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# Revised heat capacity values for topaz and staurolite based upon a better analysis of the water content of the samples[1]

By

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## Abstract

Problems with CHN elemental analysis for water using $V_2O_5$ and other lower melting point fluxes are discussed. Revised water analyses are presented for topaz, staurolite and annite.

New heat capacity measurements are reported for topaz for the temperature range of 630 to 930 K. Problems noted in earlier studies preventing measurement of heat capacities of topaz above about 800 K were resolved. The specific heat ($J \cdot g^{-1} \cdot K^{-1}$) of topaz in the temperature range of 200 to 1300 K may be calculated from the equation:

$$C^{o}_{p} = 2.6814 - 6.777\text{x}10^{-4}T + 1.784\text{x}10^{-7}T^{2} - 30.865T^{-0.5} + 6643.7T^{-2}$$

The entropy of staurolite reported by Hemingway and Robie (1984) has been corrected for the new analysis of the water content of the sample they used. The revised value is 974.4 ± 3.0 $J \cdot mol^{-1} \cdot K^{-1}$, excluding a zero-point contribution to the entropy. The specific heat of staurolite in the temperature range of 200 to 1300 K may be calculated from the equation:

$$C^{o}_{p} = 2.0226 - 2.045\text{x}10^{-4}T + 6.958\text{x}10^{-8}T^{2} - 20.811T^{-0.5}$$

## Introduction

Calculated thermodynamic properties of staurolite and topaz are dependent upon accurate information regarding the chemistry of the samples measured. For a recent study of topaz (Kirby et al., 1990), it was noted that a recent chemical analysis for water in the topaz sample did not agree with results reported for topaz from the same location analyzed at an earlier time (see Pentfield and Minor, 1894). The earlier measurements were made by the Pentfield method (Pentfield and Minor, 1894). The more recent analyses of topaz and staurolite were made using a modified Pentfield method and a CHN elemental analyzer (Perkin-Elmer 240B)[1]. Resolution of these disparate results is the subject of this communication.

## Discussion

The $H_2O$ content of topaz from the Tin Mining District, Minas Gerais, Brazil, was found to be 0.53 percent (Lee and Kirby, 1984, material also used in Kirby et al., 1990) using a modified Pentfield method ($PbO:PbCrO_4:Cu_2O$ in the ratio 10:1:1 as a flux and over a Meeker burner). This result was not consistent with other analyses of topaz from Minas Gerais (e.g., Pentfield and Minor, 1894, and Jannasch and Locke, 1894), with the reported fluorine content of 17.0 percent, or with the indices of refraction and 2V reported (e.g., Ribbe, 1980).

The water content of the topaz sample used by Lee and Kirby (1984) and Kirby et al. (1990) was verified by analyses using a CHN elemental analyzer with $V_2O_5$ as the flux (e.g., Skinner et al., 1981), and by weight loss determinations after heating a small sample of the topaz in a differential scanning calorimeter (dsc) at 1000 K. The products of these analyses were examined by near-infrared reflectance spectroscopy. The results were

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[1] Use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

inconclusive for the $V_2O_5$-topaz sample, but the dsc sample clearly showed overtone absorption bands due to oriented hydroxyl (OH and Al-OH in the 2.5 to 0.7 micron region). X-ray analysis of the $V_2O_5$-topaz sample was negative for topaz.

The results provided by the near-infrared reflectance spectroscopy suggested that the water content of the topaz sample was higher than the reported 0.53 percent and lead to an examination of the difference in the analytical procedures used by Pentfield and Minor (1894) and Jannasch and Locke (1894), and those for the CHN analyzer. Besides the obvious differences of instrumentation, the major difference observed was the temperature of melting of the flux used in each study. $V_2O_5$ melts at temperatures of 965 to 975 K while the $Na_2CO_3$ and PbO used in the studies of Pentfield and Minor (1894) and Jannasch and Locke (1894), respectively, melt at 1124 and 1161 K, respectively. The melting temperature of PbO-$PbCrO_4$-$Cu_2O$ flux is not known, but can be estimated from phase diagrams (e.g., Levin et al., 1964) as less than 1025 K.

