) and the average of those analyses are used in this paper (Table 5 and elsewhere). Kyanite-bearing rocks referred to here however are probably more Al-rich than this average.

The stratigraphic section in the Quadrilátero Ferrífero consists of three Precambrian series, separated by major unconformities: the oldest Rio das Velhas, the Minas, and the youngest Itacolomí. Four kyanite samples are from the Rio das Velhas which consists of a lower, largely mica schist and phyllite group, and separated by an angular unconformity, an upper, largely quartz sericite schist, graywacke, and quartzite.

The Minas series includes the basal Caraça Group, the Itabira Group, and the uppermost Piracicaba Group. One kyanite sample is from a vein in the basal Moeda Formation which consists of quartzite with sericite-rich beds. Six samples are from the Cercadinho, the basal formation of the Piracicaba Group. This formation is separated by a disconformity from the underlying Itabira Group and consists of ferruginous quartzite and phyllite. Phyllite in the lower part of the Piracicaba Group shows a great abundance of Al_2O_3 , averaging over 20%, which may have been largely inherited from a regolith that marked the disconformity.

One sample is from the Itacolomí Series which is largely composed of quartzite with minor phyllite.

The kyanite samples were collected in two general areas of the Quadrilátero Ferrífero: the Moeda syncline in the western part (8 samples), and

TABLE 1. SAMPLE DESCRIPTIONS

Sample Number	Locality	Description of Mineral	Inclusions	Occurrence and Associated Minerals	Notes
K-1	Lagôa Grande	Pale blue, up to 2 cm	Qz, pyr	In veins with qz, pyr rosettes, musc. Cuts Cercadinho phyllite. Chlor isograd	coll. by R. M. Wallace
K-2	Lagôa Grande	dark gray, to 0.8 mm	Qz, pyr, opaques some hex-shaped and platy, parallel ky-prism, most irregular	In Cercadinho phyllite with chlord-musc-chlor-qz	coll. by R. M. Wallace
K-3	Catas Atlas	very pale blue, to ± 1 cm	Qz, pyr	In veins with qz, pyr rosettes, musc. Cuts Rio das Velhas phyllite. Biot isograd	coll. by C. H. Maxwell
K-4	Casa de Pedra	very pale blue core, dull white rim, to +2 cm	Qz, manganese films on some grains	In veins with qz, pyr. Cuts Itacolomí qz-musc-mag phyllite with ky-gar-chlor-musc porphyroblasts	coll. by P. W. Guild, (1957)
K-5	Capanema	moderate blue or bluish green, to ± 2 cm	qz	In veins with qz. Cuts quartzite of Maquiné Group (Rio das Velhas Series). Biot isograd	coll. by C. H. Maxwell
K-6	Itabirito	elongate dark prisms, to 1 cm.	similar to K-2	In Cercadinho phyllite with musc-chlor-qz. Most ky has parallel orientation, some in rosettes	coll. by N. Herz
K-7	Lagôa Grande	pale blue, to ± 2 cm	qz, pyr	In veins with qz, pyr, musc. Cuts Cercadinho musc-chlor-ky-qz phyllite	coll. by R. M. Wallace
K-8	Itabirito	very pale blue, to ± 4 cm	qz, pyr	In veins with qz, pyr, musc and phyllite breccia. Cuts Cercadinho musc-chlor-ky-qz phyllite in brecciated area	coll. by N. Herz
K-9	Casa de Pedra	pale to moderate blue, to ± 15 cm	none	In veins with qz. Cuts Moeda quartzite and phyllite, with qz-musc-chlor-some fuchsite nearby tourmaline veins, granite contact. Chlor isograd	coll. by N. Herz (Guild 1957)
K-10	Capanema	light greenish gray, to 8 cm	Qz, pyr	In veins with musc. qz, pyr. Cuts Cercadinho ferruginous qtz and phyllite. Biot isograd	coll. by C. H. Maxwell

Localities: samples K-1 to K-12 are from the Quadrilátero Ferrífero, Minas Gerais. Quadrangles and geological formations are from Departamento Nacional da Produção Mineral, 1959.

Descriptions: colors are from the Geological Society of America Rock-Color Chart, 1951.

Inclusions and Occurrences: qz=quartz, pyr=pyrophyllite, musc=muscovite, chlor=chlorite, chlord=chloritoid, biot=biotite, mag=magnetite, ky=kyanite. Pyrophyllite replaces kyanite where listed.

