

## Staurolite-lusakite series. I. Synthetic Fe-Co staurolites

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### ABSTRACT

Cobaltoan staurolite (=lusakite if  $\text{Co} \geq \text{Fe, Mg}$ ) has been synthesized, along with intermediate staurolites at 20 mol% intervals in the composition range from pure-Fe staurolite to endmember lusakite, in a tetrahedral press at approximately 30 kbar and 750°C. All lattice parameters vary linearly with composition. There appear to be no crystal-chemical factors that would inhibit the existence of a complete solid-solution series between natural Fe-rich staurolite and lusakite. The paucity of Co in nearly all staurolites thus likely reflects the Co-poor bulk chemistry of typical staurolite-bearing rocks.

A Mössbauer spectrum obtained for the  $\text{Fe}_{30}\text{Co}_{20}$  composition shows two  $\text{Fe}^{2+}$  doublets that we attribute to tetrahedral Fe at the Fe site (~75%) and octahedral Fe at the Al(3A), Al(3B), U(1), and U(2) sites (~25%). If the site occupancies in this synthetic staurolite are similar to those in natural specimens, then the absence of 25% of the Fe from the Fe site requires the presence of some Al, even in the unlikely event that all of the Co is also in that site. Because the Al(3) and U sites are only partially occupied, 25% of the total Fe could occupy them without completely filling them, even if *no* Al entered the Fe site. We propose that local charge-balance requirements drive the exchange of Al and Fe and suggest the minimization of electrostatic repulsion between the protons and atoms in the Al(3) sites as an important factor.

### INTRODUCTION

Staurolite can be generally characterized as a hydrous iron aluminum silicate, very often containing appreciable Mg, Zn, or both. Complete analyses of natural staurolites usually also show trace to minor amounts of Ti, V, Cr, Mn, and Co (e.g., Griffen and Ribbe, 1973) and recently Li as well (Dutrow et al., 1986). Staurolite with a substantial content of Co has been reported from only one general area, although two specific localities may be involved. In 1934, Skerl and Bannister described a monoclinic mineral that is isostructural with staurolite, but has  $\text{Co} > \text{Fe, Mg}$ ; it was named lusakite because of the proximity of the locality to Lusaka, Zambia. Cech et al. (1981) described a staurolite, from the same general locale, that had  $\text{Fe} > \text{Co, Mg}$ ; proposing that the name lusakite be reserved for specimens in which  $\text{Co} > \text{Fe, Mg}$ , they called this mineral cobaltoan staurolite. Lusakite is the only silicate mineral known at present in which Co is an essential constituent.

It seems apparent from studies of synthetic staurolites (Richardson, 1966; Schreyer and Seifert, 1969; Hellman and Green, 1979; Griffen, 1981), as well as from chemical analyses of natural specimens, that more common occurrence of Mg-rich and Zn-rich staurolites is prevented only by the infrequent simultaneous satisfaction of necessary chemical and physical geologic conditions. There are no crystal-chemical factors, such as immiscibility, that would

inhibit their formation. On the other hand, staurolite with  $>1$  wt% CoO has been reported only from the Lusaka locality. This study was undertaken to determine whether a complete solid solution could be synthesized between endmember Fe staurolite and endmember lusakite.

