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Synthetic Fe/Zn staurolites and the ionic radius of $^{IV}Zn^{2+}$

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Abstract

Zinc and iron end-member staurolites, as well as three Fe/Zn staurolites with intermediate compositions, have been synthesized in a tetrahedral press at approximately 30 kbar and 750°C. All are dimensionally orthorhombic, but are assumed to be monoclinic by analogy with natural staurolites. Indices of refraction of zinc staurolite are $\alpha = 1.683$, $\beta = 1.694$, $\gamma = 1.700$. Lattice parameters for the Fe/Zn series vary linearly with composition, in general consonance with previous models of staurolite crystal chemistry. Disorder of Zn and Fe^{2+} is tentatively suggested by molar volume data. The effective ionic radius of tetrahedrally-coordinated Zn^{2+} is 0.57Å (±0.01Å) based on unit cell volumes of synthetic staurolites and on previously published data for Zn^{2+} tetrahedral oxyanions.

Introduction

Although all natural staurolites reported to date contain more iron than other metals, minor amounts of Ti, Mn, Cr, and V are nearly always present (see Smith, 1968; Griffen and Ribbe, 1973); these have comparatively little effect on the crystal chemistry of the mineral. Relatively large concentrations of Mg and Zn are common, and Skerl and Bannister (1934) have reported a cobaltoan variety. Zinc-rich staurolites have been reported in regionally metamorphosed pelites at moderately high grade (*e.g.*, Guidotti, 1970), and at unusually high grade (Ashworth, 1975); in medium grade metabasites of igneous origin (Gibson, 1978); in high pressure, medium-grade thermally metamorphosed "graywacke" (Hollister, 1969); and in pegmatites and hydrothermal veins (Tarnovskii, 1973; von Knorring *et al.*, 1979).

The staurolite crystal structure contains layers of approximate kyanite composition and atomic arrangement that alternate along *b* with "monolayers" of approximate composition $Fe_2Al_{0.7}O_2(OH)_2$ (Smith, 1968; Griffen and Ribbe, 1973). The kyanite layers contain the tetrahedral **Si** and octahedral **Al(1A)**, **Al(1B)**, and **Al(2)** sites[1], which are all nearly fully occupied. The monolayers contain the tetrahedral **Fe** site (occupancy 0.92), octahedral **Al(3A)** and **Al(3B)** sites (occupancies 0.42 and 0.28, respectively), and octahedral **U(1)** and **U(2)** sites (occupancies 0.08 and 0.04, respectively). Along the *c* direction they possess chains of edge-sharing **Al(3A,B)** octahedra with attached **Fe** tetrahedra. Along *a* the chains are separated laterally by nearly vacant **U(1,2)** sites. An "idealized" average chemical formula, necessarily imprecise because of the many partially occupied cation sites in staurolite, is $M_4Al_{17.3}(Si,Al)_8O_{48}H_4$, where M = Fe, Mg, Zn (Griffen, Gosney, and Phillips, in preparation).

The apparent preference of zinc for tetrahedral sites in silicates has often been noted (*e.g.*, Evans, 1966; Burns, 1970). The **Fe** site in staurolite (Smith, 1968) is the only tetrahedral site in common metamorphic minerals that is of appropriate size for zinc. The data of Guidotti (1970) and Ashworth (1975) suggest that the partitioning of zinc into staurolite stabilizes it (relative to zinc-free staurolite) to higher temperatures. The *P–T* stability of staurolite as a function of zinc content has not yet been investigated quantitatively.

Among natural specimens zinc content is reported to range from zero to ~7 weight percent ZnO, but is commonly between 0.1 and 2.0 weight percent ZnO. This corresponds to approximately 0.02 to 0.5 atoms of zinc on the basis of 4 metal atoms in the general-

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[1] To avoid confusion between chemical symbols and Smith's site names, the latter are printed in boldface type. Site occupancies referred to are based on Smith's (1968) structure refinement.

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ized staurolite chemical formula. A major purpose of the present study was to investigate the range of solubility of zinc in staurolite by attempting to synthesize zinc-rich specimens.