Notes: coll=collected. All are members of the U. S. Geological Survey except M(anoel) T(eixeira) da Costa and F(ernando) Peixoto, Instituto de Tecnologia Industrial, Belo Horizonte, M. G., Brazil.

TABLE 1—(continued)

Sample Number	Locality	Description of Mineral	Inclusions	Occurrence and Associated minerals	Notes
K-11	Capanema	small, dark, elongate prisms under 1 mm	musc	In fine grained Moeda or Rio das Velhas phyllite. Biot isograd	coll. y C. H. Maxwell
K-12	Capanema	fine needles in dark gray phyllite, under 1 cm	Qz, chlor	Forms rosettes on foliation plane of phyllite. Has appearance of fibrolite. Biot isograd	coll. by C. H. Maxwell
K-13	Pirajá, Brumado district, Bahia	pale blue, to 3 cm	Qz	Associated with qz at center of magnesite deposit. Fills open fissures; grown on qz crystals with beryl, tourmaline, topaz	coll. by R. M. Wallace (Bodenlos 1954)
K-14	Patrus Mine, Diamantina, Minas Gerais	very pale to light blue, to 5 cm	Qz	In veins with qz, pyr, musc. Cuts musc-rich quartzite, near Gouvêa granite	coll. by M. T. da Costa
K-15	Capelina, M. Gerais	medium dark gray, to 7 cm	Musc and opaques	In veins with musc, qz. Cuts high-metamorphic-grade schists	coll. by M. T. da Costa
K-16	Itamarandiba, M. Gerais	light medium bluish gray, to 13 cm	Musc, qz	In veins with musc, qz. Cuts high metamorphic grade schists	coll. by M. T. da Costa
K-17	Mathias Barbosa, M. Gerais	"dark blue", av. 3 cm, to 12 cm		Information not available	coll. by F. Peixoto

the region south and east of the Serra do Caraça in the eastern part (4 samples) (see map in Departamento Nacional da Produção Mineral, 1959). Both areas underwent strong structural deformation (p. 96). The general grade of metamorphism is the chlorite or biotite zones of the greenschist facies. In some places, however, especially near contacts with granitic rocks and in the eastern part, assemblages with staurolite and garnet are found.

Kyanite in metamorphosed Al-rich pelitic rocks is associated with quartz and muscovite. In low metamorphic zones, chlorite, chloritoid, pyrophyllite in part replacing kyanite, and opaque minerals, may also occur (Fig. 1); in higher metamorphic zones, garnet, and biotite or tremolite.

In veins, kyanite is found with quartz, with or without muscovite and pyrophyllite. Some kyanite is as much as 15 centimeters in length, but the largest crystals are commonly bent or broken. Where it is present, pyrophyllite is abundant, forming rosettes and appearing to replace kyanite (Figs. 2, 3).