### EXPERIMENTAL METHODS AND RESULTS

#### Syntheses

Experimental syntheses were carried out in a tetrahedral press (Hall, 1958) at  $30 (\pm 2)$  kbar and  $750 (\pm 40)$  °C. Uncertainties in operating conditions were determined from the data of Eataugh (1968). Crystalline starting materials, all reagent-grade synthetic chemicals, were CoO, FeO (wüstite), AlO(OH) (boehmite), and  $\text{SiO}_2$  (quartz). The FeO was prepared by heating stoichiometric proportions of reagent-grade Fe and  $\text{Fe}_2\text{O}_3$  in an evacuated quartz-glass tube for 12 h; although we cannot rule out the possibility that some  $\text{Fe}^{3+}$  is present, an X-ray powder photograph of the product showed only the diffraction lines of wüstite. These materials were combined in the mole proportions  $4(\text{CoO} + \text{FeO}) + 18(\text{AlO(OH)}) + 7.5(\text{SiO}_2)$ , with a small amount of water added to catalyze the reaction, and ~20 mg were packed tightly into a cylindrical graphite furnace, capped with graphite lids, and placed inside a pyrophyllite tetrahedron. The encapsulating graphite served not only to conduct the electrical current for heating the charge, but also maintained a reducing environment.

Griffen (1981) used run times of from 1 to 60 h to synthesize (Zn,Fe) staurolites with the same apparatus, but found no relation between run times and differences in run products. Subsequently, we found that run times of 20 min were sufficient to yield products indistinguishable from those of the longer runs, and so 20-min runs were used for all of the present syntheses. The product of

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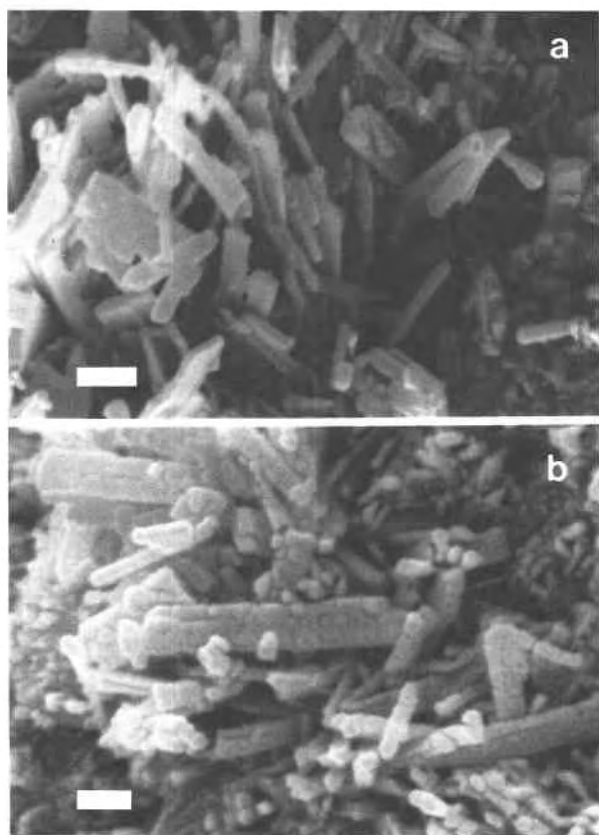


Fig. 1. Scanning-electron micrographs of (a)  $\text{Co}_{100}\text{Fe}_0$  staurolite and (b)  $\text{Co}_0\text{Fe}_{100}$  staurolite. Scale bar represents  $1\ \mu\text{m}$ .

each run was a tough compressed cylinder of reacted material, about 1 mm in diameter and 3 mm long, consisting of crystals too small to permit effective optical identification. Even with the scanning-electron microscope, most of any given specimen was compact and uniform in appearance, but tiny well-formed crystals were present in occasional "microvugs" (Fig. 1). Starting compositions, in terms of mole percent endmembers, were  $\text{Fe}_{80}\text{Co}_{20}$ ,  $\text{Fe}_{60}\text{Co}_{40}$ ,  $\text{Fe}_{40}\text{Co}_{60}$ ,  $\text{Fe}_{20}\text{Co}_{80}$ , and  $\text{Co}_{100}$ , and run products were identified from long-exposure X-ray powder photographs taken with a Debye-Scherrer camera. They consisted only of staurolite (or lusakite, as appropriate) so far as we could determine by this method, except for the  $\text{Fe}_{60}\text{Co}_{40}$  sample; that powder photograph showed three very faint lines that correspond to the three strongest lines in the powder pattern of sillimanite. In the discussion that follows, we have assumed the compositions of the starting materials as the compositions of the resulting staurolites.