Experimental methods and results

Syntheses

Synthesis experiments were carried out in a tetrahedral press (Hall, 1958) at 30 (±2) kbar and 750(±40)°C. Uncertainties in pressure and temperature were estimated from the data of Eatough (1968). Starting materials were zincite (ZnO), wüstite (FeO), boehmite (AlO(OH)) and quartz (SiO_2), in the mole proportions 4(ZnO + FeO):18 AlO(OH):7.5 SiO_2, with water added as a catalyst. All crystalline compounds used were synthetic and of reagent grade. The amount of hydroxyl in the boehmite is in excess of that needed for the formation of staurolite, but runs made with insufficient H_2O resulted in staurolite + gahnite ± corundum ± kyanite ± quartz. The ratio 4:18:7.5 was chosen instead of 4:18:8 because Richardson (1966) noted that the ratio 4:9:8 ($FeO:Al_2O_3:SiO_2$) yielded staurolite + quartz, whereas quartz was not produced in 4:9:7.5 mixtures.[2]

Run times were mostly 1 to 2 hours, although runs of up to 60 hours duration were made with no apparent differences in run products. Synthesized phases were identified by X-ray diffraction using both a Gandolfi camera and a General Electric XRD-5 powder diffractometer. Only staurolite was identified in the products of runs that started with excess H_2O. Both Zn and Fe end members were synthesized, as well as $Zn_{75}Fe_{25}$, $Zn_{50}Fe_{50}$, and $Zn_{25}Fe_{75}$ intermediate members (subscripts indicate mole percent of end members). Table 1 summarizes synthesis data.

Table 1. Summary of staurolite syntheses

Starting Materials*	P(kb)#	T(°C)#	Run duration (hrs)†	Run products**
4:0:18:7½	30	750	1-60	Zn-staurolite
3:1:18:7½	30	750	1-2	Zn/Fe-staurolite
2:2:18:7½	30	750	1-2	Zn/Fe-staurolite
1:3:18:7½	30	750	1-2	Zn/Fe-staurolite
0:4:18:7½	30	750	1-2	Fe-staurolite

* $ZnO:FeO:AlO(OH):SiO_2 + H_2O$ (excess)

\# P ± 2kb, T ± 40°C

† Several runs were made for each composition

** Runs in which only staurolite was produced are tabulated. Runs with insufficient H_2O also variously produced corundum, gahnite, kyanite, and quartz.

Microscopy

Run products were examined by both petrographic microscope and scanning electron microscope. Crystals up to ~20 μm long and of bladed habit were observed, with the zinc end member providing the largest and most well-formed examples (Fig. 1). Zinc staurolite is biaxial negative, showing positive elongation, parallel extinction, and large 2V. Indices of refraction, measured in Na_D light by standard immersion techniques, are $\alpha = 1.683$, $\beta = 1.694$, and $\gamma = 1.700$ (all ± 0.005). These properties are consistent with the optical properties of natural staurolites (Juurinen, 1956; Griffen and Ribbe, 1973), the refractive indices being smaller because the atomic refractivity of zinc is less than that of iron (Batsanov, 1961). Optical constants of Fe and Fe/Zn staurolites were not measured because of small crystal size.

Lattice parameters

Refined unit cell dimensions were obtained from X-ray powder patterns run on a General Electric XRD-5 X-ray diffractometer, using Ni-filtered Cu$K\alpha$

Fig. 1. SEM photomicrograph of synthetic zinc staurolite crystals. Length of scale bar represents 10 microns. Angles measured on this and other SEM photos suggest that the large crystal faces are (010), modified by (110), (201), and ($\bar{2}01$), with crystals elongated on c.

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[2] The deficiency of Si (that is, less than 8 atoms per unit cell) is very consistent in published staurolite analyses, even though the Si sites (8 per unit cell) are essentially fully occupied (Smith, 1968). It is likely that bond strength sums at the Si site preclude full occupancy by Si^{4+}, and require the substitution of some Al^{3+} (Griffen and Ribbe, 1973).

radiation and a goniometer scan rate of 2°2θ/minute. The internal standard was CaF_2 annealed at 800°C ($a_0 = 5.4630$Å). Peaks were indexed with reference to the calculated powder pattern of Borg and Smith (1969), and lattice parameters were refined with the least-squares program of Evans *et al.* (1963). By analogy with natural staurolites, the synthetic staurolites were assumed to be monoclinic with $\beta = 90°$, and with the *hkl* and *h0l* peaks therefore present as unresolved doublets. Each *hkl* (or *h0l*) peak was thus assigned two indices—*hkl* and $\bar{h}kl$ (or *h0l* and $\bar{h}0l$) to avoid biasing the β angle. Refined lattice parameters for the five staurolites synthesized in this study, as well as for staurolites synthesized previously by others and used in this study, are reported in Table 2.