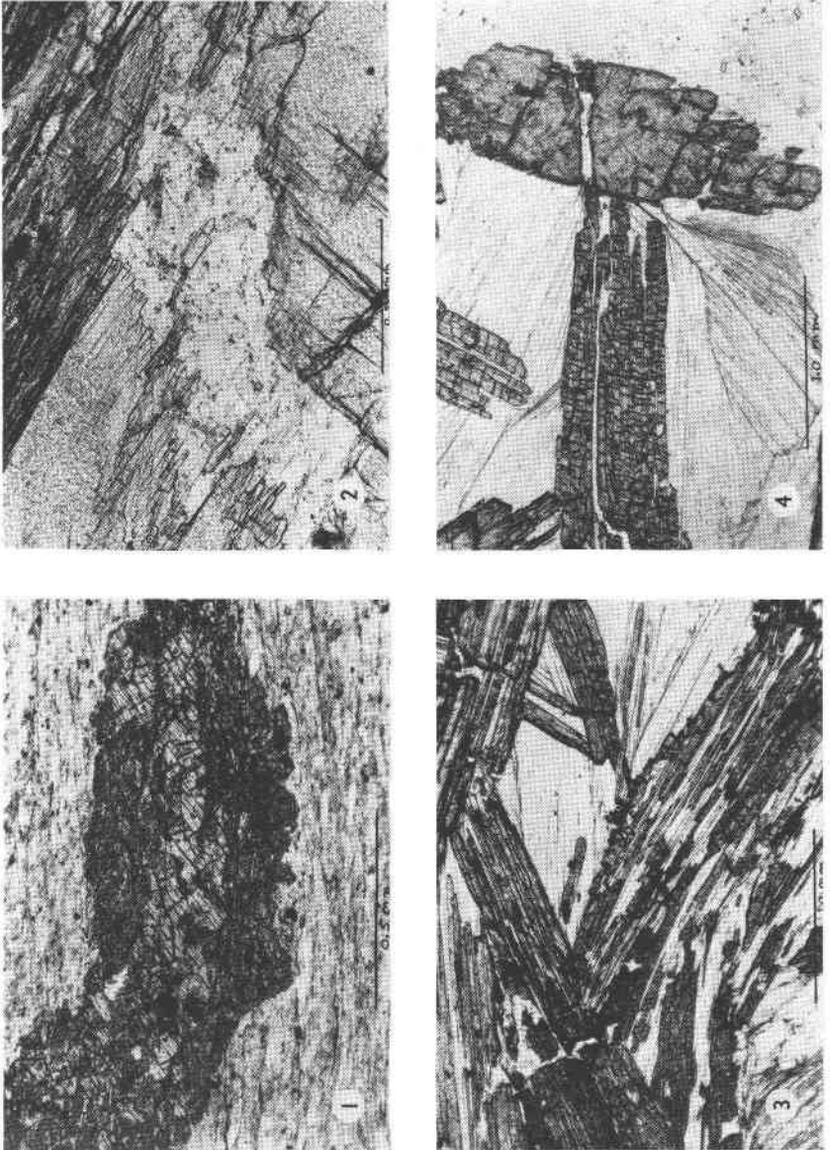


FIG. 1. Photomicrograph showing remnants of kyanite in chlorite-sericite-quartz phyllite. Kyanite partly replaced by a micaceous material that may be largely pyrophyllite. Plane light, sample from near K-2, line is 0.5 mm.

FIG. 2. Photomicrograph showing early stages of replacement of kyanite by pyrophyllite in a quartz-kyanite vein. Pyrophyllite follows fractures and cleavages in kyanite. Plane light, K-7, line is 0.5 mm.

SAMPLE PREPARATION

Samples were selected from the kyanite-rich parts of country rock, or large crystals from veins (Table 1), ground to -100 , $+200$ mesh, and then purified with heavy liquids and a magnetic separator; samples with much micaceous material were panned. Various separatory techniques were repeated until the amount of foreign grains present was less than about 3 per cent.

Much of the kyanite contained inclusions, especially of quartz, but also of opaque material and pyrophyllite. The opaque matter could not be identified with x -rays. Quartz inclusions in the purified samples, judging by excess SiO_2 in the chemical analyses (Table 3), ranges up to 6.8 per cent by weight.

The phyllite has exceptionally high K_2O , averaging 4.8 per cent (Herz, 1962), so that if it did comprise the inclusions, then K-2 should have much higher K_2O than the other samples. Actually it has less (Table 3) than samples from a vein in phyllite (K-1) and in quartz-rich rocks (K-9). If 5% of the kyanite were inclusions of phyllite then this should be contributed to the total kyanite analysis:

SiO_2	3.06%
Al_2O_3	1.02
Fe_2O_3	0.165
FeO	0.148
MgO	0.120
CaO	0.004
Na_2O	0.012
K_2O	0.240
TiO_2	0.025
P_2O_5	0.004
MnO	0.002

There is little relationship between these values and those of K-2. K-2 has higher Fe_2O_3 and TiO_2 than the above values which suggests that the inclusions may be iron and titanium oxides, also indicated by their hexagonal-appearing outlines.

FIG. 3. Photomicrograph showing various stages of replacement of kyanite by pyrophyllite. Plane light, K-9, line is 1 mm.

FIG. 4. Photomicrograph showing well crystallized pyrophyllite, in rosettes and also filling fractures in kyanite. Plane light, K-9, line is 1 mm.

TABLE 2. RESULTS OF SPECTROGRAPHIC ANALYSIS OF KYANITE FROM BRAZIL. ANALYST C. V. DUTRA, INSTITUTO DE TECNOLOGIA INDUSTRIAL, BELO HORIZONTE