#### Lattice parameters

X-ray powder patterns for determining lattice parameters were obtained with a General Electric XRD-5 X-ray diffractometer, using Ni-filtered  $\text{CuK}\alpha$  radiation and a goniometer scan rate of  $2^\circ/2\theta/\text{min}$ . Synthetic annealed  $\text{CaF}_2$  was used as the internal standard, and peaks were indexed according to the calculated powder pattern of Borg and Smith (1969). Least-squares unit-cell refinements were performed with the computer program of Evans et al. (1963). Because natural staurolites are monoclinic with  $\beta \approx 90^\circ$ ,  $hkl$  and  $h0l$  powder diffraction peaks consist of unresolved

Table 1. Lattice parameters of synthetic Fe-Co staurolites

Composition*	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	<i>V</i>
$\text{Fe}_{100}\text{Co}_0$ **	7.882(1)	16.639(3)	5.659(1)	90.00(2)	742.2(2)
$\text{Fe}_{80}\text{Co}_{20}$	7.877(2)	16.627(3)	5.658(1)	90.00(1)	741.0(2)
$\text{Fe}_{60}\text{Co}_{40}$	7.878(2)	16.606(3)	5.657(1)	90.00(2)	740.1(2)
$\text{Fe}_{40}\text{Co}_{60}$	7.870(2)	16.592(5)	5.654(1)	90.00(2)	738.2(2)
$\text{Fe}_{20}\text{Co}_{80}$	7.873(2)	16.586(3)	5.645(1)	90.00(1)	737.2(2)
$\text{Fe}_0\text{Co}_{100}$	7.865(1)	16.574(2)	5.649(1)	90.00(2)	736.3(2)

Note: Estimated standard deviations, shown in parentheses, refer to last decimal place.

\* Compositions are expressed in mole percent endmembers.

\*\* Data for pure-Fe staurolite from Griffen (1981).

$hkl$ - $\bar{h}kl$  and  $h0l$ - $\bar{h}0l$  doublets, respectively. We assumed monoclinic symmetry and, in order to avoid biasing the  $\beta$  angle, indexed each such peak both ways. Results of lattice parameter refinements are reported in Table 1.

#### Mössbauer spectroscopy

A room-temperature Mössbauer spectrum, shown in Figure 2, was obtained for the  $\text{Fe}_{80}\text{Co}_{20}$  synthetic staurolite. It was fit with two unconstrained Lorentzian doublets ( $\chi^2 = 1.21$ ). For the outer doublet, the isomer shift is 0.97 mm/s, and the quadrupole splitting is 2.35 mm/s; for the inner doublet, the isomer shift and quadrupole splitting are 1.05 mm/s and 1.20 mm/s, respectively. Isomer shifts are given with respect to the metallic Fe spectrum. The areas under the two low-velocity peaks of each doublet are slightly greater than those under the two high-velocity peaks. This asymmetry suggests the possibility that a small amount of Fe was oxidized during the syntheses (or perhaps present in starting materials), resulting in a small  $\text{Fe}^{3+}$  doublet with an isomer shift around 0.2 mm/s. We made no attempt to resolve this possible feature, but it does not appear to represent more than  $\sim 5\%$  of the total Fe present (if, indeed, it results from  $\text{Fe}^{3+}$  at all, inasmuch as the isomer shift is somewhat lower than typical values for  $\text{Fe}^{3+}$  in tetrahedral coordination and much too low to represent  $\text{Fe}^{3+}$  in octahedral coordination (Dyar, 1984)).

