

H content of staurolite as determined by H extraction line and ion microprobe

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ABSTRACT

H₂O analyses for 31 staurolites, determined using H-isotope extraction-line and ion-microprobe techniques, range from 1.43 to 2.26 wt%. The two techniques are consistent with each other. Whereas H₂O contents determined using the H-isotope extraction line are more precise, the ion microprobe has the advantage of eliminating the H₂O contributed from contaminating phases.

The staurolites fall into two groups: (1) Those that coexist with garnet and/or biotite contain 1.43 to 1.84% H₂O (2.7 to 3.4 H ions per 48-oxygen formula unit). For such staurolites the assumption of 3.06 H ions, in the absence of a good H₂O analysis, minimizes error in the remainder of the stoichiometry. (2) Staurolites that coexist with hemo-ilmenite but not with garnet or biotite contain 2.24 to 2.26% H₂O [4.09 to 4.16 H ions per formula unit (pfu)], and for such staurolites the assumption of 4.14 H ions pfu introduces little error in the stoichiometry. Consequently, knowledge of coexisting phases seems to allow reasonable estimates of H contents that provide better stoichiometry than subtraction from 100% or assumption of 2 or 4 H pfu.

INTRODUCTION

Most recent chemical analyses of staurolite have been determined using the electron microprobe and have not included light elements or Fe²⁺/Fe³⁺ ratios. Whereas the quality of analyses for the elements analyzed has increased greatly in recent years, lack of information on constituents such as H, Li, and Fe³⁺ has hampered our understanding of staurolite crystal chemistry.

Takéuchi et al. (1972), using neutron diffraction and nuclear magnetic resonance, suggested that the H positions in staurolite are located near the O(1A) and O(1B) positions at corners of the Al(3A) and Al(3B) octahedra (Ribbe, 1982). This would allow up to 8 H on a 48-oxygen basis. Other authors (Ganguly, 1972; Juurinen, 1956) have argued for 2 H per formula unit (pfu) (which allows charge balance for the simplest staurolite formula) or 4 H pfu (which is closer to some analytical determinations for H₂O). Lonker (1983 and unpub. ms.) determined H₂O contents of 42 microprobe-analyzed staurolites using a DuPont moisture analyzer; his H₂O values ranged from 0.95 to 1.92 wt% corresponding to H contents between 1.8 and 3.6 pfu, thus establishing the variability of H in staurolite.

Failure to determine the H₂O content of staurolite will lead to inaccurate stoichiometry unless the H is charge-balanced by some other ion that also is not being analyzed. If one assumes that the H in a group of staurolites is fixed

at some value, this assumption may cause variations in stoichiometry that are largely artifacts of the assumption of fixed H (Griffen et al., 1982).

Accurate analysis of H in staurolite is difficult. Apart from the primary difficulty of obtaining a pure sample, there are three analytical problems that do not occur with many other silicates. (1) Staurolite does not evolve all its H₂O even at temperatures of 1000°C. Juurinen (1956) found it necessary to use a flux to release all the H₂O from staurolite. (2) It is probable that heating of staurolite evolves H in more than one form. The presence of Fe²⁺ and, in some cases, graphite inclusions may produce H₂O, H₂, and CH₄ in relative proportions that may vary with mineral chemistry and analytical technique. (3) Not all the adsorbed H₂O is removed from staurolite at 110°C, as observed by Juurinen (1956). Analysis by ion probe eliminates most of these problems, but a new set of problems arises. Calibration must be done with the same mineral in order to minimize matrix effects (Steele, 1983); a blank correction must be made for H in the vacuum system; and matrix effects are possible between staurolites, especially when one considers that some substitution is required to balance the variation of H⁺.

As part of a larger investigation into the crystal chemistry of staurolite, we have analyzed the H₂O contents of 31 staurolite specimens using a H-isotope extraction line and an ion microprobe. We have also analyzed these same staurolites for elements heavier than F using standard electron-microprobe techniques (Holdaway et al., 1986) and for Li and F with the ion microprobe (Dutrow et al., 1986).

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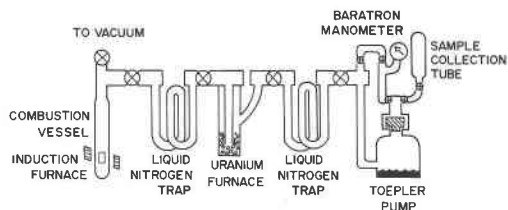


Fig. 1. Schematic diagram of the H extraction line. See text for explanation.

