

Hydrous species in zircon

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ABSTRACT

A survey of hydrous species in zircon from a number of localities with a range of occurrences and structural states was carried out using infrared spectroscopy and electron microprobe analysis. Stepwise heating experiments on a crystalline and a nearly metamict zircon were also performed. The region of IR spectra of OH-bearing crystalline zircon from 4000 to 2500 cm^{-1} exhibits anisotropic OH bands resulting from at least three OH sites, one at vacant tetrahedra and two that may be at Si-occupied tetrahedra. One site associated with Si-occupied tetrahedra is the most important, producing IR absorption bands at $\sim 3420 \text{ cm}^{-1}$ ($E \parallel c$) and $\sim 3385 \text{ cm}^{-1}$ ($E \perp c$). OH may be introduced during crystal growth by a coupled substitution of the form $[M^{3+} + H^+] \leftrightarrow [Zr^{4+}]$. The sites at vacant tetrahedra account for considerably less OH, producing relatively weak IR absorption bands at $\sim 3510 \text{ cm}^{-1}$ ($E \parallel c > E \perp c$). OH may be introduced during crystal growth by the hydrogrossular substitution of the form $[4(\text{OH})^-] \leftrightarrow [(\text{SiO}_4)^{4-}]$. An additional OH band at $\sim 3270 \text{ cm}^{-1}$ appears to be associated with an occupied tetrahedron. Heating experiments produced two more OH environments and indicate that H can migrate among the sites at high temperatures. Some crystalline samples are entirely free of OH.

IR spectra of metamict zircon exhibit broad, asymmetric, isotropic OH bands similar to H_2O bands, but the absence of the H_2O bending-mode band indicates that OH is the dominant hydrous species present. IR spectra of partially metamict zircon samples retain some anisotropy. The breadth of their OH bands is a function of degree of metamictization.

The maximum OH observed in any metamict or partially metamict zircon sample was approximately 0.1 wt%, expressed as H_2O . Such OH is probably secondary. The maximum primary OH observed is ~ 0.05 wt% in partially metamict zircon from a hydrothermal vug. Crystalline crustal zircon contains more than an order of magnitude less OH. The maximum OH content observed in crystalline zircon, ~ 0.01 wt%, is in a mantle zircon sample from a kimberlite, suggesting high activity of H_2O in the mantle.

Additional OH is present in some metamict and partially metamict zircon samples in the form of inclusions of hydrous silicates such as kaolinite. Fluid inclusions containing H_2O occur in some samples. This may be a partial explanation of the high H_2O contents reported for some radiation-damaged zircon based on loss-on-heating measurements.

INTRODUCTION

Zircon is considered to be an anhydrous mineral, but a number of studies have reported the presence of a hydrous component in natural samples (Fron del, 1953; Fron del and Collette, 1957; Coleman and Erd, 1961; Mumpton and Roy, 1961; Krstanovic, 1964; Caruba et al., 1985; Woodhead et al., 1991). The hydrous species has been attributed to H_2O or OH (or a combination of the two) in amounts up to 16.6 wt%—just over 50 mol%

H_2O (Coleman and Erd, 1961). In every case, the zircon varieties with reported H_2O (such as cyrtolite, malacon, ribierite, and naegite) have been found to be metamict or nearly so. Zircon becomes metamict as a result of accumulated damage to the crystal structure caused by radioactive decay of U and Th, which substituted for Zr during initial crystallization. Such radiation damage expands the crystal lattice and decreases crystallinity, ultimately producing an amorphous glass that may be open to the infiltration of secondary hydrous species (Mumpton and Roy, 1961) into the disturbed structure or along cracks and grain boundaries. Hydrous species in cracks or at

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grain boundaries cannot be considered true hydrous components of zircon, although they may be difficult to avoid when measuring H₂O by weight loss on heating.

