# Coupled hydrogen and fluorine incorporation in garnet: New constraints from FTIR, ERDA, SIMS, and EPMA

# JED L. MOSENFELDER<sup>1,\*</sup>, ANETTE VON DER HANDT<sup>1</sup>, ANTHONY C. WITHERS<sup>2</sup>, HÉLÈNE BUREAU<sup>3</sup>, CAROLINE RAEPSAET<sup>4</sup>, AND GEORGE R. ROSSMAN<sup>5</sup>

<sup>1</sup>Department of Earth and Environmental Sciences, University of Minnesota, 116 Church Street SE, Minneapolis, Minnesota 55455, U.S.A. <sup>2</sup>Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany

<sup>3</sup>Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Sorbonne Université, CNRS UMR 7590, Muséum National d'Histoire Naturelle, 4 place Jussieu, 75252 Paris Cedex 05, France

<sup>4</sup>Service de Physique de l'état Condensé, SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif sur Yvette, CEDEX, France <sup>5</sup>Division of Geological and Planetary Sciences, California Institute of Technology, M/C 170-25, Pasadena, California 91125-2500, U.S.A.

#### ABSTRACT

It is well known that some garnet compositions can incorporate hydrogen and/or fluorine at levels up to several wt%. However, accurate measurement of these elements can be difficult at trace to minor concentration levels, so they are frequently ignored in routine chemical analysis. Furthermore, the mechanisms of H incorporation are still under debate, and only one mechanism for F substitution is commonly considered. We employed infrared spectroscopy (FTIR), elastic recoil detection analysis (ERDA), secondary ion mass spectrometry (SIMS), and electron probe microanalysis (EPMA) to measure H and F concentrations and constrain incorporation mechanisms in ten grossular garnets. We also present SIMS data for 11 spessartine and two andradite garnets. Three grossular garnets were measured with ERDA to obtain an infrared integral molar absorption coefficient ( $\varepsilon_i$ ) for H<sub>2</sub>O of 13 470 L/(mol·cm<sup>2</sup>). Grossular H<sub>2</sub>O and F concentrations range from 0.017 to 0.133 wt% and 0.012 to 0.248 wt%, respectively. Correlations between <sup>16</sup>OH and <sup>19</sup>F and interpretation of FTIR spectra prompt us to consider various coupled substitutions of H and F for Si, which can explain some high-frequency IR absorption bands that have been attributed previously to "hydrogrossular clusters" (variably sized clusters in which 4H substitute for Si) or to inclusions of hydrous minerals. A strong correlation between <sup>16</sup>OH and <sup>19</sup>F in spessartine and similar high-frequency IR bands implies a similar role for H-F substitution. Coupled H-F substitution is also probably relevant to some andradite-rich garnets, rare pyrope from the Dora Maira massif, and some synthetic garnets. Improvements in analytical methods for trace to minor H and F open up more possibilities for using these elements to calculate the activities of H<sub>2</sub>O and F-species in fluids that were in equilibrium with garnet-bearing phase assemblages, as well as constraining the recycling of these elements into the mantle via study of xenoliths.

Keywords: Fluids and aqueous geochemistry, geochemistry, mineralogy, infrared spectroscopy, Mössbauer spectroscopy

#### INTRODUCTION

Considerable progress has been made in the last three decades in understanding how trace amounts of hydrogen can be incorporated in nominally anhydrous minerals and how this H (most commonly incorporated as structurally bound OH<sup>-</sup> groups) affects geophysical and petrologic processes in the Earth and other planetary bodies. Recent work has also highlighted the potential importance of trace fluorine (substituting for O<sup>2-</sup>) in nominally anhydrous minerals (Hervig and Bell 2005; Mosenfelder et al. 2011; 2015; Beyer et al. 2012; Bernini et al. 2013; Dalou et al. 2012; Mosenfelder and Rossman 2013a, 2013b; Crépisson et al. 2014; Roberge et al. 2015; Grützner et al. 2017; Klemme and Stalder 2018; Yoshino and Vazhakuttiyakam 2018). In the case of garnets, it has long been recognized that both H and F can be structurally incorporated at levels up to several wt% (see Grew et al. 2013 for review). Researchers have taken advantage of this phenomenon to constrain the activities of  $H_2O$  and F-species in fluids in equilibrium with garnet-bearing phase assemblages (Manning and Bird 1990; Visser 1993; Arredondo et al. 2001; Chakhmouradian et al. 2008).

Hydrogen and/or F may be almost ubiquitously present in trace to minor amounts in garnets but are commonly ignored during chemical analysis because of difficulties in measuring trace concentrations of light elements with commonly available techniques such as electron probe microanalysis (EPMA). Note that when we specify "H<sub>2</sub>O" or "H" concentrations in this paper, we are primarily referring to the equivalent in structurally bound OH<sup>-</sup> groups, because H is not incorporated in the form of structurally bound H<sub>2</sub>O groups in garnet.

Hydrogen can be detected easily using Fourier transform infrared spectroscopy (FTIR) in transmission mode, which

<sup>\*</sup> E-mail: jmosenfe@umn.edu

also provides information on incorporation mechanisms, but uncertainties remain in absolute quantification using this method (Maldener et al. 2003; Rossman 2006). One of the best microanalytical techniques for trace F is secondary ion mass spectrometry (SIMS), which is highly sensitive because of the ionization efficiency of both <sup>19</sup>F<sup>-</sup> and <sup>19</sup>F<sup>+</sup> and has benefited from technical advances that lower detection limits to less than 1 µg/g (Hauri et al. 2002; Koga et al. 2003; Mosenfelder et al. 2011). However, these measurements are most commonly made using F-bearing glasses for calibration, which can result in working curves with large uncertainties (Mosenfelder and Rossman 2013a).

SIMS measurements of H in garnets have primarily concentrated on pyrope-rich compositions representative of the mantle (Koga et al. 2003; Aubaud et al. 2007; Tenner et al. 2009), with one more recent study on grossular and spessartine (Reynes et al. 2018). Quantitative SIMS analyses of F in garnets are even more sparse (Jamtveit and Hervig 1994; Schingaro et al. 2016). In this study, we present new SIMS, FTIR, and EPMA data on the H and F concentrations of 10 natural grossular garnets, and SIMS data on 11 spessartine and 2 andradite crystals. Furthermore, based on elastic recoil detection analysis (ERDA) of three grossular samples, we reassess calibrations for the IR molar absorption coefficient for H<sub>2</sub>O derived by Rossman and Aines (1991) and Maldener et al. (2003). We demonstrate that H and F concentrations are strongly correlated in some garnets and suggest coupled H-F incorporation mechanisms analogous to those proposed for olivine by Crépisson et al. (2014). Coupled H-F substitution can rectify unexplained aspects of previous incorporation models for H in grossular, spessartine, and pyrope (Aines and Rossman 1984; Rossman and Aines 1991; Cho and Rossman 1993; Reynes et al. 2018; Geiger and Rossman 2018, 2020a, 2020b).

## ANALYTICAL METHODS

# Sample selection and preparation

Table 1 lists the localities of the grossular garnets chosen for this study. Six of these garnets, derived from granulites of the Neoproterozoic Mozambqiue belt in Tanzania and Kenya (Giuliani et al. 2008, 2011), are referred to as "East African" in this paper. Additional details on the grossular, spessartine, and andradite samples used in the study are provided in the Online Materials<sup>1</sup>.

Samples were prepared for analysis using previously described epoxy-free polishing methods and cleaning procedures (Mosenfelder et al. 2011). The garnets were fabricated into doubly polished slabs that were first measured by FTIR and then sliced using a wire saw into multiple chips for analysis by different techniques; in all cases, individual chips originated from the same single crystal.

## FTIR

Unpolarized infrared absorption spectra were collected for most of the garnets using either a Nicolet Magna 860 FTIR or Thermo-Nicolet iS50 FTIR at Caltech. All measurements employed a GLOBAR IR source, a KBr beamsplitter, and a MCT-A detector, with at least 512 scans taken at 2 cm<sup>-1</sup> resolution. Analysis areas were selected using 200 to 400  $\mu$ m diameter circular apertures, and multiple spectra for each crystal were taken to assess the possibility of zoning. Sample thicknesses were measured using a Mitutoyo digital micrometer, with a precision of ±2  $\mu$ m. JLM83a was measured at the University of Minnesota (UMN) using a Hyperion 2000 microscope attached to a Bruker Tensor 37 spectrometer, with a GLOBAR IR source, a KBr beamsplitter, and a MCT-A detector. These spectra were collected on a slab ~390  $\mu$ m thick, with 64 scans at 2 cm<sup>-1</sup> resolution, using a 100 × 100  $\mu$ m square knife-edge aperture. The video-assisted mapping feature of the OPUS 7.2 software was employed to take regularly spaced data (in a 6 × 8 grid) across the central portion of the sample slab.

The low-temperature (77 K) spectrum of GRR1386 was obtained in 1994 using a homebuilt vacuum chamber in the main compartment of the Nicolet 60SX FTIR

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that was operational at that time at Caltech. The room temperature spectrum of the sample taken in 1994 closely matches more recently acquired spectra.

Details of our baseline correction methods are provided in the Online Materials<sup>1</sup>. After baseline correction, we calculated total integrated band areas in the O-H stretching region, referred to hereafter as *Abs*<sub>tot</sub> [considered here as absorbance/cm<sup>2</sup> in one direction, rather than multiplying one measurement by three as in some studies on garnets (e.g., Libowitzky and Rossman 1997; Rossman 2006)]. Spectra were then curve fitted using the Multipeak Fitting 2 package in Igor Pro software. Table 1 also gives values for the weighted mean wavenumber (as defined by Libowitzky and Rossman 1997) for each spectrum.

### ERDA

In Table 2, we report H concentrations measured by ERDA for three grossular samples (GRR732, GRR771, and GRR1756), one synthetic forsterite (GRR1017), and three synthetic, rhyolitic glasses (NSL1, N3, and N5). The analyses were conducted at the Laboratoire d'Etudes des Eléments Légers, CEA, Saclay, France using improved methods for micro-ERDA (Raepsaet et al. 2008; Bureau et al. 2009). Analytical methods followed those outlined by Withers et al. (2012) and are detailed in the Online Materials<sup>1</sup>. GRR1017, well-characterized as an ultra-dry reference material with  $\leq 0.007 \ \mu g/g \ H_2O$  (Mosenfelder et al. 2011), was used to saxess the H background. Water contents of the rhyolitic glasses were previously reported in Tenner et al. (2009), measured using Karl-Fischer titration as described in Withers and Behrens (1999).