Discussion

Lattice parameters

As seen in Figure 2, the lattice parameters of synthetic Fe/Zn staurolites are linear or nearly linear functions of composition. The least-squares lines were calculated using both the data of this study and the synthetic iron staurolite of Richardson (1966). Linear correlation coefficients are (respectively) 0.98, 0.99, and 0.94 for *a*, *b*, and *c versus* composition, and all are statistically highly significant. This is in contrast to similar plots for twenty natural staurolites (Griffen and Ribbe, 1973), wherein the correlation between cell edge and iron content was highly significant for only the *b* dimension, while that for *c* was moderately significant for that for *a* was not significant. Assuming the metal atoms to be restricted essentially to the $Fe_2Al_{0.7}O_2(OH)_2$ monolayer, these authors rationalized that an increase in Fe (the largest of the substituent metal atoms) would expand the thickness of the monolayer independent of the kyanite layer; hence the strong correlation of *b* with Fe content. Parallel to *c*, an increase in Fe content would tend to lengthen the octahedral/tetrahedral chains in the monolayer, but this expansion would be limited by the requirement that the monolayer "fit" the presumably non-expanding kyanite layer. Along *a*, the presence of nearly empty U sites between chains would make a slight collapse of those octahedra easier than expansion of the monolayer. For the synthetic Fe/Zn staurolites the variation in *b* is four to five times that in *a* or *c*, suggesting that the

Table 2. Lattice parameters of synthetic staurolites

Composition	Number of peaks	*a*(Å)	*b*(Å)	*c*(Å)	β(°)	*V*(Å^3)	Reference
Zn_{100}	74	7.861(1)[†]	16.535(1)	5.646(1)	90.00(1)	733.9(1)	This study
$Zn_{75}Fe_{25}$	72	7.866(2)	16.555(3)	5.648(1)	90.00(2)	735.5(2)	"
$Zn_{50}Fe_{50}$	71	7.871(1)	16.580(3)	5.654(1)	90.00(1)	737.9(1)	"
$Zn_{25}Fe_{75}$	65	7.878(2)	16.606(4)	5.662(1)	90.00(2)	740.7(2)	"
Fe_{100}	62	7.882(1)	16.639(3)	5.659(1)	90.00(2)	742.2(2)	"
Fe_{100}	nr[#]	7.887(10)	16.639(8)	5.665(3)	**	743.4(10)	Richardson (1966)
$Fe_{98}Mg_2$	nr	7.891(2)	16.631(2)	5.667(1)	**	743.7(2)	"
$Fe_{90}Mg_{10}$	nr	7.881(7)	16.621(6)	5.662(6)	**	741.6(14)	"
$Fe_{80}Mg_{20}$	nr	7.890(7)	16.616(6)	5.660(2)	**	742.0(8)	"
$Fe_{70}Mg_{30}$	nr	7.887(6)	16.597(5)	5.665(2)	**	740.2(7)	"
Mg_{100}	47	7.887(1)	16.552(2)	5.635(1)	90[††]	735.6(2)	Schreyer and Seifert (1969)

* *Mole % end members*

† *e.s.d's, given in parentheses, refer to last decimal place*

\# *nr = not reported*

** *β reported as "90° within experimental error"*

†† *Orthorhombic symmetry assumed*

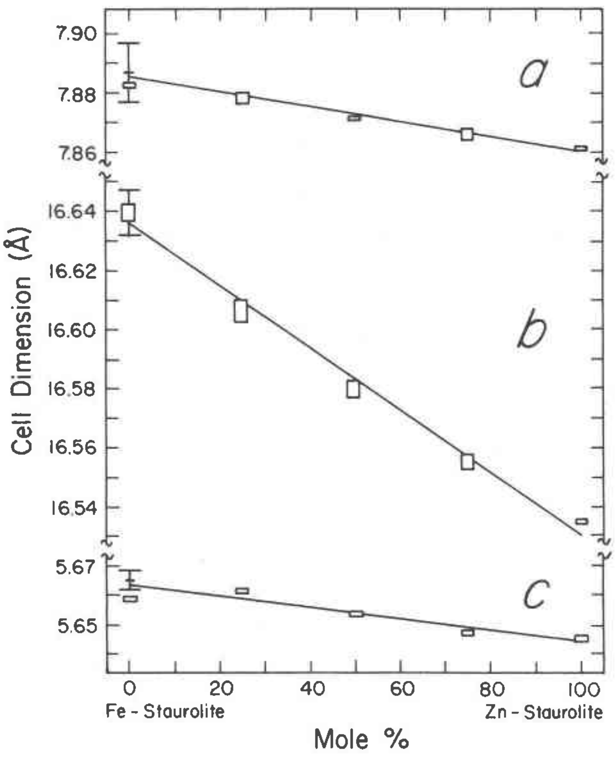

Fig. 2. Variation of lattice parameters with composition for synthetic Fe/Zn staurolites. Symbols: rectangles, this study; vertical bars, Richardson (1966). Symbols are 2 *esd*'s in height.

