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April 23, 1982

Dr. Mark D. Barton
Geophysical Laboratory
Carnegie Institution of Washington
2801 Upton Street, N.W.
Washington, D.C. 20008

Dear Mark:

I am writing to make a request on behalf of your beloved alma mater, unless someone else has. For your paper on the thermodynamic properties of fluor-topaz, you had the F content of the Thomas Range topaz reanalyzed. Could you send me a few topaz grains from the rough material remaining after your hand picking? Our present Thomas Range topaz "microprobe standard" is an undocumented sample assumed to have the composition reported by Penfield and Minor (1894). It would be much more satisfactory to have material which has been independently checked. In addition, Todd has been investigating the fluorine spectra in a variety of compounds and a better characterized topaz would be more useful when he publishes the results.

Also, I would appreciate receiving a reprint of your paper. Thank you.

Sincerely yours,

Alex Speer

J. Alexander Speer

CARNEGIE INSTITUTION OF WASHINGTON

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June 17, 1982

Dr. J. Alexander Speer
Department of Geological Sciences
V.P.I. and S.U.
Blacksburg, Virginia 24061

Dear Alex,

Sorry about the delay in answering your requests. The reprints did not arrive until yesterday. I am parting with some of my precious topaz (I only have 100 grams!) solely because of my fond memories for my beloved alma mater. A couple of chips are enclosed, let me know if you would like some more! I hope that Todd can sort out some of the fluorine problems in his study; I certainly have found fluorine analyses frustrating, even in topaz.

Say hello to everyone there for me!

Best wishes,



Mark Barton

Thomas Range topaz, Utah

		wt %
SiO ₂	31.93	Si 0.1493
Al ₂ O ₃	56.26	Al 0.2978
F	20.37	O 0.3507
H ₂ O ⁺	<u>0.19</u>	F 0.2037
	108.75	H <u>0.0002</u>
O = F	<u>8.58</u>	1.0017
	100.17	

Penfield + Minor (1894)

ideal Al₂SiO₄F₂

Si	0.1526
Al	0.2932
O	0.3477
F	<u>0.2065</u>
	1.0000

October 25, 1982

Dr. Mark D. Barton
Geophysical Laboratory
Carnegie Institute of Washington
2801 Upton Street, N. W.
Washington, D. C. 20008

Dear Mark:

Enclosed is a copy of Todd's work on the F Spectra. I have also sent you a few pieces of the topaz we had analyzed as well as its analysis. I and the analyst decided that an accurate F value would be preferred over indifferent F and H₂O values; for that reason the H₂O value is inaccurate and the preferred value (1.335 wt %) is a stoichiometric amount required to give 2(OH,F) per 6(O,OH,F).

Best regards,

J. Alexander Speer

JAS/mgs

Enclosure

The thermodynamic properties of fluor-topaz

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Abstract

The standard thermodynamic properties of fluor-topaz, $\text{Al}_2\text{SiO}_4\text{F}_2$, have been calculated from low- and high-temperature heat-capacity measurements and from high-temperature, oxide-melt calorimetry. Fluor-topaz (from Topaz Mountain, Thomas Range, Utah) containing 0.04 wt. percent water was used in all the experiments. Adiabatic calorimetry performed from 10.6 to 379.2 K gives $S_{298}^\circ - S_0^\circ$ of 105.4 ± 0.2 J/mol·K. Combined heat capacities determined by adiabatic calorimetry (200–380 K) and differential scanning calorimetry (340–800 K) were fit to the following polynomial (equation valid 200–1,000 K):

$$C_p^\circ (\text{J/mol}\cdot\text{K}) = 471.41 - 0.08165T + 1.2695 \times 10^{-6}T^2 - 5485.5T^{-0.5} (\pm 0.7\%).$$

The enthalpy of the reaction $\text{CaF}_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2 = \text{CaO} + \text{Al}_2\text{SiO}_4\text{F}_2$ was measured at 970 K by oxide-melt calorimetry and gave $\Delta H_{970}^\circ = 91.88 \pm 3.56$ kJ. From our heat-capacity measurements and ancillary data, we calculate $\Delta H_{298}^\circ = 96.12 \pm 3.95$ kJ for the reaction and $\Delta H_{f,298}^\circ = -3084.45 \pm 4.70$ kJ/mol, and $\Delta G_{f,298}^\circ = -2910.66 \pm 4.74$ kJ/mol for fluor-topaz.

Introduction

Topaz occurs frequently as an accessory mineral in fluorine-rich granitic rocks and associated hydrothermally altered rocks. As one of the principal fluorine bearing minerals, it offers a key to understanding the genesis of these rocks. Topaz is a solid solution between fluor-topaz ($\text{Al}_2\text{SiO}_4\text{F}_2$) and (hypothetical) hydroxyl-topaz ($\text{Al}_2\text{SiO}_4(\text{OH})_2$). Natural topazes vary from nearly pure fluor-topaz to about $\text{Al}_2\text{SiO}_4\text{F}_{1.4}(\text{OH})_{0.6}$, although Rosenberg (1972) has

synthesized topaz containing more than 50% hydroxyl-topaz component.