#### SIMS

SIMS data (Table 3) were obtained on the CAMECA 7f-GEO at Caltech using a Cs+ primary ion beam and previously described methods optimized for collecting low-blank H and F analyses (Mosenfelder and Rossman 2013a; Mosenfelder et al. 2011, 2015). Data are presented from two sessions, conducted in 2012 and 2016. For each analysis, we acquired either 30 cycles (in 2012) or 20 cycles (in 2016) through the mass sequence 12C, 16O1H, 18O, 19F, and 30Si, collecting negative ions with a mass resolution of ~5500 ( $\Delta$ M/M), sufficient to separate <sup>16</sup>O<sup>1</sup>H from <sup>17</sup>O and 18O1H from 19F (Burdo and Morrison 1971). Analyses from 2012 were obtained from garnets pressed into the same indium mount as the orthopyroxenes, clinopyroxenes, olivines, and F-bearing glasses (MPI-DING glasses KL2-G and ML3B-G and USGS glasses BCR-2G and BHVO-2G) reported on previously (and analyzed during the same session) by Mosenfelder and Rossman (2013a, 2013b). Some of the garnets were then extracted, repolished, cleaned, and pressed together into a new indium mount with one additional garnet (JLM83a), the MPI-DING and USGS glasses, and five additional F-bearing glasses (Fba-1, -2, -3, -4, and -5) prepared by Guggino and Hervig (2011). We used the Fba-series glasses to reevaluate the F concentrations of our MPI-DING and USGS glass splits, as described in Mosenfelder et al. (2020). The revised reference values used to establish working curves for F are given in the Online Materials1.

<sup>16</sup>O<sup>1</sup>H/<sup>18</sup>O and <sup>19</sup>F/<sup>18</sup>O ratios in Table 3 were blank corrected using <sup>16</sup>O<sup>1</sup>H and <sup>19</sup>F backgrounds monitored by analyzing "blank" reference materials: synthetic

IABLE 1. Garnet sample loc	calities and	F HR G	data
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Sample	Locality	Spectral	Abs <sub>tot</sub>	Mean
no.		class <sup>a</sup>	(cm-2)	(cm <sup>-1</sup> )
GRR42	Ramona Mine, California, U.S.A	. 2	1430(14)	3647
GRR229	Stream gravel, Merelani Hills, Tanzania	2b	1909(38)	3623
GRR732	Mindi Hills, Kenya	2b	1403(28)	3617
GRR771	Merelani Hills, Tanzania	2b	2441(73)	3622
GRR1122	Crestmore Mine, California, U.S.A.	7	1471(44)	3597
GRR1386	Stream gravel, Merelani Hills, Tanzania	2b	3589(72)	3633
GRR1386a	Stream gravel, Merelani Hills, Tanzania	2b	1592(48)	3619
GRR1429	Essex County, New York, U.S.A.	7	493(38)	3570-3579 <sup>b</sup>
GRR1756	#2 reef, Scorpion Mine, Voi, Taita, Kenya	7	591(12)	3595
JLM83a	Asbestos, Quebec, Canada	3	691–1544°	3630-3631°

Notes: Uncertainties in parentheses are estimated as discussed in text. <sup>a</sup> Classification scheme of Rossman and Aines (1991).

<sup>b</sup> Range of values for 7 spectra.

<sup>c</sup> Range measured in 48 spectra.

TABLE 2. Results of elastic recoil detection and	lysis	(ERDA)	compared to	o other H	calibration technic	ques
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Sample no.	Phase	Abs <sub>tot</sub> (cm <sup>-2</sup> )	H <sub>2</sub> O	(µg/g)	Reference	Method
			Uncorrected	Blank corrected		
GRR1756	Grossular	591(12)	308(40)	208(40)	This study	ERDA
GRR732	Grossular	1403(28)	599(76)	499(76)	This study	ERDA
			-	1062(31)	1	CFMS
GRR771	Grossular	2441(73)	1064(130)	964(130)	This study	ERDA
NSL1	Rhyolitic glass		11 133(1399)	11 033 (1399)	This study	ERDA
			-	11,600	2	KFT-FTIR
N3	Rhyolitic glass		33658 (4209)	33 558 (4209)	This study	ERDA
			-	33,000	2	KFT-FTIR
N5	Rhyolitic glass		50 549 (6313)	50 449 (6313)	This study	ERDA
	, ,		_	50 600	2	KFT-FTIR
GRR1017 <sup>a</sup>	Forsterite	0	101(14)	0	This study	ERDA
GRR53	Grossular	2877	-	1800	3, 4	MEA, MAN
GRR53F	Grossular	4796	-	2800	4	<sup>19</sup> F NRA
HESS1	Grossular	2510	-	870	5	<sup>15</sup> N NRA
		2006	-	950	5	<sup>15</sup> N NRA
TSAV	Grossular	1208	-	480	5	<sup>15</sup> N NRA
MALI	Grossular	168	-	170	5	<sup>15</sup> N NRA
GRMALI	Grossular	77	-	190	5	<sup>15</sup> N NRA

Notes: References: 1 = O'Leary et al. (2007); 2 = Tenner et al. (2009); 3 = Aines and Rossman (1984); 4 = Rossman and Aines (1991); 5 = Maldener et al. (2003). CFMS = continuous-flow mass spectrometry; KFT-FTIR = Karl-Fischer titration and FTIR; MEA =  $P_2O_5$  coulometry (moisture evolution analyzer); MAN = evolved  $H_2$  gas volume (manometry); NRA = nuclear reaction analysis. Uncertainties in parentheses are 2s in terms of least units cited.

<sup>a</sup> Blank reference material used to correct ERDA data.

#### TABLE 3. SIMS data

Sample no.	SIMS session	No. of analyses	H₂O (µg/g)ª	<sup>16</sup> O <sup>1</sup> H/ <sup>18</sup> O	<sup>19</sup> F/ <sup>18</sup> O	F (µg/g) <sup>ь</sup>
GRR1122-HT	2012	4	0	0.000338-0.000450 <sup>c</sup>	1.279(21)	508 (8)
	2016	3	0	0.001365-0.001904 <sup>c</sup>	1.325(40)	537(84)
GRR42	2012	5	529(50)	0.1244(14)	6.563(69)	2606(27)
	2016	2 <sup>d</sup>		0.1300, 0.1302	6.529, 6.584	2559, 2581
GRR229	2012	4	706(68)	0.1262(16)	3.713(48)	1474(19)
	2016	3		0.1304(49)	3.751(57)	1470(22)
GRR732	2012	4	519(50)	0.0885(16)	2.819(49)	1119(19)
GRR771	2012	4	903(90)	0.155(13)	4.14(19)	1644(75)
	2016	3		0.150(15)	3.99(10)	1565(39)
GRR1122	2012	4	544(54)	0.0956(12)	1.281(16)	508(6)
	2016	2 <sup>d</sup>		0.1183, 0.1247	1.295, 1.447	508, 567
GRR1386	2012	4	1328(128)	0.2283(31)	6.824(49)	2709(19)
	2016	3		0.2302(6)	6.694(64)	2624(25)
GRR1386a	2012	4	589(58)	0.1007(23)	2.422(48)	962(19)
	2016	3		0.1016(10)	2.423(16)	950(6)
GRR1429	2012	4	182(22)	0.0303(34)	0.465(34)	185(13)
GRR1756	2012	4	219(21)	0.0349(2)	0.602(4)	239(2)
	2016	2 <sup>d</sup>		0.349, 0.349 <sup>d</sup>	0.611, 0.615 <sup>d</sup>	239, 241
JLM83a <sup>e</sup>	2016	16 <sup>f</sup>	256-571	0.0296-0.1002	0.3502-0.8789	120-345

Notes: Numbers in parentheses are 2s uncertainties in terms of least units cited.

<sup>a</sup> Values calculated from FTIR using calibration factor of 0.37 (Eq. 1), with uncertainties propagated as described in text.

 $^{\rm b}$  Values calculated from  $^{\rm 16}{\rm O^1H}/^{\rm 18}{\rm O}$  using working curve for F-bearing glasses.

<sup>c</sup> Uncorrected ratios, given as a range.

<sup>d</sup> For samples with only two analyses, each analysis is given (separated by comma).

<sup>e</sup> Values for this sample are given as a range (for both FTIR and SIMS analyses).

<sup>f</sup> Four analyses were rejected due to a spike in the blank, as described in the text.

forsterite GRR1017 (Mosenfelder et al. 2011), a natural Cr-rich pyrope from Ugelvik, Norway (GRR332), and laboratory-dehydrated grossular (GRR1122-HT) and spessartine (GRR2215-HT). Details on characterization of these samples are provided in the Online Materials<sup>1</sup>.

#### EPMA

Electron microprobe analyses (Table 4) for most samples were acquired using a JEOL JXA-8900R at UMN. We first measured F, using MgF<sub>2</sub> as a standard; other elements were subsequently analyzed on the same spots using different analytical conditions.  $FK\alpha$  was acquired on three TAP crystals simultaneously, and intensities were then aggregated and combined with the other elements during post-processing with Probe for EPMA software (Probesoftware, Inc.). Despite its lower sensitivity for  $FK\alpha$ , we prefer TAP over LDE1 for this application, because LDE1 has the inherent problem of significant background interferences between the  $FK\alpha$  and  $FeK\alpha$ , MgK $\beta$ , and Mn $K\alpha$  X-ray lines (e.g., Witter and Kuchner 2004; Zhang et al. 2016). We found that an accelerating voltage of 20 kV optimized fluorescence yields and peak-to-background ratios for F on TAP. For most of the

garnets, a beam current of 250 nA and beam diameter of 10  $\mu$ m was used for this stage of the analysis. Analyses of JLM83a were conducted at either 200, 250, or 400 nA. Calculated detection limits range from ~40  $\mu$ g/g at the highest current to 60  $\mu$ g/g at the lowest current.

Using the procedure outlined by Donovan et al. (2011), an exponential background was fit to the F k $\alpha$  peak with parameters based on a detailed wavescan of Asbestos grossular. Counting times for each spectrometer were 400 s on peak and 350 s on each background position, resulting in aggregated times per analysis of 1200 s on peak and 2100 s on the background measurement. Time-dependent intensity (TDI) loss (or gain) was monitored for all elements, but no significant or systematic dependence was found, so the TDI correction was not used. Unknown and standard intensities were corrected for deadtime, and standard intensities were corrected for standard drift over time.

