Zn-rich staurolite from the Uvete area, central Kenya

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ABSTRACT. Zn-rich staurolite occurs in a pelitic gneiss from the Uvete area, central Kenya. The rock was metamorphosed to staurolite-kyanite grade during the Mozambique metamorphism. Microprobe analyses of the staurolite gave the following values (in wt. %): SiO₂ 26.2-27.3, Al₂O₃ 52.4-53.5, FeO 8.3-9.2, MgO 2.2-2.6, and ZnO 6.0-7.5. Cell dimensions are $a = 7.874(\pm 0.003)$, $b = 16.620(\pm 0.006), c = 5.656(\pm 0.002)$ Å and $\beta = 90.00$ $(\pm 0.002)^\circ$. Optical properties are $2V_z = 82-85^\circ$, $\alpha = 1.742$ $(\pm 0.002), \beta = 1.747(\pm 0.002)$ and $\gamma = 1.753(\pm 0.002)$. The optical dispersion is moderate and r > v. Density is $3.83(\pm 0.01)$ g/cm³. Infra-red absorption spectra were also recorded. The cation correlation suggests that the principal substitutions in the staurolite are $Zn \rightleftharpoons Fe$ in the tetrahedral sites in the hydroxide sheet and $Al \rightleftharpoons Mg$ in the octahedral sites.

KEYWORDS: staurolite, gneiss, Uvete, Kenya.

LARGE concentrations of ZnO in staurolite have been reported from many regional metamorphic terrains (Guidotti, 1970; Ashworth, 1975; Gibson, 1978; Inoue and Suwa, 1979; Stoddard, 1979; Hiroi, 1983; and others), but the ZnO content of the mineral rarely exceeds 4 wt. %. The staurolite reported by Juurinen (1956) is the highest in ZnO content (7.44 wt. %) and similar ZnO contents in staurolites were reported by Griffen and Ribbe (1973) and Kochetkova *et al.* (1981). The staurolite from the Uvete area contains 6.0 to 7.5 wt. % ZnO and is among the most Zn-rich staurolites.

The mineralogical properties of this staurolite are reported here and the substitutional relationships among cations in the staurolite are discussed.

Occurrence

Zn-rich staurolite was found in a pelitic gneiss, about 3 km southwest of Uvete $(37^{\circ} 19' 31'' E., 1^{\circ} 51'' 54'' S.)$. The locality is shown in fig. 1. The pelitic gneiss occurs in the micaceous gneiss layer which is 600 m thick (Miyake and Suwa, 1981). Abundant pegmatite veins crosscut the micaceous gneisses.

The rocks in the area were metamorphosed to staurolite-kyanite grade during the late Precam-

brian Mozambique regional metamorphism, and the P-T conditions of the metamorphism were estimated at 6.5 ± 0.5 kbar and 530 ± 40 °C, respectively (Miyake, 1983 and 1984).

The pelitic gneiss containing Zn-rich staurolite, consists of equigranular crystals of staurolite, garnet (Alm 51 mol. %, Sp 28 mol. %, Py 19 mol. %), biotite (Mg/(Fe + Mg) = 0.33), muscovite, plagioclase (An₇), quartz and an opaque mineral, and is foliated due to the parallel arrangement of biotite and muscovite. The opaque mineral has been altered into aggregations of goethite. The ZnO content of biotite is about 0.1 wt. % and those of garnet and muscovite are less than 0.02 wt. %. The gneiss in which it occurs is richer in quartz and plagioclase relative to the surrounding micaceous gneisses.

The modal abundance of staurolite in the pelitic gneiss is less than 1%. It occurs as euhedral to subhedral crystals about 0.2–1.0 mm in size and rarely contains quartz crystals less than 0.1 mm. Cleavages parallel to (010), (100), and (021) are commonly observed.

Experiments and results

Chemistry. Twelve staurolite grains were analysed with an electron-probe microanalyser, JXA-5A of JEOL. A 15 kV accelerating potential was used with a 0.01 μ A beam current and a beam diameter of about 5 μ m. The standards were synthetic materials for SiO₂, TiO₂, Al₂O₃, Cr₂O₃, MgO, and MnO, natural minerals for FeO (hematite), Na₂O (albite), and K₂O (adularia), and synthetic silicate glasses for ZnO and CaO. The X-ray intensity for all the elements was integrated over an 80 second interval. Analytical data were reduced using the method of Bence and Albee (1968). Estimated standard deviations are less than 1% of the concentrations of the major elements such as Si, Al, Fe, Mg, and Zn.

The chemical compositions obtained are shown in Table I. Chemical zoning was not found in any



FIG. 1. Locality of Zn-rich staurolite-bearing pelitic gneiss (AM 80032202).

grain, but small chemical variations were found between individual grains. The formula of the staurolite calculated on the basis of 44(O) + 4(OH)per unit cell agrees with the general formula (Fe,Mg,Zn)_{25.6-1.25x}Al_x(Si_yAl_{8-y})O₄₄(OH)₄ proposed by Griffen *et al.* (1982).