The water content of the topaz sample was redetermined by CHN analysis using PbO as the flux. The result, 1.6 percent water, is more consistent with other analyses reported for topaz (e.g., Deer et al., 1982).

Because the problem encountered with the water analysis for topaz was considered to represent a problem for all refractory silicate minerals, the water content of staurolite was redetermined. Using $V_2O_5$ as the flux, the observed water content was 1.6 percent (see Zen, 1981, sample 355-1), but using PbO, it was found to be 2.4 percent (for a portion of sample 355-1). A portion of this sample is used as a microprobe standard (J.J. McGee, personal communication). McGee reports that (historically) microprobe chemical analyses totals obtained using this sample have been lower than those reported by Zen (1981). McGee notes that this is consistent with actual $H_2O$ being higher than reported by Zen (1981).

Juurinen (1956) reported similar findings for staurolite. Juurinen (1956) used the Pentfield method with sodium tungstate as the flux and found a water content of 1.5 percent for each of six staurolite samples studied. The product of the fusion with sodium tungstate was dissolved with hydrochloric acid and examined with X-ray analysis. Juurinen (1956) found a significant amount of staurolite. He modified his procedure and used PbO as the flux and obtained values of about 2 percent water.

A portion of the topaz and staurolite samples were further examined using a Carlo-Erba elemental analyzer which has an effective column temperature for hydrogen analysis of about 1675 K. The temperature is attained by flash combustion of tin in a column maintained at about 1300 K. The total water estimated by this method was 0.29 percent and 1.65 percent, respectively, for topaz and staurolite and the results were quite variable. Methods for improving the analyses for topaz using this technique were not pursued. Lonker (1983) also determined the water content of a portion of the staurolite sample using a pyrolysis procedure that involves linear heating to about 1725 K. His value of 1.53 percent is in good agreement with that obtained using the Carlo-Erba elemental analyzer, but both values are suspect based on the discussion above. Also, Riley (1958) investigated pyrolysis procedures for determining the water content of refractory silicate phases like topaz and staurolite, and concluded that samples ground to pass 80 mesh must be held at temperatures greater than 1475 K for more than 20 minutes to obtain accurate values. Lonker's (1983) sample was above 1475 K for only a few minutes.

The water content of an annite sample (Lost Creek, Montana, Wanek and Barclay, 1966) was determined by pyrolysis (1.5 percent), and CHN elemental analyses using $V_2O_5$ (2.6 percent) and PbO (3.2 percent) as fluxes. These results suggest that underestimation of the water content of geologic materials may be a common problem.

## Revised thermodynamic properties for topaz

Barton et al. (1982) measured the heat capacity of fluor-topaz (from Topaz Mountain, Thomas Range, Utah) between 10 and 800 K. The authors noted that instrument instability prevented measurements to higher temperatures. The cause of the problems observed by Barton et al. (1982) does not arise from instrument instability, but from hydrogen diffusion in the topaz sample as discussed by Kirby et al. (1990).

The fluor-topaz sample used by Barton et al. (1982) was known to be a high fluorine topaz (Pentfield and Minor, 1894). Barton et al. (1982) had the water content redetermined by CHN analysis and found 0.04 weight percent $H_2O$. Considering the discussion above, this value is likely low.

Knowing that water in the topaz was the likely cause of the problems encountered by Barton et al. (1982), the heat capacity of a portion of their sample was remeasured using a dsc and procedures developed by Hemingway for the study by Kirby et al. (1990). The heat capacity of a portion of the topaz from Minas Gerais, Brazil, was also measured by dsc. The experimental values are listed in Table 1 and shown graphically in Figure 1. As noted by Barton et al. (1982), correction for the $H_2O$ content of the sample is not warranted.