rÅ d.l.	Ba		Ca		Co		Cr		Cu		Ga		Ge		Mg		Mn		Nb		Ni		Sc		Sn		Sr		V		Y		Zr	
	1.43 2	0.33 2	0.99 2	0.72 2	0.63 1	0.72 1	0.62 5	0.50 10	0.66 5	0.60 3	0.69 30	0.69 2	0.69 2	0.81 2	0.71 10	1.16 3	* 10	0.92 10	0.79 2															
a) K-2	7	nd	130	3.5	350	10	31	nd	420	8	35	25	4	24	16	95	25	330																
-6	0	nd	250	nd	190	13	21	nd	280	14	34	13	nd	38	15	140	39	170																
-11	0	nd	64	nd	600	1.9	13	nd	97	13	nd	39	10	nd	nd	330	19	190																
-12	3.1	nd	130	nd	410	3.7	49	nd	750	7	64	20	5.5	58	8.5	190	31	380																
K-1	nd	nd	7	nd	63	4.0	14	72	2400	7	nd	3.6	nd	nd	nd	34	nd	§																
-3	2	nd	~1.5	nd	140	13	27	nd	65	3	nd	~1.5	nd	nd	nd	65	nd	~1.5																
-7	2.7	nd	14	nd	130	3.2	30	44	72	4	nd	9	nd	12	nd	44	nd	~1.5																
-8	4.4	nd	60	2.4	120	6.4	16	67	3300	14	nd	nd	nd	nd	nd	44	nd	~1.5																
K-4	10	nd	110	~1.5	51	16	33	31	140	420§	nd	41	nd	nd	nd	30	nd	52																
-5	27	nd	150	13	2200	3.2	16	nd	160	86	nd	27	~1.5	nd	19	500	nd	13																
-9	14	2.2	64	nd	470	1.9	19	nd	280	35	nd	nd	nd	nd	19	95	nd	10																
-10	2.7	nd	7	nd	29	2.2	33	15	990	56	nd	4.4	nd	nd	nd	16	nd	5																
K-13	13	22	240	nd	330	10	36	22	460	21	84	19	nd	nd	12	900	nd	300																
K-14a	nd	nd	nd	nd	51	3.2	21	18	180	7.6	nd	6	nd	nd	nd	38	nd	nd																
-14b	3.6	nd	110	nd	34	5.3	43	10	180	25	nd	nd	nd	nd	4.2	30	nd	nd																
-15	3.6	nd	180	nd	120	4.8	28	nd	290	4	46	nd	nd	nd	4.2	30	nd	nd																
-16	nd	nd	nd	nd	96	3.2	27	28	110	8	nd	nd	~1.5	nd	170	nd	10	320																
-17	nd	nd	nd	nd	35	3.5	28	10	130	nd	nd	7	nd	nd	170	nd	10	nd																

In parts per million (ppm); rÅ = radius in Ångströms (Green, 1959). * = $V_6 = 0.74 \text{ \AA}$, $V_6 \pm = 0.59 \text{ \AA}$; d.l. = approximate detection limit (in ppm); nd = not detected; § = largely due to Mn film; looked for but not found: Ag, Au, Pb, La, Li, Mo, Ta, Th, W, and Zn.

ANALYTICAL METHODS

Twenty-eight minor elements were sought in each kyanite sample by spectrographic analysis, but ten were always below the detection limits (Table 2); the work was carried out by Dutra in the laboratories of the

TABLE 3. RESULTS OF CHEMICAL ANALYSIS OF FIVE KYANITE SAMPLES FROM BRAZIL. ANALYST: FERNANDO PEIXOTO, INSTITUTO DE TECNOLOGIA INDUSTRIAL, BELO HORIZONTE

	K-1	K-2	K-3	K-9	K-13
SiO ₂	37.3	36.7	36.9	37.77	37.0
Al ₂ O ₃	62.0	61.5	62.6	61.70	62.6
Fe ₂ O ₃	0.63	1.51	0.37	0.50	0.37
TiO ₂	n.d.	0.18	n.d.	t	t
K ₂ O	0.10	0.06	0.04	0.18	0.03
Na ₂ O	0.03	0.04	0.10	0.43	0.02
Total	100.1	100.0	100.0	100.58	100.0

Composition on the basis of 20 oxygen

rÅ						
0.40	Si	4.03	3.96	3.97	4.070	3.98
0.51	Al	7.89	7.82	7.94	7.836	7.92
0.64	Fe ³⁺	0.052	0.117	0.032	0.039	0.032
0.68	Ti	—	0.013	—	—	—
1.42	K	0.013	0.007	0.005	0.026	0.003
0.97	Na	0.007	0.007	0.019	0.091	0.003
0.66	Mg	0.065	0.011	—	0.008	0.012
0.79	Zr	—	0.003	—	—	0.002
0.99	Ca	—	0.002	—	—	0.004
0.63	Cr	—	0.005	0.002	0.006	0.004
1	V	—	—	—	0.001	0.012

