

THE CRYSTAL CHEMISTRY OF STAUROLITE: DISCUSSION

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I read with nostalgic interest the three papers by Hawthorne *et al.* (1993) on the crystal chemistry of staurolite because of the work I did on this mineral early in my career (Hollister & Bence 1967, Dollase & Hollister 1969, Hollister 1970). Although much has been written on this enigmatic mineral, no study has come as close to giving a complete understanding of the crystal chemistry of staurolite as that given in the three companion papers by Hawthorne *et al.* (1993).

Unfortunately, for me and for those interested in the evolution of ideas about staurolite, the Hawthorne *et al.* (1993) papers do not point out that some of their major conclusions were already reached in the three papers I was involved with more than 20 years ago. One possible reason for the lack of appropriate citations is given in the last page of the same issue of *The Canadian Mineralogist* that contains the Hawthorne *et al.* (1993) papers: in a one-page note, Hawthorne (1993, p. 772) apologizes for not giving proper credit in another paper owing to his "usual disorganized fashion". A second reason for the lack of citation may have been that my papers were primarily on sector zoning, and therefore their *crystal-chemical contributions* may not have been picked up in subsequent discussions of the crystal chemistry of staurolite by Donnay & Donnay (1983) and Holdaway *et al.* (1986b), which Hawthorne and his colleagues may have depended on in setting the stage for their studies.

In Hollister (1970), I used sector zoning as a "tool" to constrain site occupancies; the single-crystal work reported by Dollase & Hollister (1969) showed that different sectors in a single crystal had different degrees of order of Al and of vacancies on one site, $M(3)$, implying that a crystal could grow with two different space-groups under one set of external conditions at one time. The following specific points made in my earlier studies should have been taken into account by Hawthorne *et al.* (1993):

(1) Although I assigned most of the Mg to the tetrahedral site along with Mn, Fe^{2+} , and Zn, for the reason given below I assigned about 10% of the Mg to the $M(3)$ sites.

(2) The (001) sector has more total cations per for-

mula unit in $M(3)$ than does $M(3)$ of the sectors (010) and (110).

(3) The (001) sector has apparent orthorhombic symmetry owing to disorder of Al and vacancies in $M(3)$ in the (001) sector, whereas ordering of Al and vacancies in the (010) sector results in monoclinic symmetry.

I was able to make the first two points because of unprecedented accuracy in determining compositional differences across the sector boundaries containing growth zones that clearly must have formed under the same external conditions of P, T, fugacities of oxygen and water, and rock composition. The reason we then made exceptional effort to obtain samples of the separate sectors for single-crystal work (point 3) was that the model for the origin of sector zoning led to a prediction that there would be symmetry differences between sectors; we were pleased that this prediction was confirmed by the single-crystal X-ray work, lending support to the model for sector zoning.

I am, thus, both chagrined and pleased with the results of the new studies on staurolite. On one hand, the results confirm some of my earlier conclusions and hence some aspects of my model for sector zoning; on the other, I did not get credit for my work.

There are several loose ends remaining regarding the crystal chemistry of staurolite. I predicted that Ti enters the $M(3)$ position in a coupled substitution with Mg: $(Ti + Mg) = 2Al$. This prediction was based in part on the fact that the Mg and Ti contents changed in the same direction across the sector boundaries, whereas Al changed in the opposite direction; it was based in part on consideration of the orientation of chains of $M(3)$ octahedra with respect to growth surfaces. Hawthorne *et al.* (1993) did not define which octahedrally coordinated position Ti occupies in staurolite. Because of its relatively large atomic weight and its abundance in staurolite, I would have thought that the new single-crystal refinements would have revealed its location. Perhaps the reason Hawthorne *et al.* (1993) could not refine better the positions of Ti is that in selecting crystals to work on, they did not consider that their crystals probably contained several sectors. Data obtained for such crystals would surely

be ambiguous because of the relatively large difference in Ti content between sectors [100% between the (010) and (001) sectors: Hollister 1970, Table 1]. Similarly, the conclusions of Hawthorne *et al.* (1993) on degree of order on $M(3)$ in staurolite also would

have been better constrained if attention had been paid to the sectoral variations of degree of order in single crystals of staurolite.

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THE CRYSTAL CHEMISTRY OF STAUROLITE: REPLY

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INTRODUCTION

Hawthorne *et al.* (1993) listed 31 specific conclusions concerning the crystal chemistry of staurolite; we did not claim to be the first to prove every one of them. Indeed, our goal was to try and understand the structural chemistry of staurolite rather than to try and accrue any scientific credit. As far as the "major conclusions" claimed to have been established in previous work (Hollister 1994), these involve one site assignment and one predicted site-occupancy. Neither of these points was considered to be of sufficient importance to have been listed as one of the 31 conclusions in Hawthorne *et al.* (1993); so much for the major nature of these points of contention.

A large number of investigators have proposed a large number of possible site-assignments for staurolite. In the interests of brevity (and clarity), we chose not to cite inconclusive predictions. We also note that both reviewers of our papers commented on our constructive use of previous work in developing the crystal-chemical arguments.

SITE-OCCUPANCY DETERMINATION

Before we address the specific issues raised by Hollister (1994), it is apparent that we have to make the following point. Crystal-structure refinement can tell us the (long-range) position of an atom in the (averaged) unit-cell of a crystal, and is the only technique to do so directly. Chemical analysis tells us what atoms are present in the structure of a crystal, but does *not* tell us where that species occurs in the crystal structure. From the results of a chemical analysis, one can make inferences as to the location of a species in a

structure; such inferences may be well reasoned, or they may involve out-and-out guesswork, but they remain inferences or guesses, not proof. We wish to emphasize that only a scattering technique can incorporate the phase and amplitude information necessary to locate an atom species; spectroscopic techniques also can be important for this type of work, but they measure energy, and are normally effective through correlation of energetic information with previously derived crystal-structure data.

SPECIFIC ISSUES

We have extracted the points of contention from the text of Hollister (1994) and list them below:

(1) Hollister (1970) assigned ~10% of the Mg in the formula to the $M(3)$ sites.

The "proof" for this in Hollister (1970) consists of the statement "Furthermore, (Mg + Ti) should probably be considered with Al in the substitutions in the Al(3) site". How this unsupported statement can be considered as an established fact escapes us.

(2) Hollister (1994) notes that the (001) sector of a sector-zoned staurolite crystal has more cations per formula unit (pfu) at $M(3)$ than is the case in the (010) and (110) sectors.

Hawthorne *et al.* (1993) made no statement pertaining to sector zoning whatsoever, although we note that this aspect of staurolite is currently under investigation as part of our ongoing cooperative work.

(3) The (001) sector has "apparent orthorhombic symmetry" due to disorder of Al and vacancies at $M(3)$,