574

X-ray data. Refined unit cell dimensions were obtained from X-ray powder diffraction patterns, using Ni-filtered Cu-K α radiation and a goniometer scan of 0.5° (2 θ)/minute. NaCl was used as an internal standard. Peaks were indexed with reference to the calculated powder patterns of Borg and Smith (1969).

Table II summarizes the X-ray powder data. The empirical unit cell parameters were obtained from the reflections with the glancing angles more than 25° with a weighted least-squares procedure. The weight of sec θ was assigned to each reflection. The unit cell parameters obtained were $a = 7.874 (\pm 0.003)$, $b = 16.620(\pm 0.006)$, $c = 5.656(\pm 0.002)$ Å, and $\beta = 90.00(\pm 0.08)^{\circ}$. The estimated errors of the cell parameters, shown in parentheses, correspond to the observed errors of glancing angles ($\Delta 2\theta = \pm 0.02^{\circ}$).

According to Griffen and Ribbe (1973) and Griffen *et al.* (1982), the *b* and *c* values of staurolite vary sensitively in response to variations of chemical composition although the *a* value is almost constant (approximately 7.87 Å). The unit cell dimensions of the Zn-rich staurolite in the present study fall near the regression lines between the unit cell dimensions and the mean atomic radius in the hydroxide sheet given by Griffen *et al.* (1982).

Optical data. The refractive indices of sixteen grains were determined by the immersion method using a spindle stage. Little variation in the refractive indices was found from grain to grain. They were measured as $\alpha = 1.742 \pm 0.002$, $\beta = 1.747 \pm 0.002$, and $\gamma = 1.753 \pm 0.002$.

The refractive indices of staurolite increase with increasing Fe content, except for Zn-rich staurolite (Griffen and Ribbe, 1973). The refractive indices of the staurolite in the present study fall markedly over the regression lines for the Fe content by Griffen and Ribbe (1973) as does the Zn-rich staurolite of Juurinen, 1956 (fig. 2). The higher refractive indices of Zn-rich staurolite

Table I. Representative and average chemical compositions of staurolite in pelitic gneiss (AM 80032202) from the Uvete area.

	1 '	2	3	4	5	ave.
sio2	26.52	26.81	26.67	26,81	26.68	26.74
TiO2	0.53	0.53	0.50	0.49	0.55	0.51
A1203	52.66	52.56	52.91	52.85	53.33	52.95
cr 203	0.00	0.00	0.00	0.00	0.00	0.00
FeO*	8.51	8.93	8.36	8.83	9.07	8.80
MnO	0.72	0.71	0.67	0.79	0.91	0.75
MgO	2.26	2.61	2.32	2.57	2.46	2.39
ZnO	7.01	6.36	7.46	6.68	6.08	6.73
CaO	0.00	0.00	0.00	0.00	0.00	0.00
Na 20	0.16	0.14	0.18	0.16	0.14	0.16
к ₂ 0	0.00	0.00	0.00	0.00	0.00	0.00
Total	98.37	98.65	99.07	99.18	99,22	99.03
Formul	ae base	d on 44	(0)+4(0)	H)		
Si	7.467	7.512	7.463	7.484	7.432	7.476
Al	0.533	0.488	0.537	0.516	0.568	0.524
Al	16.924	16.873	16.919	16.875	16.943	16.924
Ti	0.113	0.112	0.106	0.102	0.115	0.107
Cr	0.000	0.000	0.000	0.000	0.000	0.000
Fe	2.004	2.093	1.957	2.061	2.113	2.056
Mn	0.173	0.167	0.159	0.188	0.215	0.181
Mg	0.948	1.089	0.968	1.070	1.020	0.994

 Zn
 1.457
 1.317
 1.542
 1.377
 1.251
 1.389

 Ca
 0.000
 0.000
 0.000
 0.000
 0.000
 0.000

 Na
 0.067
 0.075
 0.100
 0.006
 0.007
 0.067

 K
 0.000
 0.000
 0.000
 0.000
 0.000
 0.000

* Total iron as FeO.

compared with the regression lines suggest that Zn as well as Fe increases the refractive indices of staurolite.

The optic axial angles of eight staurolite grains were determined using a universal stage. The results were $2V_Z = 82-85^\circ$ and the optic axial angle calculated from the refractive indices is $2V_Z = 85^\circ$. The optical dispersion is moderate and r > v. The staurolite is pleochroic with X = Y = colourless and Z = pale yellow.

Density. Density was determined by measuring the density of Clerici solution in which the staurolite grains neither sank nor floated. The value for the staurolite grains with maximum density was used to avoid the effect of quartz inclusions. The density obtained was $\rho = 3.83 \pm 0.01$ g/cm³.

The density value is higher than any previously reported for a staurolite. The concentration of Zn increases the weight of the unit cell and decreases the unit cell dimensions because Zn is heavier than iron and smaller in effective radius ($^{V}r_{Zn} = 0.57$ Å; Griffen, 1981). This is consistent with the high density of the Zn-rich staurolite. The density calcu-

Table IJ. Powder pattern of staurolite in pelitic gneiss (AM 80032202) from the Uvete area.