6.4% quartz by weight deducted from K-1, 6.8% from K-2, 2.7% from K-3, and 2.8% from K-13. Values for Mg, Zr, Ca, Cr, and V in second part of table from spectrographic data. n.d.=not detected, t=trace, rÅ=ionic radius in Ångstroms, ¹=V³⁺=0.74Å, V⁵⁺=0.59 Å

Instituto de Tecnologia Industrial, Belo Horizonte, M.G., Brazil. The technique and precision of determination have been described elsewhere (Herz and Dutra, 1960). To minimize the difference in composition between the samples and the granite standards used in that previous study, the kyanite samples were mixed with a "sodium-quartz" base (10% Na₂CO₃+90% SiO₂) in a 1:1 proportion. These preparations were then further mixed in a ratio of 2:1 of sample to spectroscopically pure graphite.

Six major elements were determined for five samples (Table 3); the work was carried out under the supervision of Fernando Peixoto in the laboratories of the Instituto de Tecnologia Industrial. CaO, MgO, and MnO were also sought in these analyses, but were below the sensitivity of wet chemical methods. Some small amounts of MnO were detected, but

TABLE 4. OPTICAL DATA OF KYANITE FROM BRAZIL AND PYROPHYLLITE REPLACING KYANITE. n.r. = NO PYROPHYLLITE REPLACING KYANITE. SAMPLES ARRANGED AS IN TABLE 2

Sample Number	α	β	γ	$2V^\circ$	$Z/\wedge c$	2V of pyrophyllite
K- 2	1.708	1.716	1.720	82	29.5	60
- 6	1.710	1.718	1.722	80	29	60
-11	1.710	1.719	1.724	80	29	n.r.
-12	1.707	1.715	1.720	80	30	n.r.
K- 1	1.710	1.719	1.724	79.5	29.5	58.5
- 3	1.710	1.718	1.722	79.5	27.5	55
- 7	1.714	1.722	1.727	80	28.5	52
- 8	1.711	1.720	1.726	79.5	27.5	63
K- 4	1.709	1.717	1.722	79	30	n.r.
- 5	1.713	1.722	1.727	79	29	n.r.
- 9	1.711	1.719	1.724	78	30	n.r.
-10	1.710	1.719	1.724	77	29.5	61
K-13	1.714	1.723	1.728	77	31	n.r.
K-14	1.706	1.714	1.719	82	29.5	n.r.
-15	1.709	1.717	1.722	82	28.5	n.r.
-16	1.710	1.719	1.724	81	29	n.r.
-17	1.711		1.725			n.r.

the results of spectrographic analysis were used instead because of a higher precision.

Optical determinations (Table 4) were done by Herz. Indices of refraction were determined with immersion liquids having an .005 interval, using sodium light. These are believed accurate to $\pm .001$. $2V$ and $Z/\wedge c$ determinations were made with a 4-axis universal stage on grain mounts cemented on glass slides. An average of 6 determinations was made for each $2V$ and $Z/\wedge c$ value shown; the results have a precision of $\pm 1.5^\circ$.

RESULTS OF ANALYSES

There is no correlation between the optical and chemical data, nor between optical data and modes of occurrence. The total variation in the optical data is so small that much of it is mitigated by precision of the determinations. Accordingly, these data will not enter into the rest of the discussion.

The following elements were looked for and not found; their approximate limit of detection is shown in parts per million: Ag (1), Au (20), Pb (10), La (30), Li (200), Mo (10), Ta (200), Th (200), W (200) and Zn (200).

The minor element abundance in kyanite of chlorite (K-2 and K-6) and biotite (K-11 and K-12) zone phyllites are similar (Table 2a). Kyanite is dependent on the bulk chemical composition of the original metasediment and is found only in rocks with high Si and Al. Cr, Fe, V, Mg, Zr, K, Ca, Ti and Na are also relatively abundant in both the country rock and the kyanite formed in it (compare with Table 5, col. 2). Kyanite found in phyllites has the greatest amount and variety of elements substituting in the 6-coordinated Al-position.

Germanium, which suggests the intervention of aqueous fluids, was found in five of the vein kyanite samples (Table 2b, c) with an abundance about the same as in greisen, that is 35 ppm (Rankama and Sahama, 1950, p. 731). The appearance of kyanite rather than pyrophyllite as an early phase in these veins indicates, according to the experiments of Carr and Fyfe (1960), temperatures above 470° C at $P_{H_2O} = 2,150$ bars, the upper limit for pyrophyllite. The greisen-like conditions suggested by Ge abundance are consistent with these data.