ANALYTICAL PROCEDURES

Preparation of staurolite

Examination of mineral grains or thin sections showed that in several cases staurolite was filled with inclusions, especially quartz and/or ilmenite. The grain size used for analysis, which was 100–325 mesh or ≤ 325 mesh, was a function of the amount and coarseness of inclusions. All samples were elutriated repeatedly to remove the dust or finest fraction. Samples were purified first by centrifuging with methylene iodide to remove minerals with density ≤ 3.3 and then by using a Frantz isodynamic separator. Samples selected for analysis are estimated to be between 97.5 and 100% pure. In decreasing order of abundance, the contaminating minerals are quartz, biotite, ilmenite, and muscovite; all other minerals occur in very minor amounts. In some samples, quartz or ilmenite tended to dilute the amount of H_2O indicated by analysis, whereas in others, the presence of micas tended to increase H_2O content.

Purified samples, dried overnight in air at $110^\circ C$ and kept in a desiccator before weighing, were used for H-extraction-line analysis. An aliquot of between 60 and 110 mg was weighed to $\pm 10 \mu g$ using a Mettler M-5 microbalance. For ion-probe analysis, 5×5 grids were marked on the back of two 1-in.-round glass slides. Several grains of each sample were mounted in Araldite brand epoxy, one sample per grid square, polished, and coated with a $\sim 25\text{-\AA}$ thickness of gold (Steele et al., 1981). In order to test for geometrical variations in ion-probe emission of H^+ relative to Si^+ , specimens 355-1 and 356-1 were repeated throughout the grid at corners, the center, and at the centers of edges.

H extraction line

Description. The H extraction line used was that of the Stable Isotope Laboratory at Southern Methodist University. The line (Fig. 1) operates under a vacuum of $\sim 5 \times 10^{-6}$ torr and consists of six basic components. In sequence in Figure 1, these are (1) a quartz-glass combustion vessel surrounded by the coil of an induction furnace; (2) the first liquid N trap ($-196^\circ C$); (3) a U furnace at $\sim 750^\circ C$, which liberates H from H_2O and CH_4 by converting U to oxides and carbides (Bigeleisen et al., 1952); (4) a second liquid N trap; (5) a Hg Toepler pump to quantitatively transfer the H; and (6) a reservoir section of tubing attached to a Baratron brand manometer that reads the H pressure. The sample is contained in a Mo crucible mounted in a quartz-glass holder in the center of the combustion vessel that is heated by the induction furnace.

Procedure. The main justification for the present analytical procedure is that it collects and measures all the structural H from a staurolite sample and minimizes all sources of contamination. Each analysis takes between $1\frac{1}{2}$ and 2 h. General aspects of the procedure are described by Bigeleisen et al. (1952).

After forming, each sheet-metal Mo crucible was filled with

about 750 mg of a 3:1 mixture of pulverized granite and Mg olive, from which the opaque minerals had been removed. The crucible and flux were baked at maximum temperature ($1500\text{--}1600^\circ C$) and full vacuum for 10 to 20 min, until no more gas was evolved. The crucible and flux were then free of H_2 , and the flux was clear, melted, and of sufficiently low viscosity to be relatively free of bubbles. Upon cooling, the crucibles were removed from the vacuum line and stored in a desiccator. Each crucible was used within 1 or 2 d, and it was found that each crucible could be used twice.

Up to six combustion vessels, loaded with crucibles and weighed staurolite samples, were heated at $125^\circ C$ and high vacuum overnight to remove all adsorbed moisture. Without losing vacuum, a loaded combustion vessel was put into the induction coil and the induction furnace turned up slowly over a 5-min interval. Once the closed vessel had been heated to maximum temperature, the induction furnace was turned down, the valve was opened, and the evolved gas allowed to flow through the first N trap and U furnace. H_2O and other condensable gases were frozen in the first liquid N trap, whereas H_2 and other noncondensable gases (e.g., CH_4) passed through the U furnace into the measuring reservoir. Next the induction furnace was again slowly turned up to maximum heat while trapping liberated gas with liquid N, converting any CH_4 to H_2 , and pumping evolved H_2 into the measuring reservoir. Gases were pumped and trapped while heating at $1500\text{--}1600^\circ C$ for 20 to 30 min or until no more gas was evolved. At this stage the staurolite grains were at least partially immersed in melt.