Major and minor elements were measured using an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 1  $\mu$ m. Counting times for each element were 20 s on peak and 10 s at each background position. Reference materials used for calibration included synthetic forsterite (GRR1017) and

Sample no.	GRR42	GRR229	GRR732	GRR771	GRR1122	GRR1386	GRR1386a	GRR1429	GRR1756	JLM	83a
										low	high
SiO	38,59(24)	38.77(24)	40.15(39)	39.84(18)	38.69(31)	39.19(23)	39.96(5)	39.48(16)	39.70(11)	39.95(18)	39.95(18)
TiO <sub>2</sub>	_	0.40(3)	0.34(3)	0.54(2)	0.57(6)	0.64(3)	0.36(3)	0.42(3)	0.40(1)	_	_
Al <sub>2</sub> O <sub>3</sub>	21.43(12)	20.94(13)	21.97(28)	22.34(8)	17.64(7)	22.29(7)	21.90(5)	18.62(13)	20.90(12)	22.23(13)	22.23(13)
Cr <sub>2</sub> O <sub>3</sub>	-	0.28(2)	0.04(3)	-	-	-	-		0.29(2)		
V <sub>2</sub> O <sub>3</sub>	-	1.90(3)	0.88(1)	0.05(2)	-	-	-	-	1.77(5)	-	-
FeO <sup>a</sup>	3.23(2)	0.08(1)	0.06(3)	0.14(2)	7.53(26)	0.20(3)	1.36(5)	7.27(9)	0.06(1)	1.82(10)	1.82(10)
MnO	0.10(2)	0.90(5)	1.15(1)	0.27(3)	0.38(4)	0.14(2)	0.33(2)	0.21(2)	0.97(1)	0.24(3)	0.24(3)
MgO	-	0.47(2)	0.54(3)	0.34(1)	0.07(2)	0.43(1)	0.31(1)	0.14(1)	0.57(1)	-	_
CaO	35.33(6)	35.10(14)	35.44(33)	36.25(10)	34.61(20)	36.27(11)	35.78(6)	34.11(9)	35.02(5)	35.51(14)	35.51(14)
$H_2O^+$	0.0723 <sup>b</sup>	0.0706 <sup>c</sup>	0.0519°	0.0903°	0.0544°	0.1328°	0.0589°	0.0182 <sup>c</sup>	0.0219°	0.0171 <sup>d</sup>	0.0576 <sup>d</sup>
F	0.2477(36)	0.1516(30)	0.1119 <sup>e</sup>	0.1470(62)	0.0586(62)	0.2478(24)	0.0924(29)	0.0185 <sup>e</sup>	0.0343(42)	0.012 <sup>d</sup>	0.0345 <sup>d</sup>
O=F	-0.1	-0.06	-0.05	-0.06	-0.02	-0.10	-0.04	-0.01	-0.01	-0.01	-0.01
Total	98.90	99.00	100.68	99.95	99.58	99.44	100.11	100.28	99.73	99.77	99.83
					Recalcula	ated					
FeO	1.16	0.08	0.06	0.14	2.09	0.2	1.36	3.48	0.06	1.82	1.82
Fe <sub>2</sub> O <sub>2</sub>	2.30	_	_	_	6.05	_	_	4.22	_	_	_
Recalculated total	99.13	99.00	100.68	99.95	100.19	99.44	100.11	100.71	99.73	99.77	99.83
				Catio	on/anion as	signments					
Si	2.9457	2.9576	3.0015	2.9906	2.9804	2.9536	3.0037	3.0137	3.0079	3.0162	3.0138
Ti	_	0.0230	0.0191	0.0305	0.0330	0.0363	0.0204	0.0241	0.0228	_	_
AI <sup>VI</sup>	1 8978	1.8583	1,9357	1,9764	1.5924	1.9650	1.9401	1 6752	1.8663	1,9781	1,9765
Aliv	0.0301	0.0243	-	-	0.0091	0.0149	-	-	-	-	-
Cr	_	0.0169	0.0024	_	_	-	_	_	0.0174	_	_
V	_	0 1 1 6 2	0.0527	0.0030	_	_	_	_	0 1075	_	_
Fe <sup>2+</sup>	0.0738	0.0051	0.0038	0.0088	0.1346	0.0126	0.0855	0.2219	0.0038	0 1 1 4 9	0 1 1 4 8
Fe <sup>3+</sup>	0.1324	-	-	-	0.3506	-	-	0.2422	-	-	-
Mn	0.0065	0.0582	0.0728	0.0172	0.0248	0 0089	0.0210	0.0136	0.0622	0.0153	0.0153
Ма	-	0.0534	0.0602	0.0380	0.0210	0.0483	0.0310	0.0022	0.0644	-	-
Ca	2 8896	2 8689	2 8387	2 9155	2 8566	2 9289	2 8817	2 7899	2 8429	2 8726	2 8703
H.	0.0092	0.0090	0.0065	0.0113	0.0070	0.0167	0.0074	0.0023	0.0028	0.0022	0.0072
0	11 9402	11 9699	12 0027	11 9959	11 9857	11 9523	11 9850	11 9955	12 0229	12 0053	12 0031
F	0.0598	0.0366	0.0265	0.0349	0.0143	0.0591	0.0220	0.0045	0.0082	0.0029	0.0082
•	010070	0.0000	0.0205	010019	End-mem	hers	0.0220	0.000.0	010002	010025	0.0002
Katoite	0 31%	0 30%	0.22%	0 38%	0.23%	0.56%	0.25%	0.08%	0.09%	0.07%	0.24%
FCa garnet	0.50%	0.30%	0.22%	0.29%	0.12%	0.49%	0.18%	0.04%	0.07%	0.02%	0.07%
Schorlomite-Al	_	1 1 5%	_	_	0.45%	0.75%	_	-	_	_	_
Morimotoite	_	_	_	_	2 40%	-	2 04%	2 4 1 %	_	_	_
Maiorite	_	_	_	_	-	_	0.37%	0.07%	_	_	_
Goldmanite	_	5 81%	2 64%	0 1 5 %	_	_	-	-	5 38%	_	_
Livarovite	_	0.84%	0.12%	0.1370	_	_	_	_	0.87%	_	_
Spessartine	0.22%	1 94%	2 4 3 %	0.57%	0.83%	0 30%	0 70%	0.45%	2.07%	0.51%	0.51%
Durope	0.2270	1.79%	2.45%	1 27%	0.05%	1.61%	0.66%	0.4570	2.07%	0.5170	0.5170
Almandine	2 46%	0.17%	0.13%	0.29%	3.69%	0.42%	1 78%	- 6 36%	0.13%	3 64%	3 50%
Grossular	91 41%	87.22%	Q1 43%	96.02%	74 49%	94.87%	93.43%	76.83%	88 36%	94 66%	94 50%
Andradite	4 11%	-	-	-	17 5 30%	-	-	12 11%	-	-	
Remainder	1.00%	0.48%	_ 0.82%	1 03%	0.00%	1 00%	0 59%	1.65%	0.89%	_ 1 10%	- 1 18%
Total	100.01%	99 99%	100.02%	100.00%	100.01%	100.00%	100.00%	100.00%	100.01%	100.00%	100.00%
10101	100.01/0		100.02/0	100.00/0	100.01/0	100.00/0	100.00/0	100.00/0	100.01/0	100.00/0	100.00/0

TABLE 4. EPMA data and calculated garnet end-members

Notes: Cation assignments and garnet end-members calculated using Locock (2008), on an 8 cation basis (treating H as H<sup>4+</sup><sub>4</sub>). See Locock (2008) for definition of end-members. "Remainder" represents the proportion of cations that could not be allocated. Dashed lines denote oxides, elements or end-members below detection limit or calculated to be 0. EPMA data represent averages (in wt%, with 1s uncertainties in parentheses) of five to six analyses for all samples except JLM83a (average of 36 analyses).

<sup>a</sup> Total Fe calculated as FeO.

<sup>b</sup> H<sub>2</sub>O calculated from 2012 SIMS data, using fit to data for East African grossulars.

<sup>c</sup> H<sub>2</sub>O calculated from FTIR data (Table 3).

<sup>d</sup> H<sub>2</sub>O and F based on 2016 SIMS data, for two analyses at extreme ends of range.

<sup>e</sup> F based on 2012 SIMS data.

<sup>f</sup> Recalculated wt% total after calculation of Fe<sup>2+</sup>/Fe<sup>3+</sup>.

tephroite (GRR392) for Mg and Mn, respectively; a natural almandine (Harvard 112140) for Fe; asbestos grossular for Ca and Si; chromite (NMNH 117075) for Cr; ilmenite (NMNH 96189) for Ti; Brazilian spessartine (Verma 1960) for Al; and vanadium metal for V. Na and K were also analyzed but were below the detection limit in all samples.

Final data processing used the CITZAF matrix correction method (Armstrong 1988), with FFAST mass absorption coefficients (Chantler et al. 2005). The matrix correction takes into account oxygen calculated by cation stoichiometry and the oxygen equivalent from F. Cation proportions (including reassignment of total Fe to Fe<sup>2+</sup> and Fe<sup>3+</sup>) and garnet end-members were calculated using the Excel spreadsheet written by Locock (2008).

We also report EPMA data for two samples (GRR732 and GRR1429) that were acquired at Caltech using a JEOL JXA-8200. We used protocols for these analyses similar to those used at UMN but did not measure F. Reference materials for calibration included synthetic pyrope for Mg, Al, and Si; synthetic tephroite (GRR392) for Mn; synthetic fayalite for Fe; grossular (GRR1386) for Ca; and synthetic rutile,  $Cr_2O_3$ , and  $V_2O_5$  for Ti, Cr, and V, respectively.

#### RESULTS

# FTIR spectroscopy

FTIR spectra representing the full variation in O-H stretching vibrations in the grossular samples we studied are displayed in Figure 1. Following Rossman and Aines (1991), these spectra can be separated into different classes according to the most prominent absorption bands present. Class 2, represented by GRR42 (Fig. 1a), is dominated by strong peaks at 3647, 3656, 3676, and 3687 cm<sup>-1</sup>, with the highest peak at 3647 cm<sup>-1</sup>. A subset of spectral class 2 is class 2b, which exhibits the same bands at



high frequency (also with maximum absorbance at 3647 cm<sup>-1</sup>) but has multiple bands between 3600 and 3500 cm<sup>-1</sup> (Fig. 1a). Class 2b is represented by five of the East African garnets (GRR229, GRR732, GRR771, GRR1386a, and GRR1386), which have spectra with similar shapes but varying  $Abs_{tot}$  (Table 1; Online Materials<sup>1</sup> Fig. OM1). Three grossular garnets (GRR1122, GRR1429, and GRR1756) fall into class 7 in the Rossman and Aines scheme because their strongest absorption is at 3599 cm<sup>-1</sup> rather than at 3647 cm<sup>-1</sup>, but otherwise their spectra are similar to class 2b; classes 2b and 7 are compared on the same scale in Figure 1b.

