TRACE ELEMENTS IN KYANITE, SILLIMANITE AND ANDALUSITE

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Abstract

12 Kyanites, 3 sillimanites and 7 andalusites were analysed spectrographically for various minor and trace-elements. Ga, Cr, Mg, Ti, Li, Cu, V, Zr and Mn could be measured in most samples; B, Be and Ba were found in several; Ni, Co, Mo, Sn, Ag, Y, Sc, Sr and Pb were usually below detection limit. No indisputable differences in trace-element contents were found, but andalusite probably contains less Cr, whereas B, Be and Ba may be concentrated in sillimanite. It is unlikely that trace elements are factors in the polymorphic relations between these minerals.

The trace element distribution in aluminum silicates can in general be explained by crystal chemical considerations, but V is rather more abundant than might be expected. Li and B are unexpectedly rich in many samples, suggesting origin under pneumatolytic or greisen conditions: both Li and B could however have come from the parent sediments.

One of each of the minerals was analysed chemically. Slight deficiencies of Al with respect to Si can be explained by substitution of minor and trace-elements for Al. Alkali metals are present in small amounts but Jakob's hypothesis that they are essential constituents is untenable.

Introduction

The polymorphic minerals kyanite, sillimanite and andalusite present a problem in the interpretation of their stability-fields and the bearing this has on general questions of metamorphism. All three have been synthesised during the last few years but much remains to be learned of their manner of formation. It appeared worth while to examine their content of some minor and trace-elements, to enquire whether there might be any systematic differences of crystal chemical significance.

Samples

The samples are listed in Table 1: precise localities were not available for many. In two cases the specimens were visibly pure gem-quality crystals, but most of the other samples were coarse-grained aggregates, rich in the principal mineral but containing abundant impurities. In several at least two of the aluminum silicates were present.

Hand-specimens were crushed and sieved, retaining the fraction between 100 and 200-mesh stainless steel sieves. Magnetic and heavy liquid separation followed. The greatest difficulty was experienced in separating the aluminum silicates from each other, but repeated fractionation in diluted liquids gave nearly pure concentrates. Purity was checked continually by grain mounts in immersion oils, and in the final samples the grains were counted to estimate impurities and contamination.

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TABLE 1. SAMPLE LOCALITIES, DESCRIPTIONS AND PURITY

Sample	Locality	Description	Mineral ex-tracted	Impure grains %	Foreign grains %	Comments on mineral extracts
E 1	S. Dakota	Pink A with a little white mica.	A	4.2	*	S and mica inclusions
E 2	Spain	Pink A with veinlets of S and muscovite.	A S	3.5 6.5	*	S inclusions A inclusions
E 3	Switzerland	Massive A with gray K and a little muscovite.	A K	2.5 —	2.6 —	Limonite stain, K and mica inclusions Quite clean
E 4	California	Pale blue bladed K with muscovite and magnetic oxides.	K	9.0	*	A, muscovite and quartz inclusions
E 5	Germany	Blue bladed K in limonitic quartz-muscovite aggregate.	K	0.5	*	Quartz and muscovite inclusions
E 7	Wyoming	Blue gray bladed kyanite in schist also containing staurolite and micas.	K	8.4	*	Biotite, staurolite inclusions
E 9	S. Dakota	Coarse pink A with quartz and muscovite.	A	5.3	5.0	S, mica grains and inclusions
E 10	Brazil	Blue gem crystal of K with limonite stain.	K	5.0	*	Limonite stain
E 11	Brazil	Green gem crystal of A.	A	*	*	Quite clean
E 12	N. Carolina	Coarse blue K in two-mica schist.	K	20.0	*	Mica inclusions
E 13	White River Jct., Vermont	Coarse blue K with limonite stain in two-mica garnet gneiss.	K	2.0	0.1	Limonite stain
E 14	Clarkesville, Georgia	Large blue-gray crystal of limonite-stained K.	K	8.0	0.5	Limonite stain, mica inclusions
E 15	Dillon, Montana	Fibrolite with two micas, quartz and microcline.	S	*	1.7	Limonitic A grains present
E 16	White Mts., Mono Co., Calif.	Massive A with diaspore and muscovite	A	3.8	*	K and mica inclusions
E 17	Salamanca, Spain	Coarse pink-green A with muscovite and chlorite	A	12.0	3.1	Mica, chlorite grains and inclusions
E 18	Broken Hill, N.S.W.	Fibrolite-muscovite-quartz-iron oxide schist.	S	10.0	*	Muscovite inclusions
E 19	Big Joco River, 25 miles NW of Mattawa, Ont.	Kyanite-biotite gneiss.	K	14.0	*	Quartz, mica, graphite inclusions
E 20	Kake Kippawa, near Timiskaming, Ont.	Kyanite-biotite gneiss	K	7.1	*	Quartz, mica inclusions
E 21	Near E 19	Green K, green mica and pyrite	K	7.0	*	Mica, pyrite inclusions
L 73	1 mile SSE of North Thetford, N. H.	Coarse blue K in biotite gneiss	K	9.1	*	Quartz inclusions