At this point, the first N trap was isolated, the coolant was changed to dry ice-acetone slush (-71 to $-78^\circ C$), and any CO_2 or SO_2 evolved was pumped out of the system through the diffusion pump line. The first trap was then slowly warmed to room temperature and heated lightly to convert the ice to H_2O vapor, which in turn was converted to H_2 in the U furnace and then continuously pumped into the measuring reservoir. After all the gas was removed from this section of the vacuum line, the second N trap was warmed and its contents passed back through the U furnace to ensure complete reduction of all H_2O released from the staurolite. The amount of H_2O from the first trap passing through the U furnace and being trapped in the second trap was always much less than 1% of the total sample. All the evolved H_2 was pumped with the Toepler pump into the reservoir for volumetric measurement.

The pressure on the Baratron gauge was calibrated for the reservoir by running accurately measured H_2O samples through the vacuum extraction line (Table 1). Disposable $5 \mu L$ capillary pipettes were filled and sealed in such a way as to ensure loss of neither H_2O nor glass. Accurate weighing of pipettes before and after filling and sealing allowed for precise measurement of H_2O . The constant of 0.0154 mg of H_2O /torr can be applied over a wide range of pressure for H_2 and has a trivial error. An independent calibration by J. B. involves the accurate measurement of the volume of the H reservoir by weighing it filled with Hg. The H content as a function of pressure was then determined assuming ideal-gas behavior. The calibration was linear between 0 and 700 torr and agreed with the more direct calibration within 0.5% relative.

Gas samples were collected and their H isotopes measured on the mass spectrometer to check for leaks or contamination from grease. In cases of repeat analyses, the amount of H_2O and the H-isotope composition were similar between samples (Table 2). In one repeat analysis, neither the amount of H_2O nor the H-isotope composition was the same. A third analysis proved to be similar to the second, so the first was discarded.

Table 1. Calibration of H extraction line

mg H ₂ O*	torr**	mg/torr
5.063	329.3	0.01538
5.088	330.0	0.01542
5.003	325.4	0.01537
5.003	325.5	0.01537
		0.01539(2)

* Includes +0.003 mg correction for glass lost in sealing.
** Includes +1.0 torr blank correction.

Blank runs were done every 1 or 2 d. In addition, experiments were run to correct for the amount of H₂O retained in the extraction line after a completed run; most of this H₂O is believed to reside in or near the U furnace. Blank runs were also done on crucibles that had previously been used for a single staurolite analysis. The overall correction was +1.0 torr for the first use of a crucible with flux and +0.7 torr for the second use of a crucible with flux and previous staurolite sample. These corrections include a correction for contamination of the whole system (-0.2 torr) which was measured in blank runs at the beginning of the day when the U furnace was completely free of H₂O. Corrected pressure readings varied from 65 to 150 torr with all but two values above 83 torr.

Stepwise heating experiments were conducted to assure that 125°C was the optimum temperature for overnight drying. Two samples were dried overnight in air, weighed, and kept in a desiccator. Each was evacuated for 30 min in the combustion vessel before heating. Specimens 117189 (100–325 mesh) and SL-1 (≤270 mesh) were heated 3 h at 110°C producing 0.04 and 0.07% H₂O, 12 h at 125°C producing 0.03 and 0.07% H₂O, 3 h at 175°C producing 0.01 and 0.01% H₂O, and 3 h at 240°C producing 0.02 and 0.01% H₂O, respectively. (A blank was run with the same procedure, and the reported values include small blank corrections.) From these experiments, it seems that virtually all the nonstructural H₂O is evolved at 125°C and a maximum of 0.03% structural H₂O is produced at 240°C.

Six analyses were repeated on different days and at random times of the day (Table 2). The average standard deviation of each pair was ±0.023% H₂O.¹ An NBS standard biotite stated as containing 3.5% H₂O was analyzed as 3.41%. A pyrophyllite from Staley, North Carolina, provided by the Smithsonian Institution (no. 97369), has 4.90% H₂O as measured. Lonker (1983) determined 5.02% H₂O on this pyrophyllite. Robie et al. (1976) reported H₂O contents of 4.7 and 4.94% for pyrophyllites from Staley. The theoretical value is 5.00%.

Ion microprobe

The University of Chicago ion microprobe is an AEI IM-20, which uses a primary beam (10–15 μm diameter) of ¹⁶O⁻ ions at 20-keV energy and a nominal beam current of 5 nA, with instrumental conditions described by Steele et al. (1981). The sample-chamber pressure was below 2 × 10⁻⁸ torr, and the extraction system was cooled by liquid N.

Procedures for H analysis using the ion microprobe have been described by Hinthorne and Andersen (1975) and Steele (1983). Prior to analysis the two 5 × 5 grids were kept in the sample chamber at vacuum for about 10 d. Background counts for ¹H⁺ in meteoritic olivine (assumed H-free) under these conditions are

¹ Unless otherwise stated, all errors quoted are $N - 1$ weighting of one standard deviation of the population (1σ).