Ever since Holland and Gottfried's (1955) classic study of alluvial zircon from Sri Lanka, that suite has been considered prototypical of natural zircon with a wide range of crystallinities. In a detailed IR spectroscopic study of Sri Lanka zircon, Woodhead et al. (1991) found that the only detectable hydrous species is OH and that actual OH contents are quite low, approximately 0.03 wt% or less, expressed as H₂O. Zircon from Sri Lanka is thought to have formed in granulite pegmatites but has not been found in situ (Munasinghe and Dissanayake, 1981; Kröner et al., 1987). It is free of OH over the full range of structural states from crystalline to nearly metamict. OH does occur in metamict grains or zones, where it is uncorrelated with U content. Apparently, Sri Lanka zircon was initially anhydrous and took up OH only after becoming metamict. The amount of OH incorporated must depend on the conditions in the environment subsequent to metamictization and must be unrelated to H₂O present in the original crystallization environment.

Studies of synthetic zircon have demonstrated that OH can be incorporated into the structure of crystalline samples (Fron del and Collette, 1957) by the substitution $[4(\text{OH})^-] \leftrightarrow [(\text{SiO}_4)^{4-}]$. The resulting Si-deficient, hydroxylated zircon is analogous to hydrogrossular. Caruba et al. (1985) have reported samples with up to 81% of the $[(\text{SiO}_4)^{4-}]$ replaced by $[4(\text{OH})^-]$. Their IR spectra exhibit a characteristic OH-stretching band at 3515 cm⁻¹ that decreased in intensity upon heating in air. Because no crystalline OH-bearing zircon has been reported in nature and synthetic hydroxylated zircon is apparently less stable than anhydrous zircon, the relation between the speciation of OH in synthetic and natural zircon remains to be established.

Several recent studies have shown that OH is a common trace constituent in silicates normally considered anhydrous (Aines and Rossman, 1985; Rossman et al., 1989; Beran et al., 1989; Lager et al., 1989; Skogby and Rossman, 1989). Minerals such as quartz, feldspars, pyroxenes, sillimanite, and garnets exhibit sharp IR absorption bands characteristic of OH structurally incorporated at the time of growth. Some of these silicates exhibit several OH bands, indicative of multiple sites or orientations of OH. OH in pyroxenes (Skogby and Rossman, 1989) and H₂O in nepheline (Beran and Rossman, 1989) have been observed to change orientation in the course of heating experiments, indicating that the location of the hydrous species in some silicates is mutable. Rossman and Aines (1991) have found that the IR spectra of garnets with trace OH contents do not resemble those of hydrogrossular, suggesting that the speciation of trace OH in those garnets is not the same as in Si-deficient hydrogrossulars where the substitution $[4(\text{OH})^-] \leftrightarrow [(\text{SiO}_4)^{4-}]$ occurs at the tetrahedral sites. This raises the possibility that in zircon, whose structure is somewhat similar to garnet (Robinson et al., 1971), trace amounts of OH may

not follow the hydrogrossular substitution model even though such Si-deficient zircon can be produced in the laboratory.

We undertook a general survey of zircon to detect whether crystalline zircon can incorporate hydrous species and whether metamict ones can be anhydrous, as well as to determine the extent of OH incorporation, the variety of OH orientations and sites, the thermal stability of such sites, the relationship between synthetic hydroxylated zircon and natural zircon with a hydrous component, and the relationship between metamictization and hydrous species.

EXPERIMENTAL DETAILS

Natural zircon samples from several localities with a range of occurrences, parageneses, habits, colors, and structural states (Table 1) were studied by IR spectroscopy and analyzed by electron microprobe. Roughly half the samples were free of inclusions; two had inclusions in cracks that could be avoided by the IR beam; several others contained dusty, birefringent inclusions in numerous cracks or randomly distributed throughout; the Sonora zircon contained prismatic apatite(?) inclusions; and the Bedford "cyrtolite" was an intergrowth of zircon, quartz, and monazite. A pure ZrSiO₄ synthetic zircon (Chase and Osmer, 1966) was studied for comparison. Heating experiments were conducted on two samples, one crystalline and the other nearly metamict. Each sample was heated for 1 h periods at about 100 °C intervals in an open furnace. Following each stepwise annealing period, polarized IR spectra were obtained at room temperature.