Combining the new heat-capacity values for topaz with the data of Barton et al. (1982) and fitting this data set with an equation of the form suggested by Haas and Fisher (1976), yields an equation for the specific heat ($J \cdot g^{-1} \cdot K^{-1}$) of fluor-topaz from 200 to 1300 K as:

$$C_p^\circ = 2.6814 - 6.777 \times 10^{-4} T + 1.784 \times 10^{-7} T^2 - 30.865 T^{-0.5} + 6643.7 T^{-2}$$

The average deviation of the equation from the experimental values is 0.6 percent. The entropy of topaz at 1000 K calculated from the new equation differs from that given by Barton et al. (1982) by only 0.3 percent, however, the slope of the heat capacity curve is significantly different at 1000 K.

## Revised thermodynamic properties for staurolite

Hemingway and Robie (1984) published a value for the entropy of staurolite based on measurements of the heat capacity of the staurolite described above (355-1). Correction of this value to account for the revised value for the water content is necessary. The chemical analysis listed by Zen (1981) is combined with the result derived here for the water content and the idealized formula is listed in Table 2. Based on this composition (molar mass = 1655.952 g), the corrected entropy for the natural staurolite is 974.4 ± 3.0 $J \cdot mol^{-1} \cdot K^{-1}$ (both the molar mass and entropy change). No configurational entropy has been added to this value (see Hemingway and Robie, 1984).

The specific heat of the natural staurolite may be calculated from the following equation:

$$C_p^\circ = 2.0226 - 2.045 \times 10^{-4} T + 6.958 \times 10^{-8} T^2 - 20.811 T^{-0.5}$$

The equation fits the results given by Hemingway and Robie (1984) with an average deviation of 0.5 percent and is valid from 200 to 1400 K.

## Acknowledgments

I would like to thank my Survey colleagues, James K. Crowley for near-infrared reflectance spectroscopy of topaz, Floyd W. and Zo Ann Brown for CHN analyses, and William H. Orem for measurements using the Carlo-Erba elemental analyzer.

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Table 1. Specific heats for topaz from Minas Gerais, Brazil, (Series 1 - 5) and from Topaz Mountain, Utah (Series 6 and 7).