#### DISCUSSION

The variations in unit-cell dimensions and cell volume with chemistry are shown in Figure 3. Values for cell parameters of synthetic Fe staurolite were taken from Griffen (1981). Correlation coefficients for *a*, *b*, *c*, and *V* with composition are, respectively, 0.92, 0.99, 0.88, and 0.99. Although there is some scatter in the data, all trends appear to be linear. Previous rationalizations for the variations in cell parameters with chemistry (Griffen and Ribbe, 1973; Griffen, 1981) appear to hold true for the synthetic Fe-Co staurolites, although we note that the correlation of *c* with chemistry is poorer than that of *a*, in contrast to previous results.

The Mössbauer spectrum shown in Figure 2 very closely resembles that of Smith's (1968) natural staurolite from Pizzo Forno. Ignoring the possible existence of a very small  $\text{Fe}^{3+}$  doublet, we interpret the spectrum to indicate the presence of both tetrahedrally and octahedrally coordinated  $\text{Fe}^{2+}$ . The interpretation of the Mössbauer spectrum of staurolite is actually an open question. We have followed the interpretation of Bancroft et al. (1967) and Dickson and Smith (1976); others—for example, Dowty

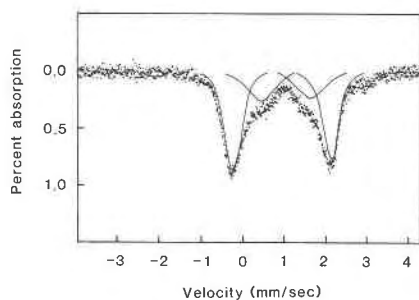


Fig. 2. Room-temperature Mössbauer spectrum of  $\text{Fe}_{80}\text{Co}_{20}$  synthetic staurolite. The spectrum is fit with two unconstrained Lorentzian doublets, and metallic Fe is the reference material.

(1972)—have interpreted the spectrum in terms of only tetrahedrally coordinated Fe. Dowty argued that both isomer shifts fall in the range typical of tetrahedrally coordinated  $\text{Fe}^{2+}$ . Yamanaka and Takéuchi (1979), however, have observed an isomer shift of 1.04 mm/s at 293 K, relative to stainless steel, for  $\text{Fe}^{2+}$  in the  $\text{Fe}^{2+}(\text{B})$  site of an ilvaite. Using the conversion factor cited by Dyar (1984), this isomer shift is 0.95 mm/s relative to Fe metal, demonstrating that such small shifts, while unusual, are known to occur for  $\text{Fe}^{2+}$  in octahedral coordination in silicates. Moreover, for a different ilvaite specimen [with an isomer shift relative to metallic Fe of 1.15 mm/s in the  $\text{Fe}^{2+}(\text{B})$  site], spectra were obtained at both 293 and 80 K, and the decrease in quadrupole splitting for that site was nearly the same as it was for Dowty's inner doublet from 294 to 77 K. We thus interpret the inner doublet in Figure 2 as due to  $\text{Fe}^{2+}$  in octahedral coordination, and the discussion that follows is obviously strongly dependent on that choice.

Peak intensities indicate that ~75% of the Fe is in tetrahedral coordination, and ~25% is in octahedral coordination. Seven octahedral sites are available, but crystal-chemical arguments (Smith, 1968) suggest that the octahedrally coordinated Fe is in the **Al(3A)**,<sup>1</sup> **Al(3B)**, **U(1)**, and **U(2)** sites of the " $\text{Fe}_2\text{Al}_{0.7}\text{O}_2(\text{OH})_2$ " monolayer, rather than the **Al(1A)**, **Al(1B)**, and **Al(2)** sites of the "kyanite" layer. Even if all of the cobalt in this  $\text{Fe}_{80}\text{Co}_{20}$  staurolite entered the tetrahedral Fe site, the absence of 25% of the Fe would yield a site occupancy of only 0.80 for that position. In fact, we would expect some Co in the octahedral sites, given that the crystal-field stabilization energy for  $\text{Co}^{2+}$  in octahedral coordination exceeds that for  $\text{Fe}^{2+}$  by  $\frac{2}{5}\Delta_0$ —about  $2600\text{ cm}^{-1}$  using the values of  $Dq$  ( $=0.1\Delta_0$ ) for  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  from Walsh et al. (1976)—and that  $\text{Co}^{2+}$  should exhibit a slight preference for octahedral coordination over tetrahedral coordination according to simple crystal-field theory. Site-occupancy refinements of natural staurolites (Smith, 1968; Tagai and Joswig, 1985; Bringham and Griffen, 1986) yield Fe sites much more nearly fully occupied than 0.80. We assume that site oc-

<sup>1</sup> 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.