The Asbestos garnet JLM83a (Fig. 1c) is typical of class 3, with a strong peak at 3631 cm<sup>-1</sup> that is not as prominent in the other garnets. JLM83a also has bands centered at ~3621, 3644, 3659, 3665, 3677, and 3689 cm<sup>-1</sup>. Garnets from Asbestos fall into both classes 3 and 4, where class 4 is defined by having its strongest peak at 3621 cm<sup>-1</sup>. Figure 1c compares spectra of JLM83a to published spectra of some other Asbestos grossular garnets (GRR53

◄ FIGURE 1. Representative FTIR spectra for grossular spectral classes 2, 2b, 3, 4, and 7. Class designations follow Rossman and Aines (1991). Spectra are plotted without baseline correction and offset from each other for clarity. Spectra in a and b are normalized to 1 cm; spectra in c are normalized to different thicknesses (as labeled) to facilitate comparison. (a) Class 2 (GRR42), with the strongest peak at 3647 cm<sup>-1</sup>, and class 2b (GRR1386). Class 2b has peaks below 3620 cm<sup>-1</sup> that are almost absent in GRR42. Room-temperature spectrum of GRR1386 (solid black curve) is directly overlain by spectrum taken at 77 K (gray dashed curve). (b) Class 2b (GRR732) and class 7 (GRR1122). Although these spectra have bands at similar positions, in class 7 the dominant peaks are at lower frequencies and the strongest peak is at 3599 cm<sup>-1</sup> rather than 3647 cm<sup>-1</sup>. (c) Class 3 and 4 spectra of natural and synthetic grossular garnets. Three representative spectra of JLM83a are displayed, with integrated absorbances (Abstot) equal to 691 (dotted line), 1118 (dashed line), and 1526 cm<sup>-2</sup> (solid line). The spectrum of GRR53 is from the slice labeled "GRR53B-F" displayed in Figure 6 of Rossman and Aines (1991). Spectra of synthetic, end-member grossular crystals are from Geiger and Armbruster (1997) and Withers et al. (1998). Spectral classes 3 and 4 are nominally distinguished by whether the strongest peak is at 3631 or 3621 cm<sup>-1</sup>, respectively. Three of these garnets (GRR53, JLM83a, and the grossular made by Geiger and Armbruster 1997) have strong peaks at 3689, 3677, 3665, and/or 3559 cm<sup>-1</sup> that are weak or absent in the other two samples (GRR1537 and the grossular synthesized by Withers et al. 1998). (Color online.)

and GRR1537) and end-member grossular crystals synthesized by Geiger and Armbruster (1997) and Withers et al. (1998).

Whereas the absorbance among different East African grossular varies widely (Table 1; Online Materials1 Fig. OM1), we failed to detect H zoning within any individual single crystal from this area. The only crystals in our study that are significantly zoned, based on FTIR, are JLM83a and GRR1429. Abstot in JLM83a varied by a factor of  $\sim 2$  in the range between 3750 and 3300 cm<sup>-1</sup>. All spectra have similar shapes, but relative intensities of the peaks at 3631 and 3621 cm<sup>-1</sup> vary (Fig. 1c). Rossman and Aines (1991) noted a comparable variation in Abstot for GRR53 from the same locality. Systematic zoning patterns (such as core-rim relationships or sector zoning) could not be deciphered in the randomly cut slab of JLM83a that we used for both FTIR and SIMS measurements. Although variations in absorbance in Asbestos garnets have been attributed previously to birefringence (Rossman and Aines 1986; Allen and Buseck 1988), our SIMS measurements (Table 3 and discussion below) demonstrate that actual differences in H concentration are a more important factor in this crystal.

GRR1429 is also birefringent, which might be the cause of the variations in  $Abs_{tot}$  (about 5% relative) in this sample. We used the average of seven baseline-corrected, unpolarized spectra taken on separate spots to estimate its H<sub>2</sub>O content.

Close examination of the spectrum of GRR1386 (Fig. 1a) reveals 12 peaks between 3700 and 3500 cm<sup>-1</sup> and the shoulders on some of the bands indicate that curve fitting should take into account more than 12 bands. Online Materials<sup>1</sup> Figure OM5 displays an example of a curve fitting for this garnet. We fit 15 bands with a pseudo-Voigt profile (mixed Gaussian and Lorentzian), at 3531, 3539, 3546, 3567, 3583, 3599, 3608, 3623, 3631, 3643, 3647, 3657, 3664, 3674, and 3688 cm<sup>-1</sup>. Although the fit is obviously non-unique, our peak positions (with initial guesses based on visual examination) are within 1 cm<sup>-1</sup> of those fit for the same sample by Geiger and Rossman (2020a), with the slight difference that

we fit an additional band at  $3539 \text{ cm}^{-1}$  not present in their fit. We used these peak positions as a basis to fit spectra for the other grossular garnets. Fitted peak centers in other samples are mostly within 1 cm<sup>-1</sup> of those for GRR1386, with a few deviations up to 3 cm<sup>-1</sup>. A table with the fit results for all samples is provided in the Online Materials<sup>1</sup>.

The cooling experiment conducted on GRR1386 demonstrates that nearly all the mid-IR absorption in this garnet can be attributed to structurally incorporated O-H, with most bands shifting to higher energies upon cooling to 77 K (Fig. 2). There is no evidence for band splitting at low T, as observed in many other garnets (Geiger et al. 1991; Geiger and Rossman 2018). However, enlargement of the baseline region reveals a broad absorption band at ~3400 cm<sup>-1</sup> that shifts to ~3240 cm<sup>-1</sup>, typical of the transition from liquid water to ice (also plotted for comparison in Fig. 2 are spectra for water and ice from Bertie and Lan 1996 and Johnson and Rossman 2003). The 3400 cm<sup>-1</sup> band is apparently also present in some of the other garnets, but quantification is hampered by high-frequency interference fringes in most spectra (not visible at the scales used in Fig. 1). The liquid water in GRR1386 is probably contained in submicrometer-sized fluid inclusions, as found in other NAMs (e.g., Johnson and Rossman 2003; Mosenfelder et al. 2011). Its contribution to Abstot for this sample amounts to 1.2%. We have elected not to correct any of the estimates for Abstot in Table 1 for the possible presence of H2O. Furthermore, we have ignored another possible contribution to Abstot in the O-H stretching region from the lowest energy spin-allowed Fe2+ transition in grossular with FeO content greater than 1 wt% (GRR42, GRR1122, GRR1386a, GRR1429, and JLM83a). This band should occur at lower energy compared to other garnets (Geiger and Rossman 1994), because the larger size of the X cation site in grossular leads to greater splitting of the Fe2+ bands (White and Moore 1972). However, its exact position is difficult to determine because of the superposition of O-H stretching vibrations (Slack and Chrenko 1971; White and Moore 1972).



**FIGURE 2.** Detailed comparison near the baselines of 77 and 298 K spectra of GRR1386. The band at  $\sim$ 3240 cm<sup>-1</sup> at 77 K is attributed to frozen H<sub>2</sub>O in fluid inclusions. Bands attributed to structural OH<sup>-</sup> groups are off scale. Spectra of liquid water from Bertie and Lan (1996) and ice from Johnson and Rossman (2003) also plotted for comparison. GRR1386 spectra are normalized to 1 cm thickness; spectra of ice and water are arbitrarily scaled. (Color online.)



**FIGURE 3.** Raw (uncorrected)  $H_2O$  concentrations determined by ERDA for three East African grossular garnets (GRR732, GRR771, and GRR1756) and blank forsterite (GRR1017), as a function of (*Abs*<sub>tot</sub>). Solid line is a York regression. Dashed lines represent 95% confidence intervals calculated from a priori errors. Equation and mean squared weighted deviation (MSWD) of the fit are also shown. (Color online.)

# ERDA

 $H_2O$  concentrations of the three grossular garnets, three rhyolitic glasses, and dry forsterite as determined by ERDA are given in Table 2. ERDA and PIXE detector maps of the analyzed areas for two of the garnets (GRR1756 and GRR732) revealed no significant heterogeneities, but a small, anomalous region of interest with high-H and Ca content in GRR771 was excluded in the calculation of its bulk H content. This "hot spot" probably represents surface contamination (Withers et al. 2012). Bulk H (ERDA) and Ca (PIXE) maps for this sample are provided in the Online Materials<sup>1</sup>.

The nominal H<sub>2</sub>O concentration measured by ERDA in GRR1017 forsterite, established as an ultra-dry "blank" material with  $\leq 0.007 \ \mu g/g H_2O$  (Mosenfelder et al. 2011), is  $101 \pm 14 \ \mu g/g$ . The bulk H concentrations for grossular are strongly correlated with  $Abs_{tot}$  (Fig. 3). We applied a York regression to the data (York et al. 2004; Vermeesch 2018), taking into account uncertainties in both  $Abs_{tot}$  and the ERDA measurements. The regression yields an intercept of  $100 \pm 13 \ \mu g/g H_2O$ , which is the value we subtract to arrive at the blank-corrected H<sub>2</sub>O concentrations. The slope of the fit line provides the following calibration for infrared measurements:

$$C_{\rm H_{20}}(\mu g/g) = 0.370(\pm 0.035, 2\sigma) \times Abs_{\rm tot}.$$
 (1)

The integral molar absorption coefficient [ $\varepsilon_i$ , in L/(mol·cm<sup>2</sup>)] can be derived by substituting the above relation into a modified form of the Beer-Lambert law (e.g., Johnson and Rossman 2004),

$$C_{\rm H20}(\mu g/g) = Abs_{\rm tot} \times 18.015 \times 10^{6}/(\rho \cdot \varepsilon_{\rm i})$$
<sup>(2)</sup>

where  $\rho$  is the density of the mineral (in g/L, or kg/m<sup>3</sup>). Assuming for simplicity a typical density for V-bearing grossular of 3615 kg/m<sup>3</sup> (Maldener et al. 2003), we derive a value for  $\varepsilon_i$  of 13470 L/(mol·cm<sup>2</sup>).

A check on the accuracy of our ERDA data on grossular is provided by the results on the three rhyolitic glasses, which are in excellent agreement with previously published total H<sub>2</sub>O concentrations determined for these samples using Karl-Fischer titration (Tenner et al. 2009). The  $H_2O$  contents of the glasses measured by ERDA are within 5% of the reference values.

### SIMS and EPMA measurements of H and F

SIMS data for the sessions conducted in 2012 and 2016 are summarized in Table 3, with complete data for all individual analyses provided in the Online Materials<sup>1</sup>. Statistics are reported in this paper using the symbology of Fitzsimons et al. (2000). Internal precision in <sup>16</sup>OH/<sup>18</sup>O (calculated from  $2s_{\bar{x}}$ , the standard error of the mean for 20 or 30 cycles through the mass sequence) ranged from 0.24 to 1.35% relative for all garnets except GRR1122-HT (the blank) and JLM83a. Measured <sup>19</sup>F/<sup>18</sup>O ratios were similarly precise (0.15 to 0.52%). The high variability in internal precision, as well as external precision (reproducibility) for JLM83a, is discussed below.

<sup>16</sup>OH/<sup>18</sup>O for each garnet with the exception of JLM83a is plotted in Figure 4 as a function of H<sub>2</sub>O concentration determined from FTIR data using the ERDA calibration. Similar plots are derived if <sup>30</sup>Si is used instead of <sup>18</sup>O as the reference mass. Uncertainties in H<sub>2</sub>O concentration were estimated by propagating the error in *Abs*<sub>tot</sub> (Table 1) and the uncertainty in the fit to the ERDA data (Fig. 3; Eq. 1). York regressions applied to the data for East African garnets (GRR229, GRR732, GRR771, GRR1386, GRR1386a, and/or GRR1756) have indistinguishable slopes for the two sessions. These regressions also fit well to the data for GRR1429 and GRR1122 measured in 2012. However, the 2016 data for GRR1122 are significantly offset from the regression line, as are both the 2012 and 2016 data for GRR42.