same general model applies. The much better correlations may be a reflection of the controlled compositional variation for the synthetic crystals. In natural staurolites a predominant substitution of Al $\rightleftarrows$ (Fe + Mg + Zn) occurs concurrently with (and nearly independent of) metal–metal substitutions (Griffen, Gosney, and Phillips, in preparation), tending to obscure the effects of the latter and to scatter the data. In the synthetic Fe/Zn staurolites the unit cell Al content was constrained at 18 by choice of starting materials, and the effects of the metal $\rightleftarrows$ metal substitution alone are evident. It is also possible that some Fe/Al substitution occurs in the kyanite layer of the synthetic staurolites, resulting in expansion of both kinds of layers.

Although substitution of Zn for Fe^{2+} clearly controls the physical and optical properties of the synthetic staurolites reported herein, the substitution does not necessarily occur at the Fe site alone. Smith (1968) inferred partial Fe/Al disorder from Mössbauer spectroscopy and crystal chemical deduction for a natural specimen from St. Gotthard, Switzerland. Figure 3 shows molar volume of the synthesized staurolites as a function of composition. The relation is either linear or very close to it, implying the possibility of thermodynamic ideality, with Zn and Fe^{2+} disordered with respect to each other. In view of the preference of Zn for tetrahedrally-coordinated sites and the absence of such a preference in the case of iron, some ordering might be expected. The apparent linearity of Figure 3 may therefore be a fortuitous result of complex site substitutions among Fe, Zn, and Al, with some Al in the Fe site, as in natural specimens.

Effective ionic radius of $^{IV}Zn^{2+}$

Shannon and Prewitt (1969) and Shannon (1976) have proposed 0.60Å as the radius of tetrahedrally coordinated Zn^{2+} in oxides, based on crystal structure determinations of inorganic compounds containing ^{IV}Zn^{2+}. Using similar data treated in a different way, Griffen and Ribbe (1979, Fig. 8) suggested 0.57Å as more likely. The present data on zinc staurolite and data available for synthetic Fe, Fe/Mg, and Mg staurolites (this study: Richardson 1966; Schreyer and Seifert, 1969) raise the possibility of an independent determination of the ^{IV}Zn^{2+} radius.

Figure 4 is a plot of the cube of the mean effective ionic radius of the metal atom (Shannon, 1976) *versus* unit cell volume. (The radii used for Fe^{2+} and Mg^{2+} were those for tetrahedral coordination; this is a possible source of error and is discussed below.) The least-squares linear fit was determined using the seven synthetic Fe, Fe/Mg and Mg staurolites, and was extrapolated to the observed unit cell volume of synthetic zinc staurolite to give r^3 = 0.17Å^3. This cor-

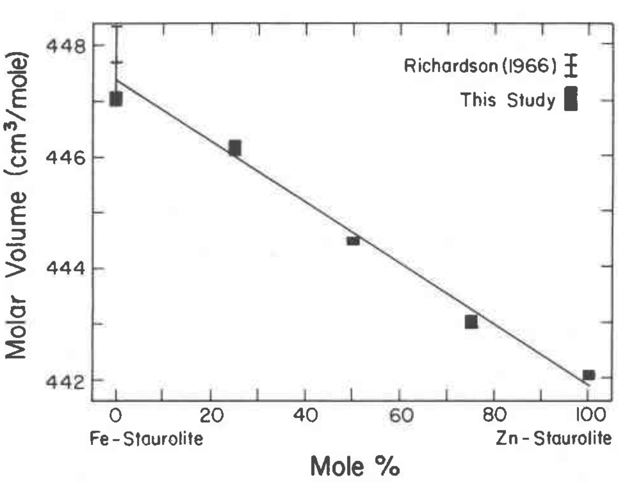

Fig. 3. Molar volume *vs.* composition for synthetic Fe/Zn staurolites. Symbols are 2 *esd*'s in height.