Rosenberg (1972, 1978) reported synthesis results involving topaz solid solutions; his is the only work from which thermodynamic data might be derived. This study was undertaken to measure the thermodynamic properties of fluor-topaz as part of a project on the thermochemistry of topaz and other fluoro-silicates and their petrological application.

Experimental methods and results

Starting materials

Natural fluor-topaz from Topaz Mountain, Thomas Range, Juab County, Utah, was collected

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from the Pliocene topaz-rich alkali rhyolites (Lindsey, 1979). This topaz is known to be very close to the fluorine end member (Penfield and Minor, 1894; Ribbe and Rosenberg, 1971) and occurs as crystals as large as 3 cm in the rhyolite lithophysae. Associated minerals include quartz, sanidine, plagioclase, biotite, fluorite, beryl, hematite, pseudobrookite, spessartine, and bixbyite (Ream, 1979). About 60 g of transparent, inclusion-free crystals and cleavage fragments were handpicked from a few hundred grams of rough material. Approximately one-third of the crystals were light brown; this color is apparently caused by electronic defect centers (Dickinson and Moore, 1967), not chemical impurities. As previously demonstrated (*e.g.*, Nassau and Prescott, 1975), the color is removed by heating to 500°C for several hours. We did not heat treat the material used for calorimetry. We did not attempt to synthesize fluor-topaz by the reaction $2\text{AlF}_3 + 2\text{Al}_2\text{O}_3 + 3\text{SiO}_2 = 3\text{Al}_2\text{SiO}_4\text{F}_2$ nor did we attempt to use this reaction for the solution calorimetry because of the tendency of AlF_3 to hydrolyze which could result in considerable uncertainty as to the compositions of the phases under study.

Several crystals were analyzed on an automated electron microprobe at the University of Chicago using a ZAF correction program written by I. M. Steele of the University of Chicago. The beam current was 15 ma at an accelerating voltage of 15 kv. Andalusite served as the standard for aluminum and silicon. The water and fluorine were analyzed at the U. S. Geological Survey with a Perkin Elmer 240B elemental analyzer (V_2O_5 flux) and a specific ion electrode respectively. The water and fluorine analyses on this material are in good agreement with the original analyses by Penfield and Minor (1894). Although we searched for other elements, none were detected. Crystallographic data were collected using powder-diffraction methods (Ni-filtered $\text{CuK}\alpha$ radiation with a corundum internal standard $a = 0.47593(1)\text{nm}$, $c = 1.29917(5)\text{nm}$). The program of Burnham (1962) was used to refine the data. The chemical and crystallographic data are given in Table 1.

Other materials used in the high-temperature oxide-melt calorimetry were CaO (prepared from reagent CaCO_3 , sintered at 1,400°C for 1 week); optically pure natural CaF_2 (southern Illinois, University of Chicago collection #1875); optically pure natural quartz (locality unknown, University of Chicago collection #2099); and $\alpha\text{-Al}_2\text{O}_3$ (prepared from reagent $\text{Al}(\text{OH})_3$, fired at 1,300°C for 2 days).

Adiabatic calorimetry

Heat-capacity measurements were made from 10.6 to 379.2 K by adiabatic calorimetry at the U.S. Geological Survey, Reston, Virginia. The cryostat and calorimeter have been described in detail by Robie and Hemingway (1972) and Robie *et al.* (1976).

The topaz sample (50.5654 g, corrected for buoyancy) was loaded into the calorimeter. After evacuation of air from the calorimeter, it was backfilled with dry helium gas at 6×10^3 pascals pressure (4.0×10^{-5} mole of He) to promote thermal equilibration, and sealed. The reported temperatures refer to the International Practical Temperature Scale of 1968 (IPTS-68).

Table 2 gives the results, corrected for curvature, for the four series (1–4) of experiments in their order of collection. The formula weight for pure fluor-topaz of 184.043 g/mol used in the calculations is based on the 1975 values for the atomic weights (Commission on Atomic Weights, 1976). Although the sample topaz contains 0.04 weight percent OH, no correction was made to the measured heat capacities because the heat capacity of hydroxyl-topaz is not known. From comparisons of the heat capacities of hydroxyl-apatite and fluor-apatite, and those of hydroxyl-phlogopite and fluorphlogopite, we estimate that the difference in the heat capacity between fluor- and hydroxyl-topaz would not exceed approximately 7 percent. The difference in $S_{298}^\circ - S_0^\circ$ between hydroxyl-apatite and fluor-apatite is 0.6 percent, and between hydroxyl-phlogopite and fluor-phlogopite is -0.5 percent. On the basis

Table 1. Chemical and crystallographic data

	Chemistry*		Cell Parameters	
	Oxide wt %	Moles**	a = 0.46475(3) nm	
Al_2O_3	56.08	1.00	b = 0.87897(4) nm	
SiO_2	32.74	0.99	c = 0.83920(4) nm	
F	20.3	1.95	V = 0.34281(2) nm ³	
H_2O	0.04	0.01†		
Total	109.16			
Less F = 0	100.61			

* Al and Si analyses by microprobe, F by specific ion electrode, and H_2O by CHN elemental analyzer.