About 350 grains counted in each case.
* Not detected.
— = No information.

TABLE 2. DETERMINATIONS OF Cr BY DIFFERENT METHODS

Sample	Analysts		Sample	Analysts	
	Shaw	Pearson		Shaw	Pearson
E 3	6 ppm	12 ppm	E 2A	* ppm	17 ppm
E 4	27	35	E 15	83	43
E 5	39	46	E 18	140	95
E 7	180	210			
E 10	50	67	E 1	*	10
E 12	11	19	E 2B	*	11
E 13	33	43	E 3A	*	14
E 14	9	8	E 9	8	7
E 19	—	105	E 11	78	62
E 20	11	21	E 16	14	17
E 21	170	200	E 17	14	11
L 73	35	72			

ANALYTICAL METHODS

The following elements were determined, using quantitative spectrographic methods: B, Be, Ga, Cr, Ti, Li, Mg, V, Cu, Zr, Mn, Ba, Sr. In addition the following were sought but were usually absent: Ge, Y, Pb, Mo, Ag, Ni, Co, Sc, Sn.

The methods have already been described (Pearson, 1955; Shaw, 1959). The latter reference describes a general method for silicates, which was modified in this instance by using standards made from a pure silica-alumina matrix. Precision was from 5–15% of amount present for most elements. Some elements (Ga, Cr, Ti, V, Cu, Zr, Mn) were determined several years apart by different analysts using different methods: the agreement was generally satisfactory, as may be seen from the example in Table 2, which gives the two sets of analyses for Cr (averages of triplicate determinations). The two sets of data were averaged in each case to give the values in Table 3. The results on Be, Mg and Ti were obtained by averaging the results on two different spectral lines.

DISCUSSION

The significance of contamination must first be discussed. The data in Table 1 showed that most of the samples were free of foreign grains, but usually contained intergrowths. In no case did the admixed mineral, whether an inclusion or alteration, constitute more than 1/20 of the host grain, as estimated under the microscope: the volume of the contamination would thus be about $(1/20)^{3/2}$ or about 1%.[1] If 10% of all grains in-

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[1] This assumes a spherical particle embedded in a larger sphere.

clude such intergrowths the total impurity amounts to about 0.1% by volume or 0.2–0.3% by weight. Thus the total contribution of the impurity to the analysis of the host mineral would be 2000–3000 ppm, including both major and minor elements.

One might therefore expect that the less pure samples, as counted with the microscope, should in fact show no clear evidence of contamination, when compared with the apparently quite clean samples. This is seen to be the case, if specimens E 3B and E 11, both of which appeared quite pure, are compared with E 12 and E 17, which contain respectively 20 and 12% of intergrowths. The trace-element suite of the latter pair show no marked differences from the previous pair, even for Mg, Ti and Li, which might be expected from mica contamination. It may perhaps be concluded that contamination is not as serious as first inspection of Table 1 would suggest, but it must nevertheless be borne in mind throughout the following discussion.

