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CRYSTAL-STRUCTURE REFINEMENT OF HYDROGEN-RICH STAUROLITE

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ABSTRACT

The crystal structures of two samples of hydrogen-rich staurolite have been refined to *R* indices of ~2% using single-crystal Mo$K\alpha$ X-ray data. Complete site-populations are derived by a combination of site-scattering refinement and mean bond-length arguments. There is considerable occupancy of the *M*(4*A*) and *M*(4*B*) sites, in line with the results of Hawthorne *et al.* (1993a). The sums of the cations for each structure are 29.48 and 29.31 apfu, respectively, in agreement with the high H contents of the crystals. The total occupancy of the *M*(3) sites [*M*(3*A*) and *M*(3*B*)] is variable in staurolite; the vacancy content of *M*(3) correlates linearly with the hydrogen content of the crystal, confirming previously suggested mechanisms of substitution (Hawthorne *et al.* 1993c) involving variable occupancy of *M*(3) in staurolite.

Keywords: staurolite, crystal-structure refinement, electron-microprobe analysis, ion-microprobe analysis, site populations, hydrogen content.

SOMMAIRE

Nous avons affiné la structure cristalline de deux échantillons de staurotide riche en hydrogène, jusqu'à un résidu *R* d'environ 2% au moyen de données de diffraction X obtenues sur cristal unique (rayonnement Mo$K\alpha$). La répartition des atomes sur les sites a été effectuée grâce à un affinement de la dispersion associée aux divers sites et des longueurs moyennes des liaisons. Ces échantillons montrent un taux d'occupation important des sites *M*(4*A*) et *M*(4*B*), en accord avec les résultats de Hawthorne *et al.* (1993a). Ces deux échantillons contiennent 29.48 et 29.31 cations par unité formulaire, respectivement, ce qui concorde avec leurs teneurs élevées en hydrogène. Le taux d'occupation des sites *M*(3) [*M*(3*A*) et *M*(3*B*)] est variable dans la staurotide; la proportion de lacunes dans cette position montre une corrélation avec la teneur en hydrogène, et confirme ainsi le schéma de substitution qu'avaient proposé Hawthorne *et al.* (1993c), impliquant un taux d'occupation variable de la position *M*(3).

(Traduit par la Rédaction)

Mots-clés: staurotide, affinement de la structure cristalline, données de microsonde électronique, données de microsonde ionique, population des sites, teneur en hydrogène.

INTRODUCTION

Hawthorne *et al.* (1993a, b, c) have examined the crystal-chemical details of the staurolite structure on the basis of refinements of 42 staurolite crystals that cover a wide range of chemical composition. However, they refined the structure of only one staurolite sample with a hydrogen content greater than 3.2 H apfu (atoms per formula unit), sample 71–62R of Holdaway *et al.* (1986a, b). As the refinement of H-rich staurolite (H > 4.0 apfu) was an important factor in unravelling the chemical and structural complexity of staurolite, particularly with regard to the variable total occupancy of the *M*(3) sites, it was considered advisable to examine some other crystals of this type (*i.e.*, with H > 4.0 apfu) in order to confirm (or deny) the stereochemical details reported by Hawthorne *et al.* (1993a, b, c).

EXPERIMENTAL

We obtained two samples of H-rich staurolite from Dr. M.J. Holdaway, samples 71–60E and 77–55C of Holdaway *et al.* (1986b), with H contents of 4.12 and 4.18 apfu, respectively, and here denoted S(43) and S(44). Crystals for X-ray work were chosen on the basis of optical clarity, freedom from inclusions, and

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TABLE 1. CELL DIMENSIONS AND STRUCTURE REFINEMENT INFORMATION FOR H-RICH STAUROLITE CRYSTALS

	S(43)	S(44)
a (Å)	7.863(2)	7.861(2)
b	16.596(7)	16.610(7)
c	5.650(2)	5.649(2)
β (°)	90.04(3)	90.18(3)
V (Å^3)	737.3(4)	737.6(4)
Sample*	77-55C	71-60E
R(sym)	2.00	2.90
N(all)	2361	2364
N(obs)	1612	1719
R(obs)	1.77	2.24
R(all)	3.56	3.48

* Sample numbers of Holdaway *et al.* (1986b).