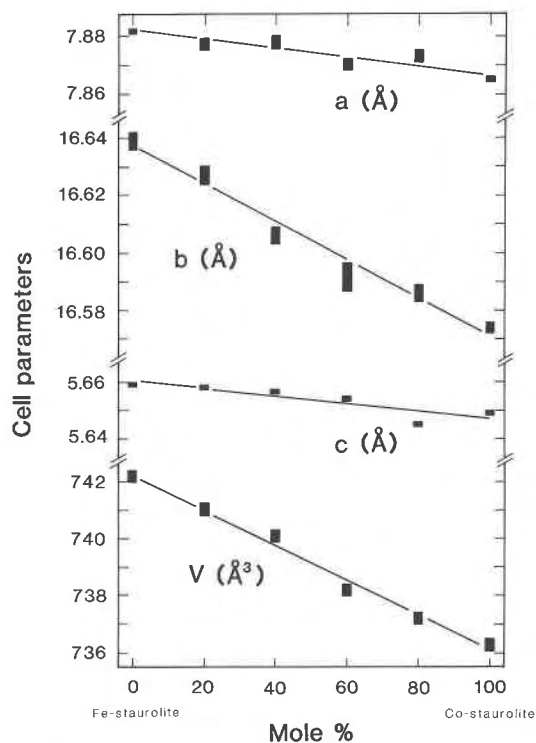


Fig. 3. Variation in lattice parameters for synthetic Fe-Co staurolites. Lattice parameters for the Fe endmember were taken from Griffen (1981). Symbols are two esd's in height.

cupancies in this synthetic staurolite are similar to those in natural specimens, and the only other element available to increase the occupancy of the Fe site in the synthetic mineral is Al. Thus, even though the Fe in the **Al(3)** sites does not "displace" any Al (because of the partially occupied state of those octahedra), there is evidently a crystal-chemical requirement that some Al enter the Fe site in staurolite "in exchange" for some Fe (not necessarily an equal amount) entering the **Al(3)** sites. Inasmuch as the protons lie on a line between the Fe and **Al(3)** sites, and closer to the latter, it may be that the Al-Fe exchange is a way of reducing electrostatic repulsion between the **Al(3)** and **P(1)** sites. [See Fig. 1 of Tagai and Joswig (1985) or Fig. 4 of Takéuchi et al. (1972) for positions of protons relative to cation sites.]

Griffen (1981) used a plot of  $r^3$  (the cube of the ionic radius) vs. unit-cell volume to estimate the radius of four-coordinated  $\text{Zn}^{2+}$  as  $0.56\text{ Å}$ , substantially smaller than the  $0.60\text{-Å}$ -radius given by Shannon (1976), and he recommended the use of  $0.57\text{ Å}$  ( $\pm 0.01\text{ Å}$ ), consistent with the data of Griffen and Ribbe (1979). Figure 4 is a similar plot, with the Fe-Co staurolites of this study included, and  $0.58\text{ Å}$  (Shannon, 1976) used as the radius of  $^{56}\text{Zn}^{2+}$ . The solid line is a least-squares fit to all of the data, and the dashed line is a least-squares fit to only the Fe-Co staurolite data. Extrapolation of either line to  $733.9\text{ Å}^3$  (the unit-cell volume of synthetic Zn staurolite) leads to a  $^{56}\text{Zn}^{2+}$  radius of  $0.56\text{ Å}$ , substantiating the earlier result (assum-