Table 2. H₂O contents and H-isotope compositions for replicate analyses using the H extraction line

Specimen	H ₂ O (wt%)	D (‰ SMOW)
EH-6-1	1.536	-62.12
EH-6-2	1.582	-65.78
356-1-1	1.615	-73.92
356-1-2	1.583	-71.72
117183-1	1.693	-61.75
117183-2	1.667	-67.61
CT-DL-1-1	1.427*	-77.51
CT-DL-1-2	1.646	-92.43
CT-DL-1-3	1.629	-94.77
117189-1	1.675	n.d.
117189-2	1.723	-72.59
78332-1	1.699	-68.42
78332-2	1.720	-75.83

* Analysis discarded.

about 300 c.p.s., compared with 11 000 c.p.s. for staurolite. Background counts for ²⁹Si⁺ are negligible. Polished staurolite grains were analyzed by counting the ²⁹Si⁺ signal and then the ¹H⁺ signal for a 10-s period each after a 3½-min burn-in. The signal for ²⁸SiH⁺ was measured and found to be less than or equal to 1% of the ²⁹Si⁺ signal. Thus ²⁸SiH⁺ has no important effect on the ²⁹Si⁺ intensity. For each specimen, two grains were analyzed. If the two ratios of ¹H⁺/²⁹Si⁺ differed by more than 5%, a third grain was counted. Any ratio differing from the average of the other two by more than 7% was discarded; 6% of the ratios were discarded. The ratio (¹H⁺ - 300)/²⁹Si⁺ was then calculated for each position on each grid.

Variations in the collection efficiency of H⁺ relative to Si⁺ of up to 9% were observed across the thin section. It was found that for 355-1 and 356-1, the average ratio (¹H⁺ - 300)/²⁹Si⁺ decreased for five of the eight corners and at the middle of two of the edges. The decreases were systematic in that where lower ratios occurred on edges, an adjacent corner also had a lower ratio. The ratios of the nine central squares of the grid were not corrected; ratios for unknowns on edges were corrected by interpolation of the corrections necessary to bring the ratios for 355-1 and 356-1 back to the average value. In every case, two adjacent values could be used for these corrections. The corrections ranged from 1 to 5% with a single correction at 7%. The corrected ratio for each staurolite was multiplied by the SiO₂ wt% as determined by microprobe analyses (Holdaway et al., 1986) to give a number that would be linearly related to H₂ or H₂O content were it not for matrix effects. All (¹H⁺ - 300)/²⁹Si⁺ ratios for 355-1 that were not decreased by edge effects were averaged. For 29 ratios, σ was ±2.8%.

RESULTS

H extraction line

H-isotope extraction-line analyses of the 31 staurolites resulted in H₂O contents from 1.39 to 2.27% (Table 3). The estimated precision of these analyses has two parts, an analytical precision and an uncertainty due to variation in impurities. Analytical precision, determined from the reproducibility of six sample pairs (Table 2), is about 0.023% H₂O. The mineral separates used in these analyses varied from almost pure staurolite to separates with a

Table 3. H₂O analyses of staurolites determined by ion microprobe, H extraction line, and weighted average

Specimen no.*	Ion-probe H-ratio**	Ion-probe analysis†	H-line analysis	Weighted average‡	H-ions 48 O§
3-3	0.0396	1.61	1.39	1.43	2.68
86	0.0391	1.57	1.42	1.45	2.71
ER-70	0.0381	1.48	1.48	1.48	2.79
M-29	0.0386	1.53	1.49	1.50	2.81
EH-6	0.0359	1.29	1.56	1.52	2.85
164	0.0405	1.69	1.53	1.55	2.91
114-1	0.0361	1.31	1.60	1.55	2.90
KF-9	0.0386	1.53	1.59	1.58	2.94
655-1	0.0392	1.58	1.59	1.59	2.98
53-2	0.0390	1.56	1.60	1.59	2.97
SL-2	0.0385	1.52	1.61	1.60	2.99
356-1	0.0398	1.63	1.60	1.60	3.00
SL-1	0.0380	1.47	1.65	1.63	3.03
106038	0.0363	1.33	1.67	1.62	3.02
117183	0.0365	1.34	1.68	1.63	3.03
36764	0.0423	1.85	1.59	1.63	3.04
CT-DL-1	0.0396	1.61	1.64	1.63	3.05
M-1	0.0434	1.94	1.59	1.65	3.09
117189	0.0372	1.40	1.70	1.65	3.10
119551	0.0424	1.86	1.71	1.73	3.23
78332	0.0438	1.98	1.71	1.75	3.27
6-3	0.0439	1.99	1.76	1.80	3.29
B14040	0.0430	1.91	1.75	1.78	3.30
GTU-104	0.0390	1.56	1.81	1.77	3.30
PF-3	0.0450	2.08	1.71	1.77	3.31
355-1	0.0422	1.84	1.77	1.78	3.32
PE-1	0.0421	1.83	1.80	1.81	3.38
PF-2	0.0413	1.76	1.86	1.84	3.41
77-55C	0.0453	2.11	2.27	2.24	4.09
71-60E	0.0459	2.16	2.27	2.25	4.15
71-62R	0.0482	2.36	2.24	2.26	4.16