In the case of GRR1122, we provisionally attribute this discrepancy to heterogeneity in the sample not recognized from FTIR data and insufficiently probed by the six SIMS analyses that were acquired. The heterogeneity could be related to the presence of fluid inclusions, indicated by a weak broad band at 3420 cm<sup>-1</sup> similar to that seen in GRR1386 (Fig. 2). As for GRR42, the consistency in values for seven analyses from the two sessions suggests a different explanation for the offset from the regression. In the discussion section, we explore the

possibility that the H concentration of GRR42 is significantly underestimated because of the frequency dependence of the IR molar absorption coefficient, which cannot be accurately constrained from our ERDA data.

Fluorine concentrations measured by SIMS and EPMA are compared in Online Materials<sup>1</sup> Figure OM9. The SIMS concentration values are tied to our redetermination of reference values for the F-bearing basaltic glasses we regularly use for calibration, not taking into account any possible SIMS matrix effect. The close correspondence between SIMS and EPMA values (with all values reasonably close to the 1:1 line) suggests that matrix effects are minimal in this case.

The heterogeneity in apparent H<sub>2</sub>O concentrations measured by FTIR in JLM83a was confirmed by the grid map of SIMS analyses taken over approximately the same area (Fig. 5). The SIMS analyses also reveal heterogeneity in F, which was additionally confirmed by EPMA (see Online Materials<sup>1</sup>). The measurements using SIMS, FTIR, and EPMA cannot be compared directly to determine a zoning pattern because the FTIR analyses are taken in transmission, whereas the SIMS and EPMA measurements sample a volume that is close to the surface (~1-2 µm deep for SIMS, and ~3 µm deep for EPMA at the analytical conditions used). However, the range in apparent H<sub>2</sub>O concentrations measured by FTIR (256–571  $\mu$ g/g) is similar to the range measured by SIMS (170-576 µg/g), calculated by applying the York regression in Figure 4b. For the sake of this comparison, we discard four analyses (marked by asterisks in Fig. 5) that were affected by the spike in background contaminant levels in the vacuum caused by the cold trap running out of liquid N2 (see Online Materials1). These analyses had <sup>12</sup>C/<sup>18</sup>O ratios one to two orders of magnitude higher than the other analyses.

Following the 2012 session, it became apparent that <sup>19</sup>F and <sup>16</sup>OH are correlated for some grossular garnets, particularly the East African samples with similar class 2b and 7 FTIR spectra (Fig. 6a). A similar correlation was noted for spessartine (Fig. 6b). An even more robust correlation exists for the data taken on JLM83a alone (Fig. 6a). The values in Figure 6a for JLM83a represent average <sup>16</sup>OH/<sup>18</sup>O and <sup>19</sup>F/<sup>18</sup>O for each analysis. How-



**FIGURE 4.** <sup>16</sup>OH/<sup>18</sup>O data from two SIMS sessions. Error bars not shown are within the symbol size. Solid lines are York regressions fit to data (circles) on the blank and East African samples only, with 95% confidence intervals (calculated from a priori errors) displayed as dashed curves. The equation and MSWD for each regression are also displayed in the graphs. (a) 2012 data. Each point represents the average of three to five measurements, with  $2s_x$  (sample standard deviation) error bars displayed for <sup>16</sup>OH/<sup>18</sup>O. (b) 2016 data. In this plot, each point represents a single analysis. Consequently, uncertainties in <sup>16</sup>OH/<sup>18</sup>O ( $2s_{\overline{s}}$ , standard error of the mean) are all within the symbol size in this plot. Some data points are obscured by overlap with other data; all original data are given in the Online Materials<sup>1</sup>. (Color online.)



ever, the internal precision of the analyses varies widely, with  $s_{\bar{x}}/\hat{s}_{\bar{x}}$  (where  $\hat{s}_{\bar{x}}$  is the precision predicted by Poisson statistics; Fitzsimons et al. 2000), ranging from 1 (ideal) to 30 (poor). We would normally discriminate against SIMS measurements with such high  $s_{\bar{x}}/\hat{s}_{\bar{x}}$  values; for instance, in Mosenfelder et al. (2011), all analyses of olivine with  $s_{\bar{x}}/\hat{s}_{\bar{x}} > 5$  were filtered out. High  $s_{\bar{x}}/\hat{s}_{\bar{x}}$  in olivine and orthopyroxene has been attributed to the presence of sub-micrometer to micrometer-sized inclusions of hydrous minerals (such as serpentine and amphibole) and/or fluid inclusions (Mosenfelder et al. 2011; Mosenfelder and Rossman 2013a). In the present case, however, we attribute the high variability to zoning in H and F within the garnet itself. Analyses with high  $s_{\bar{x}}/\hat{s}_{\bar{x}}$ show strong cycle-to-cycle covariation between <sup>19</sup>F and <sup>16</sup>OH (Online Materials<sup>1</sup> Fig. OM8), indicating that F and H are coupled on a sub-micrometer scale.

# DISCUSSION

## Molar IR absorption coefficient for H<sub>2</sub>O in grossular

In Figure 7, we compare our ERDA data to  $H_2O$  concentrations measured (as a function of  $Abs_{tot}$ ) in grossular-rich garnets using other "absolute" techniques: NRA (Rossman and Aines 1991; Maldener et al. 2003),  $P_2O_5$  cell coulometry using a moisture evolution analyzer (MEA, Aines and Rossman 1984), H manometry (Aines and Rossman 1984), and continuous-flow mass spectrometry (CFMS; O'Leary et al. 2007). Also displayed in the figure is the regression line for all of the data considered by Rossman and Aines (1991) for grossular and hydrogrossular with up to 12.75 wt% H<sub>2</sub>O (with H<sub>2</sub>O contents on the high end well-constrained using X-ray diffraction).

We have no definitive explanation for the discrepancy between H concentrations measured in GRR732 by ERDA (599  $\mu$ g/g H<sub>2</sub>O) and CFMS (1062  $\mu$ g/g H<sub>2</sub>O); we can only speculate that the blank for that particular CFMS measurement was higher than recognized. Our data show excellent agreement, however, with some of the NRA data. In particular, the analyses by Maldener et al. (2003) on their TSAV ( $480 \pm 40 \,\mu\text{g/g}\,\text{H}_2\text{O}$ ) and thin (0.0165 cm) slab of HESS1 ( $870 \pm 90 \ \mu g/g \ H_2O$ ) samples lie close to our regression line. These East African grossular garnets have IR spectra similar to those from the same area that we measured with ERDA. Our data are in poorer agreement with the analyses of Maldener et al. (2003) of a thicker (0.0312 cm) slab of HESS1 (950  $\pm$  80  $\mu$ g/g H<sub>2</sub>O) and with MALI (170  $\pm$  20  $\mu g/g H_2O$ ) and GRMALI (190  $\pm$  20  $\mu g/g H_2O$ ). The two NRA measurements of HESS1 are in agreement with each other within mutual uncertainties, which suggests that there is a discrepancy in the FTIR measurements (e.g., non-linearity of the detector for linear absorbance higher than 1.5 in the thick HESS1 sample) or perhaps unrecognized H zoning in the crystal. The discrepancies between our measurements and those on MALI and GRMALI might derive from errors made in correcting the sample thicknesses for beam convergence in the microscope. Furthermore, any inaccuracies in blank correction are also more likely to affect these low-H content samples.



**FIGURE 6.** Correlations between <sup>16</sup>OH and <sup>19</sup>F for grossular and spessartine. (**a**) SIMS data for grossular from sessions in 2012 (open symbols) and 2016 (closed symbols). Each symbol represents a single analysis ( $2s_x$  uncertainties are within the symbol size for each point). Solid lines are ordinary least-squares (OLS) regressions to data for East African grossular garnets ( $r^2 = 0.98$ ) and multiple analyses on Asbestos grossular JLM83a ( $r^2 = 0.99$ ). Data on JLM83a that were compromised by contamination (Fig. 5) are not included in this plot. (**b**) Spesartine data from 2012 session. Each data point on this plot represents an average of between 4 and 11 analyses for one sample ( $2s_x$  uncertainties are within the symbol size). Solid line is an OLS regression ( $r^2 = 0.99$ ) to all of the data. (Color online.)





**FIGURE 7.** Comparison of ERDA results (circles) to previous calibration data on asbestos grossular [GRR53 and GRR53B, triangles (Aines and Rossman 1984; Rossman and Aines 1991); diamonds (Maldener et al. 2003); and square (O'Leary et al. (2007)]. Only two data points from the compilation of Rossman and Aines (1991) are plotted (for asbestos garnets GRR53 and GRR53F), but the original regression determined for their entire data set of grossular and hydrogrossular garnets over a much wider range of H contents (up to 12.75 wt% H<sub>2</sub>O) is displayed as a dashed line. The ERDA data have been blank corrected in this graph by subtracting 100  $\mu$ g/g from the raw values plotted in Figure 3. (Color online.)

The H concentrations of asbestos grossular garnets GRR53 and GRR53F were measured using three different techniques: H manometry, MEA, and NRA (Aines and Rossman 1984; Rossman and Aines 1991). The poor agreement of our data fit with the values determined with those techniques might be related to H zoning comparable to that in JLM83a. Hydrogen manometry and MEA are bulk methods that sample a much larger volume than the FTIR measurements and thus cannot account for finescale zoning. Even though NRA is a near-surface technique, the beam size employed at that time was much larger (several millimeters) than the apparent scale of H zoning in Asbestos grossular. Furthermore, the NRA measurement of GRR53F employed a reaction with <sup>19</sup>F ions that was subsequently abandoned in favor of a more reproducible reaction employing a <sup>15</sup>N beam (Rossman 2006).

There is a large discrepancy (Fig. 7) between our data fit on relatively low-H content grossular and the regression applied by Rossman and Aines (1991), which was largely constrained by hydrogrossular garnets with high-H contents. The discrepancy cannot be attributed to the lower sample density of hydrogrossular GRR1358, which has 12.75 wt% H<sub>2</sub>O, *Abs*<sub>tot</sub> of 158750 cm<sup>-2</sup>, and a calculated density of 3050 kg/m<sup>3</sup> (Basso et al. 1983), would have an  $\varepsilon_i$  of 7354 L/(mol·cm<sup>2</sup>), lower than our new value by a factor of almost two. The data on hydrogrossular samples could have been compromised by uncertainties in sample thickness or unrecognized H zoning, but these factors are speculative and more work is needed to ascertain the reason for the large apparent difference between low-H grossular and hydrogrossular.

The possibility of a difference in calibration factor for gros-

sular and hydrogrossular was already noted by Rossman and Aines (1991), and Rossman (2006) recommended a calibration factor for low-H content grossular of 0.14 (for absorbance in three directions). That value, equivalent to 0.42 for the convention for  $Abs_{tot}$  used in this study, compares reasonably well to our new value of  $0.370 \pm 0.035$  (Eq. 1). We conclude that our new calibration is more appropriate than the Rossman and Aines calibration for grossular with less than ~1 wt% H<sub>2</sub>O.