The average trace-element contents of the three minerals are presented in Table 4, which includes abundances in the crust and in pelitic rocks (the latter from Shaw, 1954, 1956). The distribution of some elements in individual mineral groups is rather erratic (e.g. Ti in kyanite, Table 3), and the significance of the averages is therefore uncertain. In addition

TABLE 3. TRACE-ELEMENT ANALYSES OF 12 KYANITES, 3 SILLIMANITES AND 7 ANDALUSITES

Sample Number	.23	.35	.62	.63	.66	.68	.68	.72	.74	.79	.80	1.12	1.34	r Å
	10	.5	2	5	30	5	30	.5	10	5	5	10	5	Sensitivity (ppm)
	B	Be	Ga	Cr	Mg	Ti	Li	Cu	V	Zr	Mn	Sr	Ba	
E 3B	*	tr.	55	9	250	240	94	6.2	36	tr.	20	*	58	
E 4	tr.	tr.	54	31	280	2,500	190	1.3	23	85	6	130	tr.	
E 5	*	*	25	43	65	420	43	1.0	40	7	8	*	5	
E 7	*	*	34	190	1,600	580	*	1.5	100	20	29	*	14	
E 10	*	tr.	28	59	70	42	38	.2	83	tr.	7	*	tr.	
E 12	tr.	*	29	38	60	250	tr.	.1	25	92	49	*	3	
E 13	*	tr.	34	15	63	100	120	1.2	93	tr.	6	*	tr.	
E 14	*	tr.	29	9	43	58	110	8.4	31	tr.	6	*	5	
E 19	*	—	24	105	—	450	*	4.2	54	tr.	11	—	—	
E 20	*	tr.	66	16	45	150	*	.2	5	26	5	*	tr.	
E 21	*	*	61	180	170	44	*	3.1	100	22	4	*	tr.	
L 73	*	*	12	54	46	33	tr.	1.5	90	tr.	20	*	5	
E 2A	170	25	95	17	100	51	150	7.9	110	tr.	17	*	6	
E 15	20	tr.	70	63	1,900	280	140	4.1	90	11	13	tr.	77	
E 18	30	2	33	120	35	830	*	2.9	150	180	12	*	31	
E 1	25	*	210	10	130	280	250	4.5	8	tr.	11	*	tr.	
E 2B	16	2	58	11	150	81	220	1.9	45	tr.	12	*	tr.	
E 3A	—	—	61	14	—	160	190	13	56	tr.	30	—	—	
E 9	*	*	62	8	170	86	96	2.5	36	tr.	5	*	*	
E 11	*	*	75	70	160	140	tr.	3.0	46	8	5	*	tr.	
E 16	tr.	*	45	16	tr.	3,200	71	8.3	51	280	10	tr.	5	
E 17	10	*	69	13	300	110	580	2.9	35	tr.	34	54	33	

Triplicate analyses, expressed in ppm.
* Below detection limit.
— = no data.
tr. = trace.

TABLE 4. AVERAGE TRACE-ELEMENT CONTENT OF KYANITE, SILLIMANITE AND
ANDALUSITE COMPARED WITH THE CRUST AND PELITIC ROCKS

Element	Ky	Sill	Andal	C	Reference	Pelite
B	*	73	10	3	Goldschmidt (1937)	3–300
Be	tr.	9	*	2	Sandell (1952)	4
Ga	38	66	83	19	Shaw (1957)	19
Mg	220	680	160	12,500	Goldschmidt (1937)	15,120
Cr	62	67	20	100	Shaw (1954)	110
Ti	410	390	580	4,400	Goldschmidt (1937)	4,900
Li	55	110	210	29	Horstmann (1957)	55
Ni	tr.	tr.	tr.	80	Sandell & Goldich (1943)	64
Co	*	*	*	23	Sandell & Goldich (1943)	18
Mo	*	*	*	1	Kuroda & Sandell (1954)	—
Sn	*	*	*	2	Onishi & Sandell (1957)	—
Cu	2.6	5.0	5.2	70	Sandell & Goldich (1943)	18
V	57	120	40	100	Shaw (1954)	120
Zr	24	65	45	156	Degenhardt (1957)	200
Mn	14	14	15	1,000	Green (1953)	540
Sc	tr.	tr.	tr.	15	Shaw (1954)	14
Ag	*	*	*	0.1	Goldschmidt (1937)	—
Y	tr.	tr.	tr.	40	Fleischer (1955)	—
Sr	tr.	tr.	tr.	450	Turekian & Kulp (1956)	710
Pb	tr.	tr.	tr.	15	Wedepohl (1956)	16
Ba	10	38	9	250	Green (1953)	570

it seems unwise to use statistical methods to test apparent differences between species, both on this account and also because of the small number of sillimanite specimens.