* Localities and assemblages given by Holdaway et al., 1986.

** Weight percent Si \times $(^1\text{H}^+ - 300)/^{29}\text{Si}^+$.

† Standardized to H extraction-line analyses using working curve in Figure 2.

‡ $0.155 \times$ ion-probe analysis $+ 0.845 \times$ H extraction-line analysis.

§ Based on weighted average of percentage of H₂O and microprobe analyses of Holdaway et al., 1986.

maximum of about 2.5% impurities. The major impurities consisted of quartz, ilmenite, and mica. The samples with the highest abundance of impurities contained less than 1.80% H₂O. Assuming that the average impurity concentration is 1.25% and that it varies from all quartz and ilmenite to about 75% mica (i.e., from 0% H₂O to 3.6% H₂O), the uncertainty is estimated at 0.0225% H₂O ($0.0125 \times 1.80\% = 0.0225\%$). Combining this with the analytical precision gives an estimated precision of 0.045% H₂O.

Ion probe

The only accurate calibration of the ion-probe data is that of the H extraction line. As will be seen in the discussion that follows, no previously published analyses of H₂O in these staurolites can be considered to be as accurate as the H extraction-line analyses. The ratio [weight percent Si \times $(^1\text{H}^+ - 300)/^{29}\text{Si}^+$ varies from 0.0359 to 0.0482. These ion-probe numbers, plotted against the percentage of H₂O determined by the H extraction line in Figure 2, show considerable scatter. Errors in the ion-probe values are related largely to observed variation in

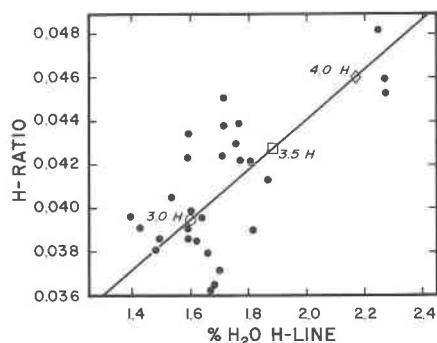


Fig. 2. Plot of [weight percent Si \times $(^1\text{H}^+ - 300)/^{29}\text{Si}^+$ (H-ratio) based on ion-microprobe analyses against percentage of H₂O based on the H extraction line. Straight line is best fit (Eq. 2, Table 4) for a working curve (see text). Open symbols identify percentage of H₂O corresponding to 3.0, 3.5, and 4.0 H pfu.

the rate of H⁺ transmission. It is hoped that in the future this can be reduced by at least a factor of two by increasing the number of analyses per sample. The problem of determining the best relationship between the two sets of data is made more difficult by the limited range of staurolite H₂O content. In the absence of matrix effects, the data must lie on a line passing through the origin, as blank corrections were made for both sets of data. The three highest-H₂O samples are somewhat unique in that they appear to be distinctly higher in H₂O by the extraction-line method than by the ion-probe method if the regression line is forced through zero.

Several statistical regressions were attempted in an effort to find the best relationship between the two data sets. In Table 4, the H extraction-line values are the x variables (abscissa of Fig. 2), and the ion-probe H ratios are the y variables (ordinate of Fig. 2). Because these trials involved three different procedures, it was necessary to compare them using a relatively simple statistic, the square root of the sum of the squares due to deviations in y , $\sqrt{SS_D}$ (Davis, 1973), divided by the number of data points used.

Several generalizations may be made on the basis of these tests: (1) the data show no statistically meaningful curvature other than that required by forcing the line through the origin; (2) all fits not constrained to pass through the origin have a substantial y intercept, and the York fits have comparable intercepts in y regardless of whether the three highest-H₂O staurolites are included. The only acceptable fits seem to be Equations 2 and 3 (Table 4), but neither curvature in the data nor $\sqrt{SS_D}/N$ support Equation 3. The only point in favor of Equation 3 is that it is constrained to pass through the origin.