TABLE 2. FINAL ATOMIC PARAMETERS* FOR H-RICH STAUROLITE CRYSTALS S(43) – TOP AND S(44) – BOTTOM

	x	y	z	$B_{eq.}$ (Å^2)
O1A	0.23371	0	0.96473	0.66
	0.23274	0	0.96383	0.61
O1B	0.23452	0	0.53382	0.65
	0.23511	0	0.53346	0.65
O2A	0.25522	0.16147	0.01526	0.44
	0.25550	0.16183	0.01473	0.42
O2B	0.25495	0.16142	0.48432	0.43
	0.25483	0.16142	0.48408	0.42
O3	0.00194	0.08881	0.24865	0.62
	0.00222	0.08912	0.24540	0.63
O4	0.02107	0.24935	0.24987	0.42
	0.02126	0.24948	0.25018	0.40
O5	0.52740	0.10026	0.24975	0.39
	0.52773	0.10014	0.24911	0.40
T(1)	0.13413	0.16612	0.24965	0.31
	0.13421	0.16628	0.24856	0.30
T(2)	0.39394	0	0.24922	1.21
	0.39548	0	0.24864	1.08
M(1A)	1/2	0.17460	0	0.38
	1/2	0.17497	0	0.36
M(1B)	1/2	0.17452	1/2	0.38
	1/2	0.17433	1/2	0.36
M(2)	0.26335	0.41038	0.25024	0.48
	0.26448	0.41009	0.25166	0.43
M(3A)	0	0	0	0.43
	0	0	0	0.42
M(3B)	0	0	1/2	0.43
	0	0	1/2	0.43
M(4A)	1/2	0	0	0.76
	1/2	0	0	0.69
M(4B)	1/2	0	1/2	0.83
	1/2	0	1/2	0.69

* standard deviations are ≤5 in the last decimal place.

TABLE 3. REFINED SITE-SCATTERING POWERS* (EPFU) IN H-RICH STAUROLITE CRYSTALS

	N**	S(43)	S(44)
M(1A)	4	52.7	52.4
M(1B)	4	52.8	52.4
M(2)	8	106.6	105.1
M(3A)	2	13.4	15.3
M(3B)	2	11.5	8.6
M(4A)	2	3.0	7.7
M(4B)	2	2.4	2.7
T(2)	4	74.5	70.3

* esds are 0.1–0.4 epfu;
** N is the number of sites corresponding to the structural formula.

equant shape. The crystals selected were mounted on a Philips PW 1100 automated four-circle single-crystal diffractometer equipped with graphite-monochromated Mo$K\alpha$ X-radiation. Unit-cell dimensions were calculated from least-squares refinement of the positions of 48 aligned reflections in the range $-35° < \theta < 35°$; values are given in Table 1, together with other information pertinent to data collection and refinement.

Intensity data were collected and the structures were refined in *C*2/*m* according to the procedure of Hawthorne *et al.* (1993a). Refinements converged to *R* indices given in Table 1. Atomic coordinates and isotropic displacement factors are given in Table 2, refined site- scattering values are given in Table 3, and selected interatomic distances are given in Table 4.

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å)* IN H-RICH STAUROLITE CRYSTALS

	S(43)	S(44)		S(43)	S(44)
T(1)–O2A	1.633	1.633	T(2)–O1A	2.042	2.052
T(1)–O2B	1.632	1.633	T(2)–O1B	2.039	2.047
T(1)–O3	1.651	1.649	T(2)–O5	1.967	1.961
T(1)–O4	1.643	1.643	<T(2)–O>	2.004	2.006
<T(1)–O>	1.640	1.640			
M(1A)–O2A	1.939	1.936	M(1B)–O2B	1.941	1.941
M(1A)–O4	1.901	1.897	M(1B)–O4	1.903	1.903
M(1A)–O5	1.887	1.890	M(1B)–O5	1.888	1.891
<M(1A)–O>	1.909	1.908	<M(1B)–O>	1.911	1.912
M(2)–O1A	1.920	1.927	M(3A)–O1A	1.849	1.842
M(2)–O1B	1.924	1.925	M(3A)–O3	2.036	2.028
M(2)–O2A	1.922	1.927	<M(3A)–O>	1.974	1.966
M(2)–O2B	1.921	1.914			
M(2)–O3	1.876	1.869	M(3B)–O1B	1.854	1.857
M(2)–O5	1.864	1.869	M(3B)–O3	2.047	2.064
<M(2)–O>	1.904	1.905	<M(3B)–O>	1.982	1.995
M(4A)–O1A	2.103	2.110	M(4B)–O1B	2.096	2.091
M(4A)–O5	2.192	2.189	M(4B)–O5	2.194	2.197
<M(4A)–O>	2.162	2.163	<M(4B)–O>	2.162	2.162

* standard deviations are ≤0.002 Å.