Indices	20 (CuKar)	29 (CuKo(1)	d _{obs} (Å)	d _{calc} .(Å)	Int.
020	10.65		8.307	8.310	30
110	12,44		7.115	7.116	30
040	21.40		4.152	4.155	40
220	25.05		3.555	3,558	40
150	29.19		3.059	3,062	30
221	29.65		3.013	3.012	80
060	32.33		2.769	2.770	70
151	33.27		2.693	2.693	100
241	35.19		2,550	2.551	30
132		37.46	2.399	2.399	70
330		37.93	2.370	2.372	70
311		38.18	2,355	2.357	50
171		42.87	2.1076	2.1092	40
062		45.83	1.9783	1,9789	50
400		46.07	1.9686	1.9685	30
460		57.35	1.6052	1.6046	30
511		61.31	1.5107	1.5108	30
004		66.01	1.4141	1.4140	20
462		66.98	1.3959	1.3956	30
0,12,0		67.57	1.3852	1.3850	10

lated from the average chemical composition and the unit cell parameters on the basis of 44(O) + 4(OH) per unit cell is $\rho = 3.81$ g/cm³.

Infra-red absorption spectra. Although there have been a few studies of infra-red absorption spectra of staurolite, chemical compositions of the staurolite in these studies were unfortunately not reported. It is important to report infra-red absorption spectra of the Zn-rich staurolite.

The infra-red absorption spectrum was taken on a JASCO A-3 infra-red spectrophotometer. The substance was used in powder form mounted in a KBr disc. The result is shown in fig. 3 together with the data by Keller *et al.* (1952) and Saksena (1961).

The bands in the regions of 802-800, 785-800and $1110-1090 \text{ cm}^{-1}$ in the earlier studies are not found in this study. Conversely the peak at 963 cm⁻¹ in the present study is not present in the earlier studies. The bands in the region of 3200- 3600 cm^{-1} in the present study are found to have lower frequency than that in Saksena (1961).

Substitutional relationships

The crystal structure of staurolite can be considered as composed of a sheet of the kyanite structure alternating with an Fe-Al hydroxide sheet (Naray-Szabo, 1929). The refinement of Smith (1968) shows that the kyanite sheet has one kind of tetrahedral site occupied principally by Si atoms and four kinds of octahedral sites occupied



FIG. 2. Relation between refractive indices and unit cell Fe content. Data are taken from Juurinen, 1956 (solid circles); Chinner, 1958 (open squares); Snelling, 1957 (solid squares); Hietanen, 1969 (open triangles); Griffen and Ribbe, 1973 (crosses); and this study (stars). The two low-iron staurolites (less than 3 Fe/unit cell) are enriched in Zn. The regression lines for low-zinc staurolites were drawn by Griffen and Ribbe (1973).

principally by Al atoms, and that the hydroxide sheet has one kind of tetrahedral site occupied principally by Fe atoms and four kinds of octahedral sites occupied principally by Al atoms. The tetrahedral site in the kyanite sheet is fully occupied by all of the Si atoms and enough Al atoms (Smith, 1968, and Griffen and Ribbe, 1973). The other sites, however, have more or less vacancies and the assignment of cations to these sites has not been established.

Griffen and Ribbe (1973) deduced the substitutional relationships among cations in the Al^{VI} sites (in the kyanite and hydroxide sheets) and Fe^{IV} sites (in the hydroxide sheet) using a statistical treatment



FIG. 3. Infra-red absorption spectra of staurolites. Full line curve, the present study; Dash curve, Saksena (1961); dot and dash curve, Keller et al. (1952).



FIG. 4. The correlations between Fe and Zn, and between Al and Mg in the Fe^{IV} and Al^{VI} sites in staurolite in pelitic gneiss (AM 80032202) from the Uvete area. The contents of the atoms are presented as the numbers per unit formula. The Al atomic content in those sites is 'total Al'-(8-Si).

of correlations among cations in many staurolites with various chemical compositions. The present study gives the substitutional relationships in the Zn-rich staurolite in the Uvete area.

Fig. 4 shows the correlations among Al, Fe, Mg, and Zn atoms in Al^{VI} and Fe^{IV} sites. The negative correlation between the Fe and Zn atoms suggests that the Zn \Rightarrow Fe substitution is the principal one in the Fe^{IV} site. The preference of the Zn atom for the tetrahedral site has often been reported (Guidotti, 1970; Hollister, 1970; Hollister and Bence, 1967; Griffen, 1981).

On the other hand the negative correlation between the Al and Mg atoms suggests that the Mg \Rightarrow Al substitution is the principal one in the Al^{VI} sites. With respect to the assignment of the Mg atom there have been various opinions and the substitution in the Al^{VI} sites possibly varies according to the chemical compositions of staurolite. Acknowledgements. I wish to thank Professor K. Suwa of Nagoya University for his critical comments on the manuscript. I am also indebted to Dr K. Suzuki and Mr H. Noro of Nagoya University for invaluable advice on experiments. The infra-red spectroscopy was used with the invaluable assistance and guidance of Professor K. Nagasawa of Shizuoka University.

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