In the absence of any firm evidence to the contrary, we have chosen Equation 2 (Table 4) as the best regression line for the two sets of data. The selection of a regression line with a substantial y intercept implies some kind of matrix effect on the ion-probe signal for H; however, we were not able to establish one with certainty. The H₂O analyses based on the ion-probe determinations using Equation 2 (Table 4, Fig. 2) as a working curve are pre-

Table 4. Statistical data on H extraction-line vs. ion-probe H values

Equation	Parameters		$\sqrt{SS_p/N}$	
	28 pts.*	31 pts.	28 pts.*	31 pts.
(1) $y = mx$	$m = 0.0245(19)$	$0.0241(22)$	0.00056	0.00068
(2) $y = mx + b$ (York, 1966)	$m = 0.0168(52)$	$0.0115(13)$	0.00048	0.00042
	$b = 0.0124(189)$	$0.0214(50)$		
(3) $y = ax^e + mx$ (York, 1966)	$a = -0.0136(30)$	$-0.0071(8)$	0.00047	0.00043
	$m = 0.0467(110)$	$0.0361(31)$		
(4) $y = ax^e + mx + b$	$a = 0.0207(274)$	$0.0042(71)$	0.00044	0.00041
	$m = -0.0591(891)$	$-0.0057(266)$		
	$b = 0.0809(724)$	$0.0380(244)$		

* Excluding the three highest-H₂O analyses.

sented in Table 3. The ion-microprobe 2σ of 5.6% in sample 355-1 translates to an error of ±0.21% H₂O or about twice that of the H extraction line (2σ = 0.09% H₂O).

Best values

Whereas the H extraction-line determinations are clearly more precise than the ion-microprobe determinations, it is important to emphasize that the variable content of impurities produces effects on the extraction-line determinations that do not occur in the ion-microprobe determinations. Although the results of the two analytical methods are not completely independent, the H₂O analyses can be combined in a weighted arithmetic mean. The estimated variances (at the 95% confidence level) for each method were used as weights. The weighted average (Table 3) is 0.155 of the ion probe value plus 0.845 of the H extraction-line value. These analyses vary from 1.43 to 2.26% H₂O. They are accurate to about ±0.1% H₂O. These are probably the best available values for H₂O content of these staurolites.

COMPARISON WITH OTHER RESULTS

Table 5 compares our H₂O analyses with previous results on the same or similar material. The specimens of Juurinen (1956) cannot be definitely correlated with the present specimens, as he reported no specimen numbers. However, because some of his specimens were supplied by the Smithsonian Institution, at least some of the specimens used by us may be from the same samples. His analyses are between 0.3 and 0.6% H₂O higher than our results. Two possible explanations for this are the failure of Juurinen to remove all the H₂O from the PbO flux, and failure to remove all adsorbed nonstructural H₂O from the staurolite. Stepwise-heating analyses by Juurinen (1956, p. 31, 32) on Pizzo Forno staurolite, presumably similar to B14040, PF-2, or PF-3, produced a 0.57% H₂O loss at 240°C and no additional loss at 460°C. Most of this 0.57% H₂O could have been evolved at temperatures as low as 125°C, as drying was the only previous step. Our own heating experiments, discussed above, indicate that a maximum of 0.03% structural H₂O is produced at 240°C. Thus the structural H₂O of this staurolite is about 2.37 —

0.54 = 1.83%, in good agreement with our results (\bar{x} = 1.80%).

Analyses of staurolites from the Errol quadrangle (Green, 1963) are very similar to the analysis of specimen ER-70, and the H₂O content is also similar. The analyses quoted by Zen (1981) are 0.2 to 0.4% H₂O lower than our analyses of staurolites from the same specimens. Table 3 shows that, using either the H extraction line or the ion probe, 356-1 contains about 92% as much H₂O as 355-1. As the analyses given by Zen indicate that 356-1 contains 74% as much H₂O as 355-1, it seems reasonable to assume that not all the H₂O was evolved in the microcombustion train used by the U.S. Geological Survey and that sample 355-1 came closer to evolving all its H₂O than did sample 356-1.