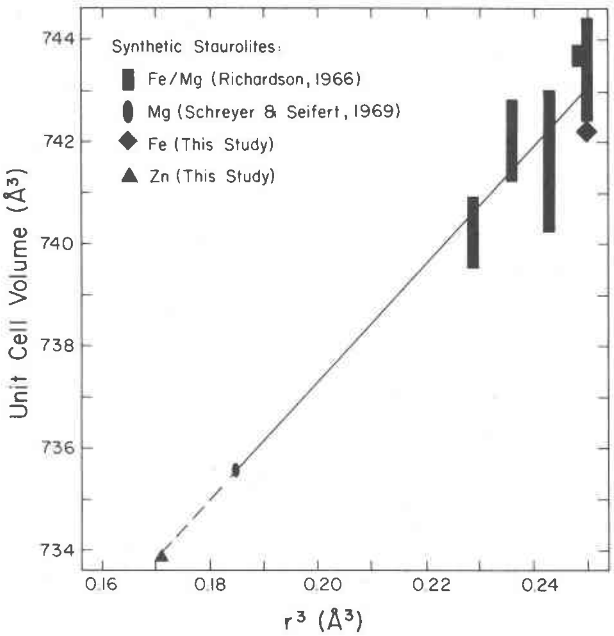

Fig. 4. Unit cell volume of synthetic Fe/Mg staurolite as a function of the cube of the mean effective ionic radius of the metal atom (Shannon, 1976). The value of r^3 for $^{IV}Zn^{2+}$ is determined by extrapolating the least-squares line to the observed unit cell volume of zinc staurolite (Table 1). Symbols are 2 *esd*'s in height.

responds to a radius of 0.56Å for $^{IV}Zn^{2+}$. The average value of r obtained from unit cell volumes of all four zinc-bearing staurolites is also 0.56Å.

Three possible sources of error in the radius determination are apparent. (1) The accuracy of the radius for Zn^{2+} estimated in this way is limited by the accuracy of the radii used for Mg^{2+} and Fe^{2+}. Griffen and Ribbe (1979, Figure 8) confirm Shannon's (1976) radius for $^{IV}Fe^{2+}$, but Griffen and Ribbe did not include $^{IV}Mg^{2+}$ in their study. The paucity of crystal structure data involving $^{IV}Mg^{2+}$ makes its radius somewhat less certain than that of $^{IV}Fe^{2+}$. (2) The precision of Richardson's (1966) cell volumes is not sufficient to determine whether the r^3 *vs.* *V* plot is linear or curvilinear. The unit cell volumes of zinc and magnesium staurolites are close enough, however, that no reasonable nonlinearity would change the estimate of the $^{IV}Zn^{2+}$ radius by more than ~0.01Å. (3) If there is any disorder between the metal atoms and aluminum, then some of the metals are in octahedral coordination and use of the tetrahedral radii is not strictly correct. Nevertheless, the differences between the four- and six-coordinated radii of Fe^{2+}, Mg^{2+}, and Zn^{2+} are nearly the same, so that the method is approximately valid in any case. The more nearly alike the degree of metal/aluminum order for the various staurolites plotted, the less error would arise from this source.

For reasons cited above the r^3 *vs.* *V* plot must be considered less reliable than the crystal structure refinements used by Griffen and Ribbe (1979). Nevertheless, it tends to confirm the $^{IV}Zn^{2+}$ radius of those authors. The value of 0.57Å (±0.01Å) for r($^{IV}Zn^{2+}$) is therefore recommended for use with Shannon's (1976) radii, which are based on an assumed $^{VI}O^{2-}$ radius of 1.40Å. The effective ionic radii proposed by Whittaker and Muntus (1970) are based on r($^{VI}O^{2-}$) = 1.32Å, and are a more suitable set for radius ratio considerations. The $^{IV}Zn^{2+}$ radius consistent with that set is 0.65Å.

Conclusion

The synthesis of both Zn staurolite and Fe/Zn staurolite at approximately 30 kbar and 750°C suggests that there are no apparent crystal chemical limitations to the amount of zinc incorporated in staurolite. Availability of zinc in various geologic environments or possible thermodynamic limitations to the stability of Zn-containing staurolites may govern the concentrations of zinc observed in natural specimens. All unit cell dimensions for the Fe/Zn series vary linearly with composition, but the large variation in *b* (compared to that of *a* and *c*) indicates that the decrease in thickness of the metal-containing (020) monolayer, as Zn is substituted for Fe, is much more important than contraction parallel to the monolayer. The explanation given by Griffen and Ribbe (1973) for lattice parameter variations in natural staurolites thus applies with little modification to these synthetic analogs. The known preference of Zn for tetrahedral coordination suggests that the apparent linearity of the molar volume *vs.* composition plot (Fig. 3) may be a fortuitious result due to partial metal/aluminum disorder combined with partial iron/zinc order.

An effective ionic radius of 0.57Å for $^{IV}Zn^{2+}$ is proposed for use with the radii of Shannon (1976). This corresponds to a radius of 0.65Å for use with the radii of Whittaker and Muntus (1970).

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