Looking first at differences between the three minerals, the data of Tables 3 and 4 show that the elements Ga, Ti, Cu, Zr and Mn are clearly at about the same concentration-level in each. However B, Be, Cr, Li, Mg, V and Ba appear to show differences. In calculating the averages in Table 4 all analyses were used, including those where the element in question was below the detection limit (*tr* was assigned a figure equal to the sensitivity limit). This procedure appears reasonable where an element is distributed in a fairly regular manner, but in the case of Li, for example, the range in concentration in kyanite is so great that the average calculated in this manner (55 ppm) differs considerably from that obtained from averaging only the analyses where Li was detected (99 ppm). In consequence, the averages for B, Be, Li and Ba have little real value. Inspection of the individual analyses does however suggest that sillimanite might be richer in B, Be and Ba than either kyanite or andalusite, but that is the most that can be said.

Every analysis however showed presence of Cr, Mg and V. Andalusite

definitely contains less Cr than either of the other two. The three silli-manite analyses suggest that the mineral may be somewhat enriched in V, but that the Mg-average is unduly affected by one high value.

It must be concluded that the results show no indisputable differences in trace-element values between the three minerals, but there is a possible concentration of B, Be and Ba in sillimanite and a probable paucity of Cr in andalusite. These results suggest that minor and trace-elements can not be considered as factors influencing the polymorphic behaviour of the minerals.

Comparing the minerals with the crust of the earth, the elements studied fall into three groups:

Ga, B, Li are distinctly enriched in the aluminum silicates,

Be, Cr, V show about the same abundance in both,

Mg, Ti, Ni, Co, Mo, Sn, Cu, Zr, Mn, Sc, Y, Sr, Ba are more abundant in the crust.

Comparing with the average pelitic sediment, the position is the same, except for B and Li which have passed into the category of elements with no clear enrichment either way. In addition, if the Al_2O_3 contents of aluminum silicate, the crust and pelitic rocks are taken as 62.2, 15.34 and 16.95% respectively, then the Ga/Al ratios are 1.7, 2.3 and 2.1×10^{-4}.

In part these results are what would be expected. Thus the larger ions Sc, Y, Sr, Ba, would not be expected to find lattice sites in these minerals, where the largest major metal is Al, and whose coordination numbers are 6 and 6 in kyanite, 6 and 5 in andalusite, and 6 and 4 in sillimanite.

Mn occurs in only small amounts in the minerals analysed and does not exceed 50 ppm. It should be noted however that manganandalusite containing 3.63% MnO_2 has been reported by Odman (1950), from a manganese-rich environment. Other occurrences of manganandalusite are also known, but the writers know of no occurrences of Mn-kyanite or Mn-sillimanite. It is probable that Mn^{+2} cannot substitute for Al^{+3} to any notable extent and that extensive Mn-Al substitution requires the smaller ion Mn^{+4} which forms only in strongly oxidising environments.

The elements Mg, Ti, Ni, Co, Mo, Sn, Cu, Zr, Li and V customarily oc-cupy 6-coordinated positions in ferromagnesian minerals, and might therefore be expected to substitute for Al. All except the last two however show concentrations much lower than the parent pelitic rocks from which these minerals usually form. This must be attributed to a greater attrac-tion to the micas and garnets, which generally form at the same time. Al^{+3} is a smaller ion than Mg^{+2}, and even in 6-fold coordination the lattice sites must be "smaller" than in most ferromagnesian minerals. This also accounts for the fact that Cr^{+3} and Ga^{+3} (both small ions) show average and high concentration in the aluminum silicates. The usual close co-

herence of Ga and Al however does not explain why Ga concentrates less than Al in these minerals (see Ga/Al ratios).

The data are not adequate to discuss Be with profit. The remaining elements are Li, V and B. The concentration of Li may in part be attributed to a prior concentration in pelitic rocks with respect to the crust. The figures in Table 4 however suggest that there is in many cases a further concentration into the aluminum silicates formed during recrystallisation of shales, etc. It may be that the source rocks of the silicates with high Li-values were themselves richer than normal, but in any case one would again expect Li to be preferentially concentrated in the accompanying micas. It should be added that the quantities of Li involved are much too great to be explained by mica contamination, even if the mica were lepidolite. The radii of Li^{+1} and Al^{+3} are .68 and .51 Å respectively and mutual substitution would hardly be expected on crystal chemical grounds. The overall Li average is 110 ppm if all samples are included, and 170 ppm if the samples with undetectable Li are discarded.