S. W. Lonker kindly supplied samples of staurolite to enable us to crosscheck results. We observe two kinds of differences between the staurolite H₂O analyses (Table 5). The more H₂O-rich staurolites analyzed by Lonker (1983

Table 5. Comparison of staurolite H₂O analyses with results of previous workers

Specimen	This study	Juurinen (1956)	Green (1963)	Zen (1981)	Lonker (1983, ms.)	ΔL†	CO ₂ ‡
86	1.45				1.01	0.44	450
ER-70	1.48		1.60**				
164	1.55				0.95	0.60	425
655-1	1.59				1.04	0.55	330
356-1	1.60			1.19	1.27	0.33	300
36764	1.63	1.98*					
M-1	1.65	1.92*					
355-1	1.78			1.61	1.53	0.25	85
B14040	1.78	2.37**					
PF-2	1.84	2.37**					
PF-3	1.77	2.37**					
71-60E	2.25				1.92	0.33	160
71-62R	2.26				1.92	0.34	140

* No specimen number given, may not be from same specimen.

** Not from same specimen. Green, specimen ER-101B from same quadrangle.

† ΔL indicates percentage of H₂O from this study less percentage of H₂O from Lonker (1983, and unpub. ms.).

‡ Pressure (μm Hg) of noncondensable gases (CO₂, SO₂) in dry ice-acetone trap, this study. Higher values may result from CO₂ produced by traces of graphite.

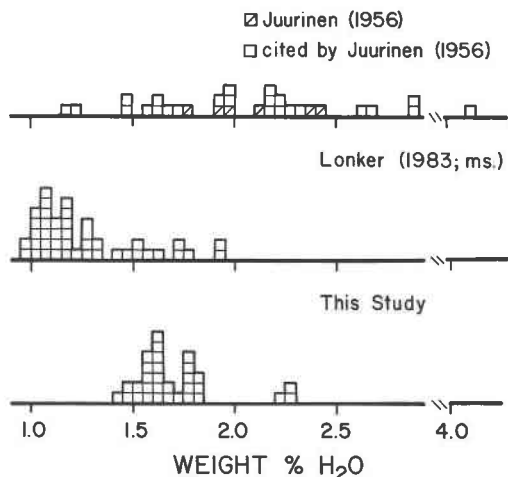


Fig. 3. Group comparison of staurolite H₂O analyses. Note the approximate agreement between the present results and those listed by Juurinen (1956). The present data represent a slightly narrower range of H₂O content than indicated by previous studies unless the six analyses by Juurinen are taken alone. A single analysis of 0.0% H₂O cited by Juurinen is not represented.

and unpub. ms.) are lower by 0.25 to 0.34% H₂O than our data, and the staurolites with less H₂O are lower by 0.44 to 0.6%. There are several possible explanations for these discrepancies: (1) The DuPont moisture analyzer approach used by Lonker did not involve a flux. In our own experience, we could not be certain of evolving all the H₂O without a flux. Even when grains were not totally dissolved by the flux, the flux provided good thermal conduction of temperatures near 1500–1600°C. (2) Lonker oxidized any H₂ evolved by reaction with oxygen in the carrier gas at the Pt furnace. It is possible that not all the H₂ was oxidized, especially gas produced at lower temperatures. In the H extraction line, 25–30% of the gas is evolved directly as H₂, but all H-bearing gases are ultimately reduced to H₂. (3) Many staurolites with low H₂O contents apparently crystallized in the presence of graphite, as indicated by our thin-section study of the staurolites from Maine. Traces of graphite inclusions in the staurolite may well have produced CO₂ and caused some H₂O to be reduced to CH₄. The CH₄ may not all have oxidized back to H₂O in the DuPont moisture analyzer. In our studies, the gas pressure in the dry-ice trap was higher in low-H₂O staurolites than in those with higher H₂O content (Table 5). This gas is likely to be predominantly CO₂, as CH₄ would not freeze in the initial N trap but would pass through the U furnace, liberating H₂. The probable evolution of more CO₂ from the low-H₂O staurolites supports the possibility of traces of graphite in these samples and may provide a partial explanation for the lower H₂O contents found by Lonker in low-H staurolites.

Figure 3 gives a group comparison of our H₂O analyses with those cited and determined by Juurinen (1956) and the measurements of Lonker (1983 and unpub. ms.). The group of analyses done by Juurinen are higher by 0.15 to

0.35% H₂O and are otherwise similar to the present results. The results cited by Juurinen occupy a wider range, as would be expected for staurolite from several sources, some of them quite old. However, only 7 of 24 analyses cited by Juurinen (1956) and 1 of the 6 analyses done by Juurinen fall more than 0.1% H₂O outside the range of the present analyses. On the other hand, 29 of the 42 analyses determined by Lonker fall at least 0.1% H₂O below the range of the present analyses; none of them are higher. The highest analyses by Lonker (1983 and unpub. ms.) fall 0.35% below the highest values in the present study. We conclude that the H extraction-line procedure measures all the structural H in staurolite without contamination by sources other than the impurities in the sample. The ion-probe analyses, although less precise, are useful in improving the quality of the H₂O analyses of staurolites that contain impurities of up to 2.5% of quartz, ilmenite, and/or micas.

