

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

FRANK C. HAWTHORNE, LUCIANO UNGARETTI, ROBERTA OBERTI,
FRANCA CAUCIA AND ATHOS CALLEGARI

CNR Centro di Studio per la Cristallografia e la Cristallografia, via Abbiategrasso 209, I-27100 Pavia, Italy

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 $M(3)$,

whereas order of Al and vacancies in the (010) sector results in monoclinic symmetry (Hollister 1994).

Again, we note that we made no statements concerning sector zoning. Dollase & Hollister (1969) showed that, in sector-zoned crystals of staurolite, the (001) sector has orthorhombic symmetry, and the (010) sector has monoclinic symmetry. They did not establish that this difference in symmetry is due to different degrees of order between Al and vacancies at the $M(3)$ sites. It was a contention of Smith (1968) that major deviations from orthorhombic symmetry are due to Al–vacancy order over $M(3A)$ and $M(3B)$, together with ordering over $M(4A)$ and $M(4B)$.

(4) Ti was predicted to occur at the $M(3)$ sites according to the coupled substitution $\text{Ti} + \text{Mg} \rightarrow 2\text{Al}$.

As with point (1), no proof was provided for this assertion. Indeed, recent XAS work (Henderson *et al.* 1993) suggests that Ti orders at the $M(2)$ site. Furthermore, the suggestion that crystal-structure refinement could locate ~ 0.10 Ti apfu in a mineral containing ten major and minor scattering species and ~ 30 apfu displays a complete lack of understanding of

X-ray scattering and crystal-structure refinement.

GENERAL DISCUSSION

Contrary to the suggestion of Hollister (1994), we did examine the published literature on staurolite back to Náray-Szabó (1929), including the papers of Hollister & Bence (1967), Dollase & Hollister (1969) and Hollister (1970). While not wishing to disparage the significance of this work with regard to sector zoning, it contained no results of any substance on site occupancies in staurolite. In this regard, we note that recent major contributors to the resolution of crystal-chemical problems of staurolite (Holdaway *et al.* 1986a, b, Dutrow *et al.* 1986, Holdaway *et al.* 1991, Dutrow 1991, Henderson *et al.* 1993) did not feel compelled to recognize the “major conclusions” of Hollister (1970). While not normally subscribing to the idea of “science by acclamation”, we feel that the similar attitude taken by these authors endorses our original actions.

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