V would not be expected to substitute for Al any more than would Li, if in its usual valence state V^{+3} (radius .74 Å): its radius however changes to .63 and .59 Å for V^{+4} and V^{+5}, respectively. These smaller ions are closer to the size of Al^{+3}, but there is no evidence that V is in an oxidised state except in supergene and sedimentary minerals. In any case the concentration of V in the minerals is less than in the crust, and is noticeable only by contrast with such an element as Ni, which is completely excluded.

The data is rather equivocal for B, but six samples showed values well in excess of the crust. These almost certainly reflect formation from marine shales, which are well-known to be rich in B, but the location of the B-atoms, ions or radicles in the minerals is uncertain. Minute tourmaline inclusions could readily be the explanation, but although tourmaline occurs very commonly with sillimanite none was observed under the microscope in these samples.

The concentration of both Li and B in several samples suggests crystallisation in the presence of fluids similar to those which form greisen or pneumatolytic deposits (the same effect is more prominently displayed by scapolite, which also is rich in B and Li).

It may be concluded that all the elements examined, with the exception of B, Be and Ba, probably occur at Al lattice sites: Be might alternatively replace Si, while the significance of B and Ba is uncertain.

Two kyanites and one andalusite were analysed for Ba, Cr, Cu, Ga and V by Hietanen (1956). She found similar amounts of Ba and Cu, but lesser amounts of Cr, Ga and V, by comparison with the writer.

Major element analyses of three samples are given in Table 5. The only

noteworthy constituents in addition to SiO_2 and Al_2O_3 are Fe oxides and H_2O+: the sillimanite (E 18) also contained a little CaO, K_2O and TiO_2 (the last is greater than the amount determined spectrographically). Densities were determined using a pycnometer: refractive indices were measured by immersion methods, using sodium light.

TABLE 5. CHEMICAL ANALYSES

	Sillimanite E 18	Andalusite E 9	Kyanite E 14
SiO_2	36.61	37.25	36.85
Al_2O_3	61.54	61.90	62.26
Fe_2O_3	.22	.29	.21
FeO	.14	.04	.03
MgO	.04	.06	.03
CaO	.40	.08	.08
Na_2O	.06	.08	.07
K_2O	.25	.08	.11
H_2O^+	.33	.39	.41
H_2O^-	.11	.09	.05
TiO_2	.22	.05	.04
F	.02	.01	.01
Less			
$0=F$	.01		
Sum	99.93	100.27	100.15
Al_2O_3/SiO_2	1.68	1.66	1.69
G	—	3.02	3.69
α	1.655	1.629	1.710
β	—	—	—
γ	1.673	1.641	1.725
$\gamma - x$	.018	.012	.015

Analyzed at the Rock Analysis Laboratory, University of Minnesota: Director, Dr. S. S. Goldich: Analysts, D. Thaemlitz, (E 18) and E. H. Oslund (E 9, E 14).

Other data by G. R. Pearson.

The theoretical value of the ratio Al_2O_3/SiO_2 is 1.70. In all three of the analysed specimens the ratio is a little less than this figure. This suggests a deficiency of Al with respect to Si (analytical error can be disregarded, in the opinion of the writers), which is entirely reasonable if the substitution of small amounts of Fe, Ti, Mg and trace-elements for Al be allowed. Such substitution can hardly be extended to the much larger elements Na and K, however, and the significance of alkalies in aluminum silicates has

been discussed by many authors (in particular—Jakob, 1937, 1940, 1941; Henriques, 1957; Eigenfeld & Machatski, 1957). Jakob believed the alkali metal and water content of these minerals to be essential constituents, in the sense that one or two molecules of each were combined with 40 SiO_2 and 40 $(Al_2O_3 + Fe_2O_3)$. With the present three samples, however, the proportions are as follows:

	SiO_2	$(Al_2O_3 + Fe_2O_3)$	$(Na_2O + K_2O)$	H_2O
Sillimanite	100	100	1	3
Andalusite	160	160	1	6
Kyanite	160	160	1	6

It is most unlikely that these large figures represent a formula in the accepted sense, and Jakob's hypothesis appears untenable. The problem of the significance of Na and K however remains, and the quantities appear too great to be explained by mica contamination. Some kind of concealment in lattice voids seems the best explanation at present.

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