** Based on 5 oxygens.

† As hydroxyl.

Table 3. Enthalpy of solution measurements

Material	ΔH_{970}° kJ	Experimental data in chronological order ΔH_{970}° (kJ/mol); Sample wt (mg) in parentheses
$\text{Al}_2\text{SiO}_4\text{F}_2$	$76.57 \pm 1.67^*$	74.74(29.88), 74.21(44.77), 79.68(41.84), 80.16(47.96) 72.46(41.28), 78.64(35.32), 80.39(50.80), 71.54(28.32) 74.56(37.60), 78.04(42.71), 78.88(36.29), 79.53(24.50)
CaO	-55.06 ± 4.10	-62.10(13.78), -57.59(12.71), -54.30(10.44), -45.68(15.11) -49.97(16.22), -64.68(14.50), -63.32(13.10), -48.54(15.44) -60.33(13.06), -50.11(13.99), -49.02(14.85)
$\text{CaO} + \text{Al}_2\text{SiO}_4\text{F}_2$	29.83 ± 3.05	20.96(29.58), 29.19(26.69), 38.67(34.10), 31.67(56.75) 29.01(50.10), 26.60(47.48), 28.81(66.64), 39.10(50.63) 29.48(45.00), 23.11(53.18), 32.37(73.24), 29.25(44.86)
$\text{CaF}_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2$	121.71 ± 1.80	121.33(30.00), 122.31(30.74), 124.72(36.39), 118.52(30.50) 121.21(30.50), 127.65(38.90), 122.20(40.78), 120.26(46.13) 120.35(40.79), 117.79(39.05), 118.32(40.45)
addition of CaO to $\text{Al}_2\text{SiO}_4\text{F}_2$	21.51 ± 4.44	
$\text{CaF}_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2 = \text{CaO} + \text{Al}_2\text{SiO}_4\text{F}_2$		$\Delta H_{970}^{\circ} = 91.88 \pm 3.56 \text{ kJ}$ $\Delta H_{298}^{\circ} = 96.12 \pm 3.95 \text{ kJ}$

* Two standard errors of the mean; errors are propagated assuming they are independent; possible systematic errors have been neglected.

** Using the value for the mechanical mix of $\text{CaO} + \text{Al}_2\text{SiO}_4\text{F}_2$; see text.

$\text{Pb}_2\text{B}_2\text{O}_5$ glass from a single homogeneous batch was used in all the experiments. The topaz, CaO , Al_2O_3 , SiO_2 , and CaF_2 were sized to -150 to +350 mesh and kept in a desiccator.

A 2 month exposure to air in the desiccator reduced the heat of solution of CaO by about 10 percent, apparently because of the formation of small amounts of Ca(OH)_2 and/or CaCO_3 . Brief heating to 1,300°C before each experiment eliminated this perturbation. The final value obtained for ΔH_{soln} at 970 K of CaO in this study (-55.06 kJ/mol) agrees very well with that reported by Newton *et al.* (1977) (-55.15 kJ/mol). None of the other materials showed a time dependence in their heat effects. In addition, consecutive measurements on the same material in a given batch of melt showed no significant variation with increasing concentration of solute. In no series of experiments,

however, was more than 200 mg of material dissolved in any given 30.5 g batch of melt.

Two different values were obtained for the heat of solution of the $\text{Al}_2\text{SiO}_4\text{F}_2 + \text{CaO}$. The linear combination of the heat of solution of $\text{Al}_2\text{SiO}_4\text{F}_2$ and the heat of solution of CaO ($21.5 \pm 4.44 \text{ kJ/mol}$) differs significantly from the heat of solution for the mechanical mixture ($29.83 \pm 3.05 \text{ kJ/mol}$). Consecutive dissolution experiments of stoichiometric proportions of $\text{Al}_2\text{SiO}_4\text{F}_2$ followed by pure CaO in the same aliquot of melt confirmed the mechanical-mixture value. Therefore, the value of the mechanical mixture is used in the evaluation of the enthalpy of fluor-topaz. We have considered the effect of systematic errors, including those resulting from hydrolysis (of topaz, CaF_2 , CaO), reaction of the mechanical mixture before the experiments, and impurities (e.g., 0.04 percent H_2O in the topaz).

is 0.7 percent. This equation is considered to be accurate to within 1.4 percent to 1,000 K. Above 1,050 K ($dC_p/dT < 0$) so this equation should not be used for extrapolation to higher temperatures. The thermodynamic properties at 298.15 K (Table 5) were derived given the heat of reaction (1), the ancillary data for the other phases (taken from Robie *et al.*, 1979), and the entropy and heat capacities obtained here. The uncertainty in the enthalpy and Gibbs free energy arises mostly from the uncertainty in the heat of solution of the $\text{CaO} + \text{Al}_2\text{SiO}_4\text{F}_2$ mixture.

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