DISCUSSION

Although the 31 staurolites analyzed do not necessarily represent the total range of H content in staurolite, they clearly represent a substantial amount of the range. The staurolites selected for comparison with Lonker's (1983) analyses include those specimens with the lowest and highest H₂O content according to Lonker's analyses. The present H₂O contents thus represent the range of 66 staurolite analyses in terms of H₂O content. That range is from 1.43 to 2.26% H₂O or from 2.68 to 4.16 H ions per 48-oxygen formula unit (Table 3). The present results strongly indicate that the H content of staurolite is indeed variable, as shown previously by Lonker (1983). However, the range given by Lonker was 0.95 to 1.92% H₂O or from 1.79 to 3.57 ions pfu.

Our staurolites can be broadly subdivided into two groups (Table 3, Fig. 2). Twenty-eight of the staurolites analyzed coexist with biotite and/or garnet and contain 1.43 to 1.84% H₂O (2.68 to 3.41 H ions pfu). Three staurolites do not coexist with biotite or garnet but instead coexist with hemo-ilmenite and contain 2.24 to 2.26% H₂O (4.09 to 4.16 H ions pfu). This second group might be extended to somewhat lower values if more such staurolites were analyzed (e.g., those from Black Mountain, New Hampshire; Rumble, 1978). The average H₂O content of the first group is 1.64(11)% [3.06(21) H ions pfu], whereas that of the second group is 2.25(1)% [4.14(4) H ions pfu].

As we show in a companion paper (Holdaway et al., 1986), there is evidence for the substitution $2\text{H}^+ + \square = 2\square + \text{R}^{2+}$. Those staurolites with 2.7 to 3.4 H ions pfu had their R²⁺ activity controlled at high levels by biotite and/or garnet. At these conditions, staurolite R²⁺ is high and staurolite H is low. Where biotite or garnet is absent, the hematite component of ilmenite is higher, and chloritoid may also occur (71-60E and 71-62R). Under these conditions the activity of R²⁺ is maintained at a lower value and the staurolite has more H. The upper limit of H₂O content of the present analyses corresponds to 4.16

H ions pfu. The 2σ error of the H₂O analyses ($\pm 0.1\%$ H₂O) corresponds to ± 0.18 H ions. If F is included with H, the total of (F + OH) reaches a maximum value of 4.25, implying that more than half of the 8 H positions suggested by Takéuchi et al. (1972) are occupied.

It is likely that petrologists who study staurolite will not routinely have the capability to analyze them for H₂O. However, one must understand that inappropriate assumptions as to H content will lead to errors in the stoichiometry calculated from microprobe analyses. On the basis of the results presented here, the following approximations may be useful: (1) If biotite and/or garnet occurs with the staurolite, assume that it contains the average value of 3.06 H ions pfu. This value should be within 0.38 H ions of the correct value and should not produce serious errors in the remainder of the stoichiometry. (2) If the staurolite does not occur with biotite or garnet, but does occur with hemo-ilmenite (not pure ilmenite), assume that the staurolite contains 4.14 H ions pfu. This value is probably within 0.10 of the correct one. It is important to emphasize that the H content of staurolite is not fixed; it varies over at least the range 2.7 to 4.2 H ions pfu.

SUMMARY AND CONCLUSIONS

1. Staurolites have been analyzed for H₂O content to within 0.1% using a weighted average of H extraction-line and ion-microprobe analyses. Whereas the H extraction-line procedure is about twice as precise, the ion-microprobe technique, if well calibrated, avoids contamination by impurity minerals.

2. Comparison of present results with previous analyses indicates that great care must be taken to exclude non-structural H and measure all structural H in staurolite. Structural H is not detected if not all H is evolved, if not all H is converted back to H₂O, or if some H is lost as CH₄.

3. The analyzed staurolites fall into two groups. Staurolites that occurred with biotite and/or garnet vary from 2.7 to 3.4 H pfu, whereas those that formed only with hemo-ilmenite (and possibly with chloritoid) vary from 4.1 to 4.2 H pfu.

4. For staurolites coexisting with biotite or garnet, an estimated value of 3.06 H pfu may be used, whereas for staurolites that grew only with ilmenite-hematite, 4.14 H pfu may be estimated. These estimated values allow calculation of approximate staurolite stoichiometry from microprobe analyses.

5. Staurolite analyses with H₂O contents below 1.35 or above 2.35 wt% should be questioned.

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