Empirical and theoretical studies consistently show an increase in  $\varepsilon_i$  with decreasing frequency for O-H absorption bands (Paterson 1982; Libowitzky and Rossman 1997; Balan et al. 2008; Mosenfelder et al. 2015). This means that an IR calibration based on grossular with relatively low-mean wavenumber might underestimate the H2O contents of grossular with higher mean wavenumber. Whereas our ERDA calibration was performed on grossular with mean wavenumbers between 3595 and 3622 cm<sup>-1</sup> (Table 1), GRR42 is dominated by bands with significantly higher frequency (with a mean wavenumber of 3647 cm<sup>-1</sup>; Fig. 1a; Table 1). A frequency dependence to  $\varepsilon_i$  can therefore explain the offset of SIMS data for this sample in Figure 4, but the magnitude of the dependence is poorly constrained. For the sake of calculating formula units and garnet end-members (Table 4), we assume a H2O concentration for this sample based on the York regression shown in Figure 4a. Further work is needed to constrain the frequency dependence of  $\varepsilon_i$  to determine whether this assumption is justified. Our calibration also might underestimate H<sub>2</sub>O concentrations for JLM83a and other asbestos grossular garnets, which also have a higher mean wavenumber (Table 1). Unfortunately, the zoning in some (or all?) of these class 3 and 4 garnets will make this goal challenging, and class 2 garnets with spectra like that of GRR42 are rare in our experience. A better way forward might entail synthesizing grossular crystals at high P-T (Geiger and Armbruster 1997; Withers et al. 1998) and establishing their homogeneity using a technique such as ERDA.

## Previous models of H and F incorporation mechanisms

Hydrogen incorporation in garnets is classically assumed to take place via the "hydrogarnet" substitution, whereby four H atoms bond to the O atoms surrounding a vacant Si site. Hereafter, we refer to this substitution as  $(4H)_{Si}^{x}$ , which is a commonly used, abbreviated form of the following defect associate written in Kröger and Vink (1956) notation:

$$[V_{\rm Si}^{\prime\prime\prime\prime\prime} - 4(\rm OH)_{\rm O}^{\cdot}]^{\rm x}$$
(3)

Here, V represents a vacancy; the superscripts <sup>x</sup>, , and ' represent null, positive, and negative charges relative to the perfect structure, respectively; and the subscripts refer to Si and O crystallographic sites. We recognize that some mineralogists might object to using point defect symbolism to refer to both trace and high concentrations of elements, but we use it in the following discussion for the sake of convenience.

The  $(4H)_{s_i}^s$  mechanism is well established for H-rich garnets along the grossular-katoite join (for review see Beran and Libowitzky 2006; Grew et al. 2013; Geiger and Rossman 2020a), not only from chemistry but from NMR, X-ray diffraction (XRD), and neutron diffraction (Cohen-Addad et al. 1967; Lager et al. 1987, 1989; Cho and Rossman 1993). An analogous substitution of four F atoms substituting for O surrounding a vacant Si site is well documented for F-rich garnets, based on XRD (Smyth et al. 1990; Chakhmouradian et al. 2008) and negative correlations between Si and F concentrations (Flohr and Ross 1989; Visser 1993; Chakmouradian et al. 2008). This substitution can be written as:

$$[V_{\rm Si}^{\prime\prime\prime\prime\prime} - 4F_{\rm O}^{\,\prime}]^{\rm x}.$$
(4)

This substitution differs structurally from  $(4H)_{Si}^{s}$  in the sense that F atoms can occupy the regular site of O atoms, whereas the H atoms in  $(4H)_{Si}^{s}$  are bonded to O that is displaced from its normal position because of the expansion of the tetrahedron (e.g., Lager et al. 1989).

Other substitution mechanisms for H and particularly for F in garnet have received somewhat less attention. Valley et al. (1983) considered the possibility, in addition to mechanisms 3 and 4, of F and H incorporation in grossular via the coupled substitution:

$$(Al,Fe)^{3+} + O^{2-} \leftrightarrow (Mg,Fe)^{2+} + (F,OH)^{-}$$
(5)

where the cations are located in the six-coordinated Y site. They recognized that verification of this substitution relies on accurate determination of Fe<sup>2+</sup>/Fe<sup>3+</sup> as well as H and F content, beyond the scope of their study. Various mechanisms involving coupled substitution of Ti and H have also been considered, primarily for pyrope (Bell and Rossman 1992; Khomenko et al. 1994; Geiger et al. 2000) but also for grossular (Reynes et al. 2020). Partial substitution of H for the Y-cation in a hydrogrossular was inferred by Kalinichenko et al. (1987), based on NMR, and at least two studies have inferred substitutions other than (4H)x in H-rich garnets based on crystal-chemical arguments (Birkett and Trzcienski 1984; Basso and Cabella 1990). In principle OHor F- can replace O in the dodecahedral X-site in garnet if it is vacant or contains a monovalent cation (e.g., Andrut et al. 2002). For instance, a Ca vacancy in grossular can be compensated by two H, which we notate as (2H)<sup>x</sup><sub>Ca</sub>. A similar substitution for the Y cation can be notated as  $(3H)_{Al}^x$  or  $(3H)_{Fe}^x$ , depending on the garnet composition.

Early on in the study of nominally anhydrous minerals it was recognized that the mid-IR spectra of some garnets are incompatible with the (4H)<sup>x</sup><sub>si</sub> mechanism, because too many peaks are present (Aines and Rossman 1984). The (4H)<sub>si</sub> substitution sensu stricto (cf. Geiger and Rossman 2020a; see below) can result in a maximum of four O-H stretching vibrations, or two if the symmetry of the garnet is maintained (Harmon et al. 1982; Aines and Rossman 1984). The IR spectra of many pyrope, almandine, and andradite garnets are dominated by a broad, asymmetric band that splits into two bands at low temperature (cooled by liquid  $N_2$ ), thus consistent with  $(4H)_{S_i}^x$  (Geiger et al. 1991; Geiger and Rossman 2018). Differences in band positions as a function of composition can be explained by the presence of different neighboring X and Y cations, and the broad width of the bands can be explained by a combination of proton disorder and variations in local cation configuration. On this basis, Geiger and Rossman (2018) assigned bands at 3629, 3613, 3598, and 3563 cm<sup>-1</sup> in pyrope, almandine, grossular, and andradite, respectively to (4H)<sup>x</sup><sub>si</sub>. However, in grossular, as well as many spessartine garnets (Aines and Rossman 1984; Arredondo et al. 2001) and some rare pyrope garnets from the Dora Maira massif (Rossman et al. 1989), the multitude of sharp peaks cannot be explained by this mechanism alone.

Additional constraints on H incorporation in grossular and garnets on the grossular-andradite join come from experimental studies of H diffusion (Kurka et al. 2005; Phichaikamjornwut et al. 2012; Reynes et al. 2018). All of these studies support the idea that there are multiple sites for O-H incorporation, because various O-H bands decrease at different rates during dehydration. In general, dehydration kinetics for bands at higher frequency have a lower activation energy  $(E_a)$  than those at low frequency. For instance, Reynes et al. (2018) measured  $E_a$  for a grossular-rich garnet in the range between 157 and 185 kJ/mol for bands at 3628, 3645, 3657, and 3686 cm<sup>-1</sup>, and in the range between 216 and 275 kJ/mol for bands at 3533, 3576, and 3604 cm<sup>-1</sup>. A positive dependence of the diffusion coefficient on  $f_{0_2}$  as well as observations of color changes in sample rims in the experiments by Reynes et al. also support a key role for Fe<sup>2+</sup> in dehydration. Reynes et al. identify a fast diffusion mechanism, analogous to that identified in many other nominally anhydrous minerals (Ingrin and Blanchard 2006), that is limited by the availability of Fe2+:

$$M^{2+} + OH^{-} + \frac{1}{4}O_2 \rightarrow M^{3+} + O^{2-} + \frac{1}{2}H_2O$$
 (6)

where M represents either Fe or Mn, which may or may not be directly tied to a defect responsible for incorporating H. Our failed attempt to fully dehydrate GRR1122 (Online Materials<sup>1</sup> Fig. OM4) at low  $f_{02}$  (with virtually no change in spectra between dehydration steps 1 and 2) is consistent with this interpretation. We will return to this point when we discuss our model for coupled H-F substitution in the next section.

Another critical constraint on H incorporation in grossular comes from the study of Cho and Rossman (1993), who performed solid-state <sup>1</sup>H NMR measurements on a synthetic endmember katoite [Ca<sub>3</sub>Al<sub>2</sub>D<sub>3</sub>(OH)<sub>12</sub>] powder and single crystals of GRR1386 (Fig. 1a), GRR53 (Fig. 1c), and GRR1537 (Fig. 1c). From their analysis of multiple-quantum spectra, Cho and Rossman (1993) concluded that the protons in katoite occur in closely spaced groups of four, as expected for (4H)<sup>x</sup><sub>Si</sub>. However, the best fit to the multi-quantum spectrum of GRR1386 was for a cluster size of two protons, and the best fit to the data for GRR1537 was for two separate clusters consisting of two and four protons each. The class 4 IR spectrum of GRR1537 is dominated by a band at 3621 cm<sup>-1</sup> (Fig. 1c), which is the position of the main band in a synthetic hydrogrossular with composition Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>2,28</sub>(O<sub>4</sub>H<sub>4</sub>)<sub>0.72</sub> (Rossman and Aines 1991). Therefore, Cho and Rossman (1993) assigned this band to (4H)<sup>x</sup><sub>Si</sub> and other, less intense bands to a different, unspecified defect containing two closely spaced protons.

Geiger and Rossman (2020a, 2020b) offered a novel explanation for the sharp, high-frequency bands in natural grossular. They hypothesized that bands at 3599, 3612, 3622, 3634, and 3641 cm<sup>-1</sup> correspond to clustered groups of  $(4H)^{x}_{Si}$  with cluster sizes of one, two, three, four, and five, respectively. A band at 3657 cm<sup>-1</sup> was tentatively assigned to a cluster size of six, and a band at 3660 cm<sup>-1</sup> was assigned to a "finite-size katoite cluster" based on the fact that the main absorption in pure katoite (GRR1059; mislabeled as "Si 2.28" in Fig. 7 of Geiger and Rossman 2020a) occurs at this frequency (Rossman and Aines 1991). Bands at 3674 and 3688 cm<sup>-1</sup> were attributed to inclusions of hydrous minerals. This model explains all the features in IR spectra of class 2, 3, and 4 grossular and all absorptions above  $\sim$ 3600 cm<sup>-1</sup> in class 2b.