TABLE 5. RESULTS OF ELECTRON AND ION MICROPROBE ANALYSES, AND UNIT FORMULAE* OF STAUROLITE CRYSTALS

	S(43)	S(44)
SiO_2	27.93	27.64
Al_2O_3	55.28	54.60
TiO_2	0.33	0.40
Cr_2O_3	0.03	0.04
FeO	12.97	12.67
MgO	0.18	0.75
MnO	0.10	0.32
CoO	0.02	0.03
ZnO	0.01	0.06
Li_2O	0.56	0.24
H_2O	(2.24)	(2.25)
Sum	99.65	98.77
Si	7.708	7.691
Al	0.292	0.309
Sum	8.000	8.000
Al	17.687	17.598
Cr	0.006	0.009
Ti	0.068	0.084
Fe	2.993	2.949
Mg	0.074	0.311
Mn	0.023	0.075
Zn	0.002	0.012
Co	0.004	0.007
Li	0.621	0.269
CATSUM	29.480	29.313
H	4.123	4.176

* calculated on the basis of 48(O,OH,F)

TABLE 6. SITE POPULATIONS IN STAUROLITE CRYSTALS

Site		S(43)	S(44)
M(1)	Al	7.86	7.87
	Mg	0.02	0.07
	Fe*	0.12	0.06
M(2)	Al	7.80	7.92
	Mg	0.00	0.02
	Fe*	0.20	0.06
M(3)	Al	1.91	1.84
	Mg	0.01	0.03
	□	2.08	2.13
M(4)	Fe*	0.21	0.40
	□	3.79	3.60
T(1)	Si	7.71	7.69
	Al	0.29	0.31
T(2)	Fe**	2.58	2.61
	Mg	0.04	0.19
	Li	0.62	0.27
	Al	0.12	-
	□	0.64	0.93
Sum T(2)		4.00	4.00

* Fe* = Fe^{3+} + Cr + Ti
** Fe** = Fe^{2+} + Mn + Zn + Co

Subsequent to the collection of the X-ray-diffraction data, the crystals were mounted in epoxy and analyzed by electron microprobe according to the procedure of Hawthorne *et al.* (1993a). Average compositions (10 points) for each crystal are given in Table 5; the cell contents were calculated on the basis of 48 atoms of oxygen using the H_2O and Li_2O values of Holdaway *et al.* (1986a).

DISCUSSION

Background information to the points addressed here is given in Hawthorne *et al.* (1993a, b, c).

Site populations

Site populations were assigned as in Hawthorne *et al.* (1993a); values are given in Table 6. The $T(1)$ populations are consistent with the observed $<T(1)\text{–O}>$ distances as expressed by Hawthorne *et al.* (1993a, their Fig. 6). The $<M(1)\text{–O}>$, $<M(2)\text{–O}>$ and $<M(3)\text{–O}>$ distances agree very closely with the correlations developed by Hawthorne *et al.* (1993a, their Figs. 7, 11 and 12), and the Mg site-populations were assigned on this basis. The refined site-scattering values at the $M(1)$ and $M(2)$ sites show a slight enrichment in transition metals (stronger scatterers) at the $M(2)$ site; site populations for the transition metals (expressed as Fe^{*} = Fe + Cr + Ti) were assigned on the basis of the refined site-scattering values. The $M(4)$ site-populations were assigned on the basis of the refined site-scattering values at these sites, assuming occupancy by Fe^{*}. Remaining cations (including Zn, Co and Li) were assigned to the $T(2)$ site.

Total cations in staurolite

A key aspect of compositional variation in staurolite is the substitution

$$^{M(4)}Fe^{2+} + {}^{T(2)}\square_2 \rightarrow {}^{M(4)}\square + {}^{T(2)}Fe^{+} \qquad (1)$$

TABLE 7. END-MEMBER AND EXCHANGES INVOLVING VARIATION IN M(3) SITE POPULATIONS IN STAUROLITE

	End member								exchange vector
	Heterovalent exchanges involving hydrogen								
(1)	$\square_4$	Fe^{2+}_4	Al_{16}	$(Al_2\square_2)$	Si_8	O_{40}	$(OH)_2$	O_6	Additive component
(3)	$\square_4$	Fe^{2+}_4	Al_{16}	$(\square_4)$	Si_8	O_{40}	$(OH)_8$	–	$\square(OH)_6(AlO_3)_{-2}$
*(7)	$\square_4$	Al_4	Al_{16}	$(Al_{0.67}\square_{3.33})$	Si_8	O_{40}	$(OH)_2$	O_6	$Al_4\square_{1.33}(Fe_4Al_{1.33})_{-1}$

* note that the end member could be simplified to $\square_4Al_4Al_{16}\square Si_8O_{40}[(OH)_4O_4]$ at the expense of complicating the exchange vector: $Al_4\square_2(OH)_2[Fe^{2+}_4Al_2O_2]_{-1}$.