Minor elements that are abundant in both the phyllite and its kyanite are generally less abundant in vein kyanite (Table 2a, b) except for Mg in K-1 (2400 ppm) and in K-8 (3300 ppm). Vein kyanite in phyllite may represent a continuation of the period of crystallization of kyanite in the country rock, similar to the "recrystallization pegmatites" of Ramberg (1952). The fact that these veins are restricted to rocks that already contain kyanite and commonly occur in shear zones suggests this. Kyanite in other veins studied are in quartz-rich rocks that had an excess of Si and perhaps also excess Al compared to alkalis. Apparently crystallizing in veins, under pneumatolytic conditions the kyanite accommodated fewer minor elements than it did in phyllites.

Minor elements in vein kyanite cutting quartz-rich rocks (Table 2c) are, in general, similar to those in veins in phyllite. The major differences are high Cr in K-5 (2200 ppm) and K-9 (470 ppm) which has the only Be found in any Cuadrilátero Ferrífero sample (2.2 ppm). The vein kyanite

in quartz-rich rocks also has generally higher Zr, V, Ni, Mn, alkalies and alkaline earths.

The high value for Cr in K-5 was confirmed by a re-run which showed 2300 ppm. The greenish color of this sample is also evidence for a high Cr content. High Cr, K and Na and the presence of Be in K-9 may be attributed to pneumatolytic solutions from a nearby granitic intrusion; fuchsite, associated with the kyanite, also suggests a high Cr in these solutions.

The sample from Bahia, K-13, occurs in an open fissure vein lined by quartz crystals in a magnesite deposit and is assumed to have crystallized at low pressures (Bodenlos, 1954).

Precise data on the geologic settings of the samples from highly metamorphosed areas (Table 2e) are not available. These kyanite samples are taken from veins and, in four of the five analyses, Ge was found which suggests pneumatolytic processes. In general, the variety and abundance of minor elements are low.

DISCUSSION OF MINOR ELEMENTS

Only Be and Ge probably occupy Si-sites in the kyanite lattice, because both have small radii and 4-fold coordination. Ga, Cr, Fe, Mg, Ni, Mn, Ti and Nb may substitute in the Al-sites; Ba, Ca, K, Na, Sc, Sr and Y are too large to substitute; and Co, Cu, Sn and Zr may also be too large. V can substitute for Al, if it is in a highly oxidized state (5+).

Averages shown for minor elements in kyanite (Table 5) are both as parts per million, and as a percentage of the amount present in the average pelite of the Cuadrilátero Ferrífero. The elements are grouped below in order of increasing ionic radius (from Green, 1959).

Ionic radius 0.60–0.69 Å, 6-fold coordination. Cr, Ga, and Fe³⁺ are expected to substitute easily for Al since they have a 3+ charge, 6-fold coordination, and ionic radii similar to Al. Ga occurs in about the same abundance in both country rock and kyanite; Cr is relatively abundant in all kyanite. Quantitatively, Fe is one of the most, if not the most, abundant accessory element. These elements, and most of the others are more abundant in kyanite in phyllite than in kyanite from any other environment.

Ga is known to follow Al closely so that the order of abundance in kyanite should be about three-fold more than in the phyllite. However, phyllite with 10.7 per cent Al has 30 ppm Ga (Table 5); kyanite with 32.9 per cent of Al only averages 26 ppm of Ga. Pearson and Shaw (1960, p. 814) also noted a deficiency of Ga in all three Al₂SiO₅ polymorphs, with kyanite having the least of all, 38 ppm.

Mg and Ni have 6-fold coordination and ionic radii similar to Al, but only a 2+ charge. Mg is abundant in all samples and is the most abundant minor element in many. Ni is also relatively abundant except in the higher temperature vein kyanite.