It is well known from studies of hydrous minerals that the strengths of O-H bonds (and thus their vibrational frequencies) are affected by different cations sharing bonds with the same O atom (i.e., second nearest neighbors to the H atom). For example, the frequencies of O-H bonds in amphibole, which vary by up to ~50 cm<sup>-1</sup>, can be assigned reliably to different cation environments (e.g., Burns and Strens 1966). Recent work has also explored the effects of neighboring cations on O-H stretching frequencies in olivine (Blanchard et al. 2017). The cluster model of Geiger and Rossman (2020a, 2020b), however, relies on an assumption that comparable shifts in O-H bond frequencies are influenced by bonds in other (4H)x that are not directly adjacent because the tetrahedra in garnet are isolated from each other. Geiger and Rossman justify this assumption as a consequence of the increase in Ca-O bond lengths between the end-members grossular (Geiger and Armbruster 1997) and katoite (Lager et al. 1987). It remains to be shown by first-principles modeling or other methods whether or not this relaxation in Ca-O distances for the end-members also operates on a localized scale within small, isolated clusters of (4H)<sup>x</sup><sub>si</sub> in garnets with trace amounts of H. It should also be noted that the model of Geiger and Rossman ignores the results of Cho and Rossman (1993) that indicate some grossular garnets contain a significant fraction of defects with only two protons. Furthermore, the assignment of bands at 3674 and 3688 cm<sup>-1</sup> to inclusions of hydrous phases is problematic because of geological and spectroscopic reasons that we elaborate in the Online Materials<sup>1</sup>. In the following sections, we offer alternative explanations for some of the absorption bands that call on coupled H and F substitution for Si as well as substitution of H (and possibly F) for cations in octahedral and/or dodecahedral sites.

#### Coupled substitution of H and F

Our first clue that incorporation mechanisms of H and F in grossular might be entangled came from correlations between <sup>16</sup>OH and <sup>19</sup>F in grossular (Fig. 6a) and spessartine (Fig. 6b), prompting us to consider coupled substitution of H and F for Si (or other cations). While it is possible that these correlations are coincidental and reflect nothing about coupled H-F substitution, interpretation of the IR spectra combined with quantitative data on H and F concentrations (Table 4) suggests otherwise.

Consider first the comparison between GRR42 and GRR1386: these crystals have the same F content (0.25 wt%), but GRR1386 has nearly twice as much H<sub>2</sub>O (0.13 wt%) as GRR42 (0.07 wt%; based on SIMS). The other obvious difference (Fig. 1a) is that both garnets have significant absorbance at lower frequencies. This suggests that some of the high-frequency bands are related to defects containing both H and F unless all F is bound in anhydrous defects (e.g., via Eq. 4). We draw a similar conclusion from the comparison between GRR732 and GRR1122 in Figure 1b: these garnets have nearly the same H<sub>2</sub>O content (0.052–0.054 wt%), but GRR732 has almost twice as much F (0.11 wt%) as GRR1122 (0.06 wt%) and has stronger

absorbance above  $\sim$ 3620 cm<sup>-1</sup>, whereas GRR1122 has stronger absorbance at lower frequencies. Furthermore, the strongest correlation between <sup>16</sup>OH and <sup>19</sup>F is evident in JLM83a, which has virtually no absorbance at frequencies lower than  $\sim$ 3600 cm<sup>-1</sup> (Fig. 1c)—again suggesting that the higher-frequency O-H bands are related to F incorporation. An attempt to quantify these general observations is summarized in Figure 8, where we plot F (per formula unit; Table 4) against the band areas derived by spectral curve fitting for nine out of ten of the grossular garnets in the study (JLM83a is excluded from this analysis because it is difficult to compare any given spectrum to a precise F content in this zoned garnet).

Motivated partly by these observations and partly by the experiments and first-principles density functional theory (DFT) calculations of Crépisson et al. (2014) on forsterite, we propose that some of the bands at frequencies >3600 cm<sup>-1</sup> represent coupled H-F substitution for Si. Following Cho and Rossman (1993) and Withers et al. (1998), we start with the assumption that the band at 3621 cm<sup>-1</sup>, with a shoulder at ~3610 cm<sup>-1</sup>, represents (4H)<sub>Si</sub>. The asymmetry of the stretching vibration in this region is consistent with the band structure in other garnet compositions previously assigned to (4H)<sub>Si</sub> (Geiger and Rossman 2018), although the bands in grossular are narrower. Some or all of the bands at higher frequencies are then assigned to defect associates involving both OH<sup>-</sup> and F<sup>-</sup>:

$$[V_{\rm Si}^{\prime\prime\prime\prime\prime} - (\rm OH)_{\rm O}^{\cdot} - 3F_{\rm O}^{\cdot}]^{\rm x}$$
<sup>(7)</sup>

$$[V_{\rm si}^{\prime\prime\prime\prime} - 2(\rm OH)_{\rm o}^{\rm o} - 2F_{\rm o}^{\rm o}]^{\rm x}$$
(8)

$$[V_{\rm Si}^{\prime\prime\prime\prime} - 3(\rm OH)_{\rm O}^{\cdot} - F_{\rm O}^{\cdot}]^{\rm x}$$
<sup>(9)</sup>

Calculations made by Crépisson et al. (2014) indicate that some of these clumped OH-F defects in forsterite lead to O-H vibrations at higher frequencies than those assigned by previous studies to the (4H)<sup>x</sup><sub>Si</sub> defect. For instance, the single O-H stretching vibration corresponding to defect (7) is at 3674 cm<sup>-1</sup>, as opposed to the four O-H vibrations predicted for the most stable (4H)<sup>x</sup><sub>si</sub> configurations, which are between ~3400 and 3625 cm<sup>-1</sup> (Balan et al. 2011; Umemoto et al. 2011). In general, the frequencies of bands assigned to the various clumped OH-F defects decrease as the number of F atoms decreases, but complexities arise because of the three non-equivalent crystallographic sites for O in the olivine structure. A positive frequency shift is also predicted for a clumped OH-F defect in an octahedral site, compared to a fully protonated vacancy. The positive O-H frequency shifts for sites where F- replaces O<sup>2-</sup> are presumably a consequence of the influence of F- (which is more electronegative than O<sup>2-</sup>) on the geometry of the polyhedron (Crépisson et al. 2014). The theoretically derived frequencies of the clumped OH-F defects represented by Equations 7-9 are consistent with IR spectra of natural olivines known to contain relatively high-F concentrations (Sykes et al. 1994; Libowitzky and Beran 1995; Mosenfelder et al. 2011), which have bands at 3670, 3637, and 3620 cm<sup>-1</sup> that are not present in olivines with lower F contents.

Precise assignment of individual high-frequency bands in grossular to defects represented by Equations 7–9 is difficult. We tentatively assign the band at 3687–3688 cm<sup>-1</sup> to Equation 7 by analogy to the corresponding defect in olivine. This attribution helps to reconcile the H diffusion behavior observed by Kurka

et al. (2005), who found that this band and the band at 3600 cm<sup>-1</sup> decrease more rapidly than bands at 3645 and 3568 cm<sup>-1</sup>. Specifically, H diffusion of the defect associated with Equation 7 can take place rapidly via the reaction:

$$[V_{Si''}^{''''} - (OH)_{O}^{\circ} - 3F_{O}^{\circ}]^{x} + Fe_{Ca}^{x} + \frac{1}{4}O_{2} = (V_{Si''}^{''''} - O_{O}^{x} - 3F_{O}^{\circ})' + Fe_{Ca}^{\circ} + \frac{1}{2}H_{2}O.$$
(10)

This reaction is similar to the generalized redox reaction represented by Equation 6 but is defect-specific. In this case, F diffusion—which is inherently slower than H diffusion—is not needed to maintain charge balance because dehydration involves oxidation of Fe<sup>2+</sup> in the dodecahedral site. Many studies have found that oxidation reactions of this type are faster than reactions that require counter-diffusion of cations to maintain charge balance (Ingrin and Blanchard 2006), and Reynes et al. (2018) provide direct evidence from color changes in dehydrated crystals and experiments at variable  $f_{02}$  that oxidation of Fe<sup>2+</sup> plays a key role in dehydration of grossular.

The effect of dilute F substitution on local symmetry of the grossular structure is unknown, so it is not straightforward to use group theory to predict how many bands should be present for defects containing more than one O-H bond (Eqs. 8 and 9). Significant proportions of cations other than Ca and Al in neighboring X and Y sites, such as V or Fe (present in some of the grossular garnets in this study; Table 4), could also shift the frequencies of the O-H bands because these frequencies largely depend on the masses, ionic radii, and electronic states of the neighboring cations (Burns and Strens 1966; Berry et al. 2007; Geiger and Rossman 2018, 2020a). This effect is likely to be minor but may explain the small shifts up to 3 cm<sup>-1</sup> for some peaks in our curve fits for different grossular spectra. The imperfect correlation of F to the integrated absorbance of the high-frequency bands (Fig. 8a) could be related to the additional presence of F in sites with no OH (e.g., Eq. 4), vagaries of the fitting exercise, or perhaps other mechanisms completely unrelated to F-such as the cluster model of Geiger and Rossman (2020a,b) or coupled substitution of H and Ti (Reynes et al. 2020), which we discuss below. Therefore, more work, including ab initio calculations, is needed to verify our hypothesis that clumped OH-F defects are present in grossular. One attractive feature of our model is that the presence of a significant proportion of defect 8 could partially explain the finding of Cho and Rossman (1993) that H is predominantly present in clusters of two closely spaced protons in GRR1386, and by extension to other class 2b grossular garnets.

#### Low-frequency O-H absorption bands

No study has yet offered a satisfactory explanation for all the bands below ~3600 cm<sup>-1</sup> in class 2a and 7 grossular (some of the bands are also present in class 5 and 6 grossular; Rossman and Aines 1991). Geiger and Rossman (2020a) assigned the band at 3563 cm<sup>-1</sup> to a localized "hydroandradite group" consisting of a single  $(4H)_{s_i}^x$  adjacent to Fe<sup>3+</sup> in the octahedral site, based on comparison to the most intense O-H band frequency in andradite IR spectra (Amthauer and Rossman 1998; Geiger and Rossman 2018). Furthermore, they speculated that their model for hydrogrossular clusters could be extended to assign other bands at 3581 and 3594 cm<sup>-1</sup> to different-sized hydroandradite clusters. This hypothesis is difficult to assess because the total Fe content in many grossular garnets is too low to accurately determine Fe2+/Fe3+ using established methods. Our cation assignments (Table 4) based on stoichiometry using the calculation scheme of Locock (2008) indicate that all of the Fe is Fe<sup>2+</sup> for our garnets with 0.06 to 1.8 wt% FeO, but this method for calculating Fe2+/Fe3+ suffers from considerable uncertainty, and Fe<sup>3+</sup> may also be present.