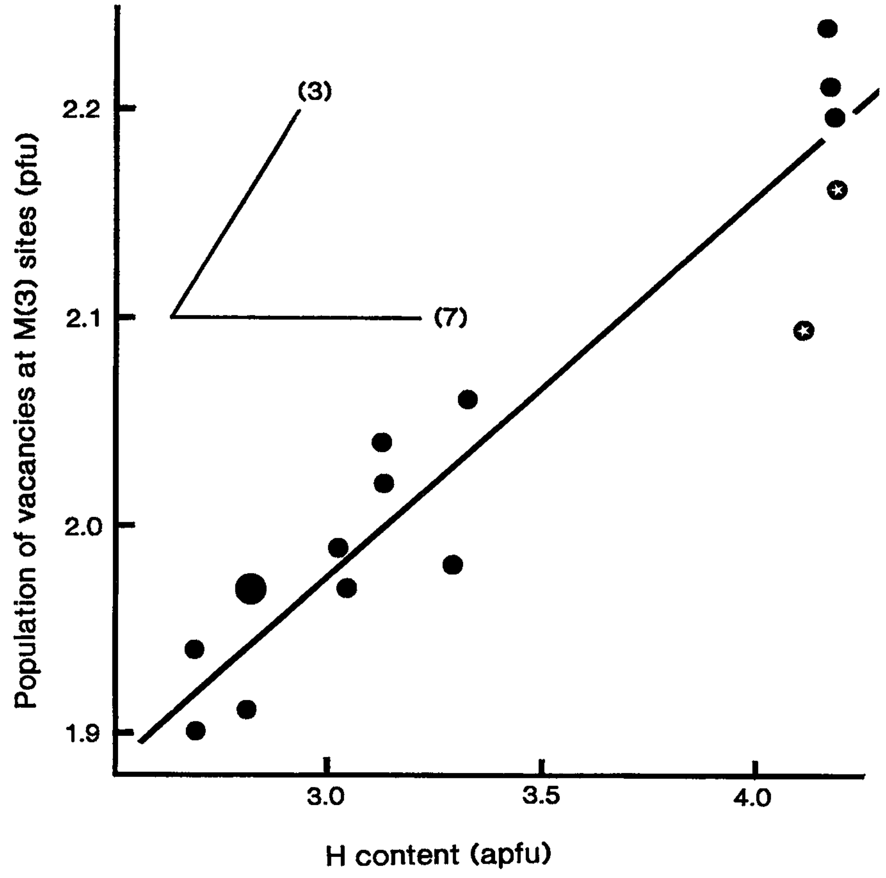

FIG. 1. Variation in vacancy population of M(3) *versus* H content in staurolite; circles are data from Hawthorne *et al.* (1993a), stars are data from this work, and the large circle shows two overlapping data-points. The ideal trends for exchanges (3) and (7) (Table 7) are shown by the lines in the top left of the figure.

which is coupled to a □ → H substitution to maintain electroneutrality, where □ denotes a vacancy. The extent of this substitution controls the total number of cations in the unit formula of staurolite, CATSUM. Hawthorne *et al.* (1993c) showed that CATSUM is related to the total H and Li contents of the structure by the relation

$$\text{CATSUM} = 31.333 - 0.495(22)\text{H} + 0.321(38)\text{Li} \quad (2).$$

Using the H and Li contents of S(43) and S(44) given in Table 5, this equation predicts the CATSUM values to be 29.49 and 29.35 apfu, respectively, in close agreement with the observed values (Table 5). This agreement confirms equation (2) for unusual values of H and Li contents.

Vacancies at the M(3) sites

Hawthorne *et al.* (1993c) proposed nine heterovalent exchanges in staurolite. Seven of the exchanges leave the cation content of the *M*(3) sites [*M*(3*A*) + *M*(3*B*)] unchanged at a value of 2 apfu [+ 2□ pfu]. The other two exchanges (Table 7) involve changes in the total cation content of the *M*(3) sites. For exchange (3), the vacancy content of the *M*(3) sites should show a linear correlation with the H content, with a slope of 0.333 □/H; for exchange (7), the vacancy content of the *M*(3) sites should be independent of the H content. Figure 1 shows the variation in vacancy (pfu) at *M*(3) *versus* the H content for the staurolite crystals examined by Hawthorne (1993a) and in this work. There is a linear relationship developed, albeit with quite a lot of scatter, with a slope of 0.18. Also shown in Figure 1 are the ideal trends for exchanges (3) and (7). It is apparent that exchange (3) seems dominant.

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