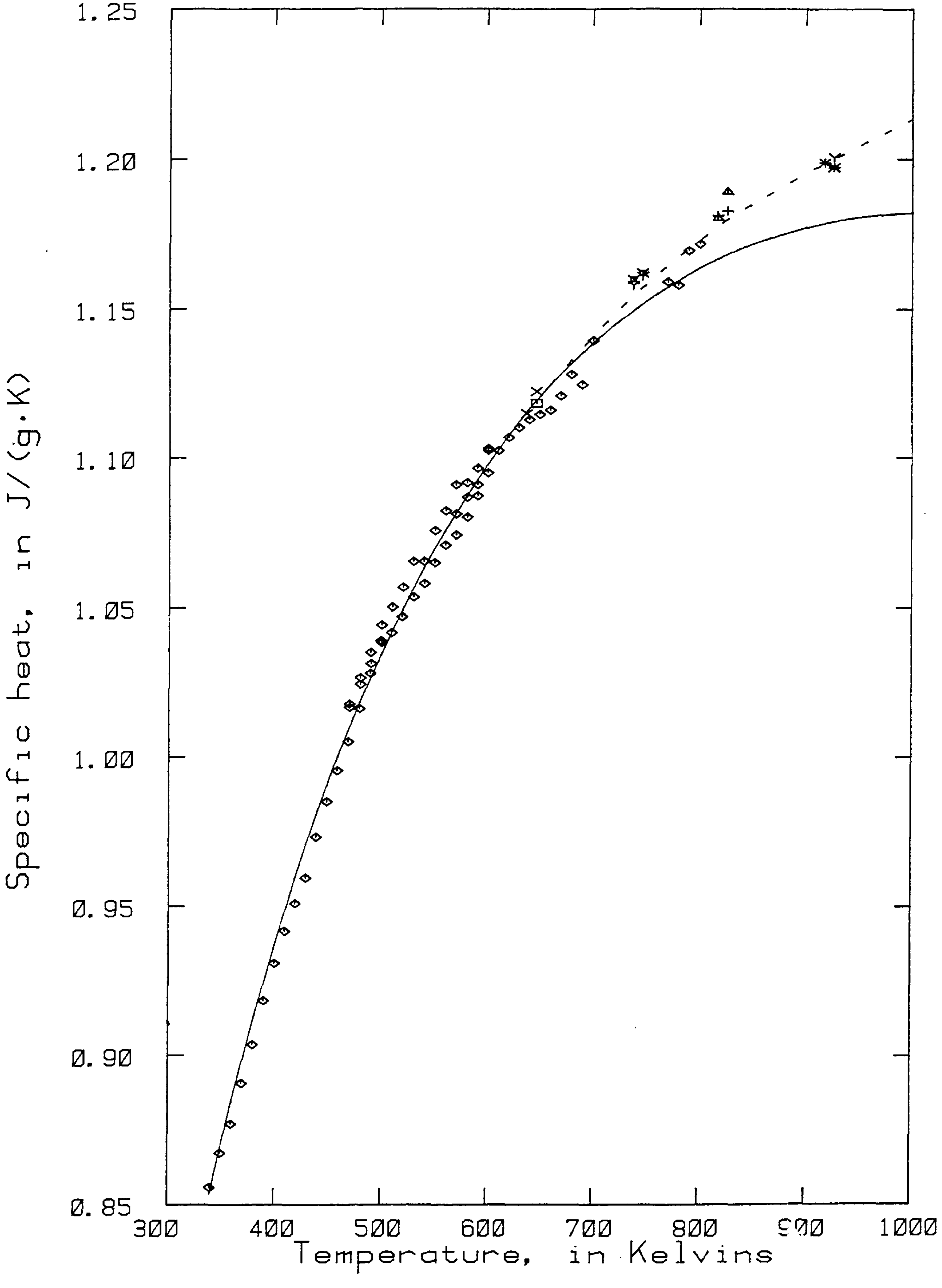
| Temp. K | Specific heat $J\cdot g^{-1}\cdot K^{-1}$ | Temp. K | Specific heat $J\cdot g^{-1}\cdot K^{-1}$ | Temp. K | Specific heat $J\cdot g^{-1}\cdot K^{-1}$ |
|---|---|---|---|---|---|
| Series 1 | | Series 4 | | Series 6 | |
| 638.0 | 1.115 | 817.3 | 1.181 | 737.6 | 1.158 |
| 647.0 | 1.122 | 826.3 | 1.183 | 746.6 | 1.161 |
| Series 2 | | Series 5 | | Series 7 | |
| 737.6 | 1.160 | 917.0 | 1.199 | 926.0 | 1.200 |
| 746.6 | 1.162 | 926.0 | 1.197 | | |
| Series 3 | | | | | |
| 817.3 | 1.180 | | | | |
| 826.3 | 1.189 | | | | |

Table 2. Staurolite composition based on the chemical analysis reported by Zen (1981) for sample 355-1 and on the value for water determined in this study.

| Element | Number of ions based on 48 (O, OH) | |
|---|---|---|
| Si | 7.85 | 8.00 |
| Al | 0.15 | |
| Al | 17.17 | 18.00 |
| Mg | 0.44 | |
| Ti | 0.08 | |
| $Fe^{3+}$ | 0.31 | |
| $Fe^{3+}$ | 0.21 | 2.94 |
| $Fe^{2+}$ | 2.62 | |
| Mn | 0.02 | |
| Ca | 0.03 | |
| Zn | 0.05 | |
| P | 0.01 | |
| H | 4.39 | 4.39 |

# List of Figures

Figure 1. Experimental specific heats for topaz: diamonds, results from Barton et al. (1982) for fluor-topaz from Topaz Mountain, Utah; Y, results from this study for a portion of the sample used by Barton et al. (1982); and the remaining symbols represent results from this study for the topaz sample from Minas Gerais, Brazil. The solid curve is from the equation given by Barton et al. (1982). The dashed curve is from this study.


1.25
1.20
1.15
1.10
1.05
1.00
0.95
0.90
0.85
300
400
500
600
700
800
900
1000
Temperature, in Kelvins
Specific heat, in J/(g·K)