TABLE 5. AVERAGE ABUNDANCE OF ELEMENTS IN KYANITE

Expressed as (a) ppm. and (b) percentage of abundance of element in Quadrilátero Ferrifero pelites (column 2). Elements in each group arranged according to increasing ionic radius. Based on Tables 2 and 3

Element	Average pelite	Average 2a		Average 2b		Average 2c		Average 2e ²		Method of Substitution
		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	
Be	1	nd	0	nd	0	nd	0	nd	0	ad } Si-site cam }
Ge	2	nd	0	46	2300	12	600	(13)		
Ga	30	29	97	22	73	25	83	29	97	cam } Al-site
Cr	300	390	130	110	37	(690)		(65)		
Fe	46,000	10,600	23	3500	8	3500	8	na		Al-site
V	200	190	95	45	23	(160)		130	65	
Mg	1400	390	28	(1500)		390	28	180	13	ad } Al-site
Ni	100	24	24	4	4	(18)		3	3	
Cu	20	7	35	7	35	6	30	(12)		Al-site
Co	9	nd	0	nd	0	(4)		nd	0	
Mn	300	11	4	7	2	59 ¹	20	(7)		cap } Al-site
Ti	3000	1080	36	nd	0	t		na		
Nb	nd	(33)		nd	—	nd	—	nd	—	Al-site
Sn	nd	(30)		nd	—	nd	—	nd	—	
Zr	200	270	135	2	1	(20)		nd	0	
Sc	9	5	56	nd	0	nd	0	nd	0	? ? radius ion >>>
Y	30	29	97	nd	0	nd	0	nd	0	
Na	1800	300	17	480	27	3200	178	na		Al
Ca	500	140	28	(21)		(83)		(59)		
Sr	300	(10)		nd	0	(10)		2	0.7	
K	40,000	500	1.5	580	1.5	1500	4	na		
Ba	900	7	0.8	2	0.2	13	1.4	1	0.1	

() = value not meaningful, difference between high and low > 10 × (nd counts as 1)

nd = 3 or 4 analyses showed nd (not detected)

na = not analysed for

¹ = excluding K-4.

² = K-14a, K-14b count as 1 sample

t = trace

ad = admission, cam = camouflage, cap = capture.

Mn⁴⁺ and Ti⁴⁺ are much less abundant in most kyanite compared to the country rock.

Nb⁵⁺ is abundant in kyanite in phyllite and is not found in either the country rock or in the vein kyanite. Nb only occurs when Zr is above 170 ppm; samples with Nb below its detection limit (about 30 ppm) also have less than 52 ppm Zr with only one exception, K-11 with 190 ppm Zr. The

enrichment of Nb compared to Zr in kyanite (Table 6) is higher than the 1/10 ratio observed by Goldschmidt for igneous rocks (1954, p. 504).

Ionic radii 0.71–0.81 Å, 6-fold coordination. Co²⁺ was rarely found in kyanite, probably because of its low tenor in the country rock (9 ppm). Cu²⁺ was detected in all kyanite samples; the country rock averages 20 ppm Cu.

V is one of the most common trace elements in kyanite, found in about the same order of abundance as in country rock (200 ppm).

Sc³⁺ is neither abundant in the kyanite nor in the country rock. Sn⁴⁺ was only detected in 3 samples from phyllite and 1 from a vein in phyllite and is not found in the country rock.

TABLE 6. Nb/Zr RATIOS

Sample	Nb/Zr
K- 2	.106
K- 6	.200
K-12	.168
K-13	.280
K-15	.144

Zr⁴⁺ is as abundant in kyanite in phyllite as it is in the phyllite itself (200 ppm). It is greatly reduced in abundance in other environments except for one high metamorphic grade sample and the sample from Bahia.

Ionic radius > 0.92 Å. Y³⁺ was found only in kyanite from phyllite and in one high metamorphic grade sample. It commonly occurs together with La (Rankama and Sahama, 1950, p. 517) but La was not detected in any sample, perhaps because of the limit of detection of the method used (30 ppm).

Ca²⁺ ionic radius 0.99 Å, Sr²⁺ 1.16 Å, and Ba²⁺ 1.43 Å, are all present to some extent. They are much more abundant in phyllite than in kyanite, and their relative abundance in kyanite decreases in order of increasing ionic radius. To a large extent, Sr follows Ca and is only present when at least 64 ppm of Ca is also found.

Na¹⁺ and K¹⁺ are among the most abundant of the accessory elements. Other authors also noted this (as Pearson and Shaw, 1960) but without any satisfactory explanation of the mechanism of substitution. Most probably, very large ions occupy voids in the lattice rather than substitute for Al in a 6-coordinated position.

PYROPHYLLITE REPLACING KYANITE

In many samples pyrophyllite replaces some kyanite (Figs. 1-4). In thin sections, kyanite is first replaced around its edges and along cleavages (Figs. 1, 2). With advancing replacement, kyanite becomes more ragged and pyrophyllite better crystallized (Fig. 3). Initially, pyrophyllite occurs in small flakes, but with advanced replacement, it assumes larger forms that are in optical orientation (Fig. 4).