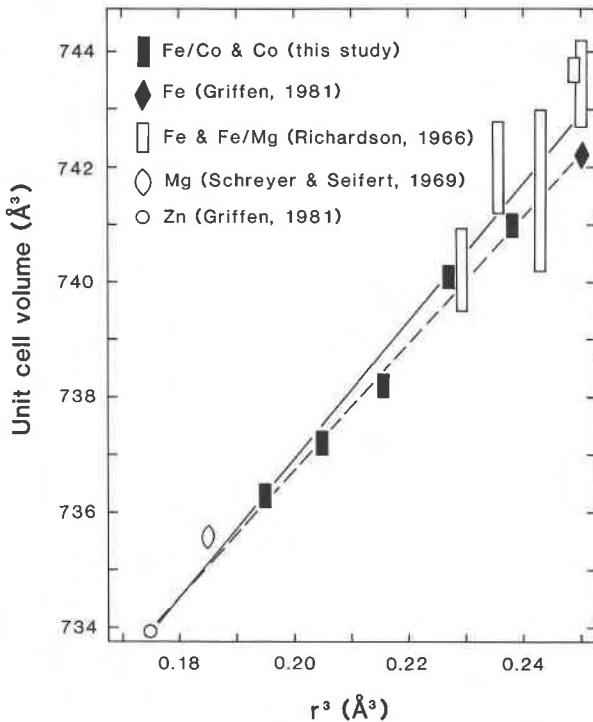


Fig. 4. Plot of the unit-cell volume as a function of the cube of the ionic radius of the metal atom. Radii were taken from Shannon (1976). The solid line is at least-squares fit to all data, and the dashed line is a least-squares fit to only the syntheses done at 30 kbar. The lines are extrapolated to 733.9 Å<sup>3</sup>, the cell volume of Zn staurolite (Griffen, 1981). Symbols are two esd's in height.

ing, of course, Shannon's radii for <sup>IV</sup>Fe<sup>2+</sup>, <sup>IV</sup>Mg<sup>2+</sup>, and <sup>IV</sup>Co<sup>2+</sup> to be accurate). Because the staurolites represented by solid symbols were all synthesized at pressures higher than those represented by open symbols, we might have expected them to yield smaller effective radii. It is interesting, if inexplicable, that higher-pressure syntheses (dashed line) fall, on the average, to the high-radius side of the lower-pressure syntheses (solid line) in Figure 4.

### CONCLUSIONS

The successful synthesis of pure-Co staurolite ("end-member" lusakite), as well as four compositions nominally uniformly distributed in composition between the Fe and Co endmembers, demonstrates that crystal-chemical factors do not prohibit a complete solid solution between pure-Fe staurolite and lusakite. Apparently the rarity of such specimens in nature simply reflects the paucity of Co in pelitic rocks. The fact that the sole reported natural cobaltoan staurolite contains a greater weight percent Co than, and about the same cation percent Co as, accompanying magnetite, hematite, ilmenite, and chlorite (Cech et al., 1981) suggests that Co, like Zn (Guidotti, 1970), may preferentially partition into staurolite.

Our interpretation of the Mössbauer spectrum of the staurolite with composition Fe<sub>80</sub>Co<sub>20</sub> leads us to conclude

that some Fe<sup>2+</sup> always enters octahedral Al sites, and that some Al occupies the tetrahedral Fe site, despite the fact that composition does not require either substitution. We suspect that local charge-balance considerations are important in driving the exchange and suggest that reduction of electrostatic repulsions between protons and atoms at the Al(3) site may be an important factor.

The unit-cell volumes of synthetic lusakite-staurolite solid solutions, either alone or when combined with the cell volumes of other synthetic staurolites, substantiate the conclusion by Griffen (1981) that <sup>IV</sup>Zn<sup>2+</sup> has a smaller effective ionic radius than <sup>IV</sup>Mg<sup>2+</sup>.

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