The role of Ti in H incorporation in grossular and andradite was recently studied by Reynes et al. (2020). They proposed coupled substitution of Ti on the Y site and 2H for Si, as follows:

$$[V_{\rm Si}^{\prime\prime\prime\prime} - 2(\rm OH)_{\rm O}^{\cdot}]^{\prime\prime} + 2T\dot{i}_{\rm Al,Fe}^{\cdot}$$
(11)

FTIR spectra of the grossular studied by Reynes et al. are unusual compared to most grossular garnets surveyed by Rossman and Aines (1991), containing only three bands at 3546, 3595, and 3652 cm<sup>-1</sup>; the closest match is to GRR1359, a grossular from a metarodingite in the Gruppo di Voltri, Italy (probably from a similar geologic setting as the rodingite grossular



**FIGURE 8.** Results of spectral curve fitting plotted as function of calculated F (per formula unit). Frequencies of fitted bands vary by up to  $3 \text{ cm}^{-1}$ . Symbols (see inset legend in **a**) correspond to those in Figure 7. (**a**) Integrated absorbance vs. F for fitted bands centered at ~3631, 3643, 3647, 3657, 3664, 3674, and 3688 cm<sup>-1</sup>. (**b**) Integrated absorbance vs. F for fitted bands centered at ~3530, 3539, 3545, 3560, 3567, 3582, 3600, 3608, and 3622 cm<sup>-1</sup>. (Color online.)

studied by Reynes et al.). Bands at similar frequencies are also present in spectra of the class 2b grossular samples in this study, centered at 3546, 3599, and 3657 cm<sup>-1</sup> in GRR1386. Therefore, this mechanism may also be important in these garnets, which contain between 0.3 to 0.6 wt% TiO<sub>2</sub> (Table 4). The presence of a band at 3652–3657 cm<sup>-1</sup> related to defect 11 could also partially explain the imperfect correlation of F content to high-frequency absorption in Figure 8a.

Another possibility is that some of the low-frequency bands represent H substitution in dodecahedral and/or octahedral sites via defects such as  $(2H)_{Ca}^{x}$  or  $(3H)_{Al}^{x}$ , respectively. This attribution could further help to explain the identification of two-proton clusters in GRR1386 by Cho and Rossman (1993), if a large fraction of the H is located in the defects 8, 11, and  $(2H)_{Ca}^{x}$  combined. Substitution of H via defects such as (2H)<sup>x</sup><sub>Ca</sub> would also be consistent with the higher  $E_{\rm a}$  measured for lower frequency O-H bands by Reynes et al. (2018) if dehydration requires counter-diffusion of Ca to take place (as opposed to dehydration via a fast-redox mechanism). Although this hypothesis is highly speculative, DFT calculations for nominally anhydrous minerals to date indicate that the (4H)x defect gives rise to O-H absorptions at higher frequencies than substitutions involving octahedral cation vacancies. This phenomenon applies to olivine (Balan et al. 2011; Umemoto et al. 2011), enstatite (Balan et al. 2013), wadsleyite (Blanchard et al. 2013), and ringwoodite (Blanchard et al. 2009).

In principle, clumped OH-F defects in octahedral or dodecahedral sites are also possible, as are coupled substitution mechanisms like those put forth by Valley et al. (1983) (Eq. 5). The intensity of the low-frequency bands in East African grossular also correlates positively with F content (Fig. 8b). By analogy to our argument with the high-frequency bands, this might suggest a role for such defects in addition to clumped OH-F in tetrahedral sites. One weakness with this idea is that the presence of isolated, clumped OH-F defects in octahedral or dodecahedral sites would require the presence of Si-F bonds, because all O sites in the garnet structure are shared between the tetrahedral site, two dodecahedral sites, and the octahedral site. As noted by Smyth et al. (1990), there are no known mineral structures in which F bonds directly to tetrahedral Si. However, some NMR studies provide evidence for Si-F bonding in aluminosilicate glasses (e.g., Zeng and Stebbins 2000; Liu and Nekvasil 2002). It is probably more likely that any defect associate involving clumped OH-F in an octahedral or dodecahedral site would be paired with a neighboring defect associate in the tetrahedral site (e.g., three H and one F substituting for Si).

### Coupled H and F substitution in other garnet compositions

Our model of coupled H and F substitution for Si in grossular likely applies to garnets with other compositions. Data from our 2012 session show strong correlations between <sup>16</sup>OH and <sup>19</sup>F in 11 spessartine garnets (Fig. 6b), similar to the correlations seen for East African grossular (Fig. 6a). These spessartine garnets have peaks at ~3582, 3595, 3615, 3625, 3640, and 3649 cm<sup>-1</sup> (Arredondo et al. 2001). Bands at similar frequencies are also present in spectra of a spessartine with up to 3.8 wt% F studied by Smyth et al. (1990). Aines and Rossman (1984) recognized that these six peaks (which can be fit with even more bands) cannot

be explained by  $(4H)_{s_i}^s$  alone. It is tempting to assign the band at 3595 cm<sup>-1</sup> (with a shoulder at 3582 cm<sup>-1</sup>) to  $(4H)_{s_i}^s$ . The lower frequency compared to katoite or grossular can be explained by the high mass of  $Mn^{2+}$  (compared to  $Ca^{2+}$ ) in the X-site (Geiger and Rossman 2018). However, relative peak heights at 3582 and 3595 cm<sup>-1</sup> vary considerably in garnets from different parts of the pegmatite and in spessartine from the Himalayan Mine (Arredondo et al. 2001), which is not easily reconcilable with a single O-H site being responsible for both bands. Taken together, these observations suggest the possibility that some or all of the bands represent clumped OH-F defects analogous to those we propose for grossular.

The presence of high-frequency bands in some garnets along the grossular-andradite join (Phichaikamjornwut et al. 2012; Geiger and Rossman 2020a) was already noted. In the Online Materials1, we provide IR spectra of a Grs26Adr74 garnet (GRR1830) and a nearly end-member andradite (GRR2103) that we analyzed by SIMS in 2012. GRR1830 has at least eight bands, with peaks at 3560, 3580, 3589, 3617, 3640, 3653, 3660, and 3677 cm<sup>-1</sup>. The band locations are similar to those in the garnets from Thailand studied by Phichaikamjornwut et al. (2012). The spectrum of GRR2103 is dominated by a strong peak at 3563 cm<sup>-1</sup> (with a shoulder at about 3547 cm<sup>-1</sup>) and has only weak absorbance above 3600 cm<sup>-1</sup>. Published spectra of other garnets close to end-member andradite also typically do not have these bands (e.g., Amthauer and Rossman 1998; Geiger and Rossman 2018). However, Amthauer and Rossman (1998) noted spectral complexity in a near end-member andradite from Stanley Butte, Arizona, U.S.A. (GRR1137). Again, the number of bands in GRR1830 and the grossular-andradite garnets studied by Phichaikamjornwut et al. (2012) raises the possibility that some of them represent clumped OH-F defects. This inference is also consistent with SIMS data. Whereas GRR1830 yielded an average <sup>19</sup>F/<sup>18</sup>O ratio of 0.191, equivalent to 76 µg/g F, measurements during the same session on GRR2103 yielded 19F/18O ratios just barely above the detection limit (<1 µg/g F; Mosenfelder and Rossman 2013a).

Coupled H-F substitution is less likely to be important in pyrope, if only because it typically contains significantly lower concentrations of both elements compared to other garnet compositions. Mosenfelder and Rossman (2012) report 0.2 to 10  $\mu$ g/g F in pyrope garnets from mantle xenoliths that contain up to 135  $\mu$ g/g H<sub>2</sub>O (using the IR calibration of Bell et al. 1995). These xenoliths also contain other phases (olivine, orthopyroxene, and/or clinopyroxene) that can partition much of the available F (Mosenfelder et al. 2011; Mosenfelder and Rossman 2013a, 2013b). Nearly endmember pyrope from the Dora Maira massif represents an unusual case; its IR spectra are unlike those of other pyrope-almandine garnets, with sharp peaks at 3602, 3641, 3651, and 3662 cm<sup>-1</sup> (Rossman et al. 1989). As noted above, similar bands are present in a pyrope synthesized by Geiger et al. (1991).

On the one hand, Lu and Keppler (1997) attributed the bands in Dora Maira pyrope to O-H defects associated with Li and B substitution, based on Li<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> concentrations measured by inductively coupled plasma atomic emission spectroscopy. On the other hand, our attribution of high-frequency bands to clumped OH-F defects is particularly apropos in this case because some Dora Maira garnets contain inclusions of phlogopite with up to 1.6 wt% F as well as other F- and Cl-bearing phases, unequivocally indicating that they formed in a halogen-rich environment (Philippot et al. 1995). Furthermore, SIMS analyses of Dora Maira pyrope by Tenner et al. (2009)—while uncalibrated for F concentration—yielded a <sup>19</sup>F/<sup>30</sup>Si ratio of 0.215, approximately one order of magnitude higher than ratios measured in pyrope garnets from mantle xenoliths (0.008–0.025). A rough estimate of 30  $\mu$ g/g F can be derived by comparing to our SIMS data on pyrope (Mosenfelder and Rossman 2012), including MON9 from Bell et al. (1995), which was also measured by Tenner et al.

# IMPLICATIONS

This work highlights technical advances in analytical methods for F and H that could facilitate future studies using garnets to constrain the activities of  $H_2O$  and F-species in fluids in equilibrium with garnet-bearing phase assemblages. The present study—including our new calibration for the IR molar absorption coefficient in grossular—most directly applies to geologic problems in the Earth's crust. However, measurements of trace F and H in garnets from mantle xenoliths may also provide additional constraints on recycling of these elements into the mantle, already a topic of interest addressed by studies of F and H in olivines and pyroxenes.

Fine-scale zoning of H in garnets such as those from Asbestos or the garnets studied by Jamtveit and Hervig (1994) or Reynes et al. (2020) is probably best studied using micro-analytical techniques such as SIMS or FTIR conducted with a focal plane array (FPA) detector, which is becoming more widely available (the FPA detector has a higher spatial resolution than normal MCT detectors such as those we used; e.g., Reynes et al. 2020). We have also demonstrated that F can be measured reliably with EPMA at levels down to  $\sim$ 50 µg/g, and it should be possible to achieve higher analytical throughput at a lower cost with EPMA compared to SIMS. Furthermore, in principle, minimum estimates for F concentrations in garnet could be constrained from FTIR spectra alone once band assignments for coupled H-F defects are confirmed and controversy over incorporation mechanisms is settled. We expect that theoretical calculations will shed additional light on coupled H-F substitution in garnets and other nominally anhydrous minerals.

#### Acknowledgments

The manuscript was improved by helpful reviews from Andrew Locock, Jörg Hermann, and an anonymous reviewer. We also thank Yunbin Guan for assistance with SIMS analyses and John Beckett for help operating the gas-mixing 1 atm furnace. Campbell Bridges, Peter Flusser, Robert Gaal, Peter Keller, William Larson, Gary Novak, and Julius Petsch are thanked for providing garnet samples that were used in the work.

#### FUNDING

Financial support for this research is gratefully acknowledged from NSF grants EAR-0947956 and EAR-1322082 to George Rossman, EAR-1347908 to Jed Mosenfelder, NASA 80NSSC19K0959 to Marc Hirschmann, the Gordon and Betty Moore Foundation, and the White Rose Foundation.

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Manuscript received November 2, 2020 Manuscript accepted March 10, 2021 Manuscript handled by Anne Peslier

#### **Endnote:**

<sup>1</sup>Deposit item AM-22-47880, Online Materials. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2022/Apr2022\_data/Apr2022 data.html).