The reaction $\text{Al}_2\text{SiO}_5 + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ would be favored by decrease in temperature or increase in partial pressure of water. The appearance of pyrophyllite must be correlated with some stage after kyanite formed during the main folding (with maximum tectonic overpressure) or subsequent pneumatolytic activity (vein formation). Coexistence of relict kyanite and pyrophyllite suggests incomplete reaction while the system cooled along the curve of univariant equilibrium on a $P_{\text{H}_2\text{O}}\text{-T}$ diagram. Such a course implies difficulty of access of water in a rock rendered impermeable by metamorphic recrystallization.

CONCLUSIONS

The data suggest some general conclusions regarding a) the formation of kyanite at low grades of metamorphism and b) the replacement of Al by minor elements in the kyanite lattice.

Formation of kyanite and pyrophyllite. The pelitic rocks of the Quadrilátero Ferrífero are characterized by high Al_2O_3 , averaging 20.3 per cent, and low CaO, averaging 0.07 per cent (Herz, 1962). A compositional plot on an ACF diagram would fall near the A-F join. The rocks containing kyanite have probably even higher Al than this average. The basal Cercadinho Formation, which lies on an unconformity and contains the highest amount of kyanite of any rock, may have originated as a saprolite which lost most of its alkaline earths and alkalis, except for K_2O . Elsewhere, where aluminum silicates and quartz comprise the bulk of the country rock, a similar origin has been suggested (Zen, 1961).

This rock was metamorphosed at high pressures and moderate temperatures coexistent with the greenschist facies. Kyanite formed from country rock that had unusually high Al and Si in troughs of synclines, where the tectonic overpressure was greatest. The vein kyanite later formed under lower pressures, but with perhaps higher temperatures. This vein kyanite also fills breccia zones and may be related to Ramberg's (1952, p. 252) "recrystallization pegmatites," which crystallize in shear zones, under the influence of pneumatolytic solutions, but with little introduction of new material. The following assemblages with kyanite resulted:

- a) quartz-kyanite
- b) quartz-muscovite-kyanite
- c) quartz-muscovite-kyanite-pyrophyllite
- d) quartz-muscovite-kyanite-chlorite-(pyrophyllite)
- e) quartz-muscovite-kyanite-chlorite-(chloritoid)-(pyrophyllite)

a), b), and c) are typical of veins; d) and e) of phyllite.

Replacement of aluminum by minor elements. Contrasting the quantity and abundance of minor elements in kyanite in various geologic settings (Tables 2, 5), replacement took place most readily under comparatively low temperatures and high pressures that prevailed during the earlier metamorphic phases in the Quadrilátero Ferrífero. Under these conditions, minor elements substituted in the kyanite lattice with great ease by camouflage, admission, capture, and even unknown processes. Apparently under high nonhydrostatic stress, the kyanite lattice was more disordered and admitted more exotic ions. Furthermore, such stress effectively augments the "load" pressure, and so favors a higher coordination of ions, reflected by the abundance of ions whose radius is much greater than aluminum.

For kyanite that crystallized in veins, under probable pneumatolytic conditions, that is lower total pressure, and perhaps higher temperature, Ga, Cr, V and Fe, which substitute Al by camouflage, are all important minor elements.

Mg is the most abundant of the elements that may be admitted to or capture Al-sites. This is in apparent contradiction to the Goldschmidt rules of trace element behaviour (1954) which predict that higher charged ions substitute more readily, but is explained by Ringwood's (1955) extension of the Goldschmidt rules, that is, electronegativity is the most important factor governing substitution after similarity of ionic radii. Ions with smaller electronegativities, that is a greater tendency to form ionic bonds, will be preferentially incorporated into the lattice. The electronegativity of Mg is 1.2, compared to 1.5 for Al, which is lower than any of the other elements in Table 5 except for the alkalis and alkaline earths (Pauling, 1948 p. 65), all of which, however, have exceptionally large ionic radii.

Except for Na and K, elements with radii appreciably greater than Al are not abundant.

In veins, Ge is abundant, substituting presumably for Si.

Other studies by Pearson and Shaw (1960), probably largely on vein material and from high grade schists, and by Hietenan (1956), on kyanite from schists of high metamorphic grade, have revealed relatively high Mg, Cr, V and Ga. The only other elements found by Hietenan were K,

Ba, Fe and Cu. The results of both studies agree very well with the results presented here.

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