A Nicolet 60SX FTIR spectrometer was used to obtain IR spectra of most zircon samples. Polarized absorption spectra in the range 9500–1850 cm⁻¹ were obtained on doubly polished, single-crystal zircon plates cut parallel to the c-axis. A Perkin-Elmer model 180 double-beam grating infrared spectrometer was used to obtain spectra in the range 4000–1400 cm⁻¹ for the metamict zircon heating experiment. The absorption bands observed for each sample between 4000 and 2500 cm⁻¹ are listed in Table 2.

A JEOL 733 electron microprobe was used for chemical analyses of the polished, single-crystal zircon plates. Proportions of 13 elements were determined. The standards used for the analyses were mineral samples or synthetic oxides—Al and Ca, anorthite; Si, Zr, and Hf, Pacoima Canyon pegmatite zircon; P, Durango fluorapatite; Ti, rutile; Mn, manganese olivine; Fe, fayalite; Y, synthetic Y₂O₃; Nb, synthetic NbO; Th, synthetic ThO₂; and U, synthetic UO₂. X-ray peaks for the minor and trace elements were chosen to avoid interference by those of the major elements as well as mutual overlaps. Backgrounds on each side of the measured peaks were chosen away from peaks of the other elements. The intensities of the K α lines of Al and Si, of the L α lines of Y and Zr, and of the M α line of Hf were measured using a TAP crystal. Intensities of the K α lines of P and Ca, of the L α

TABLE 1. Zircon sample descriptions

Sample	Locality/description	Occurrence/ paragenesis	Color	Inclusions	Structural state	Donor/source
274	Reinbolt Hills near Amery Ice Shelf, Antarctica (EG556)	granulite pegmatite	black		metamict	Ed Grew
339	Chantaburi, Thailand	alluvial	pale red	no inclusions	crystalline	Leon T. Silver
340	Ratnapura, Sri Lanka (Ceylon 6500)	alluvial (granulite peg)	black		metamict	Leon T. Silver
341	Chantaburi, Thailand, "RED"	alluvial	red	no inclusions	crystalline	Leon T. Silver
485	pure synthetic ZrSiO ₄ *	Li ₂ MoO ₄ -MoO ₃ flux grown	colorless	no inclusions	crystalline	Armond Chase
576	Bedford, Westchester, New York, U.S.A. (Harvard 100833)	"cyrtolite"	brown	xl intergrowth	metamict	Karl Francis
1218	Southeast Asia (CIT 10011)B		lt. blue	no inclusions	crystalline	
1222-1	Thailand (sample Siam M21-30) (unheated)		colorless	no inclusions	crystalline	Grieger's
1222-2	Thailand (sample Siam M21-30) (heated)		colorless	no inclusions	crystalline	Grieger's
1223	Strangway, Northern Territory, Australia (NMNH 117288)**		colorless	no inclusions	crystalline	U.S. Nat. Mus. Nat. Hist.
1224	Ampanobe, Flanarantsoa, Madagascar (brown)	coarse syenitic gneiss	brown	hi biref in cracks	partially metamict	Demethius Pohl
1225a	Ampanobe, Flanarantsoa, Madagascar (black)	coarse syenitic gneiss	black	no inclusions	partially metamict	Demethius Pohl
1225b	Ampanobe, Flanarantsoa, Madagascar (black)	coarse syenitic gneiss	clriss tip	no inclusions	partially metamict	Demethius Pohl
1226	Tanzania				crystalline	Peter Keller
1228-1	Poças de Caldas, Minas Gerais, Brazil (CIT 4095)†	hydrothermal vug	green	opq in cracks, avoided	partially metamict	Ed Swaboda
1228-2	Poças de Caldas, Minas Gerais, Brazil (CIT 4095)	hydrothermal vug	green	no inclusions	partially metamict	
1229	Kimberley, South Africa	kimberlite	colorless	no inclusions	crystalline	Warren Hamilton
1230	La Panchita, Mexico		violet	in cracks, avoidable	partially metamict	Leon T. Silver
1231	Golding Keene, Ontario, Canada (no. 108)	nepheline syenite peg	straw	no inclusions	partially metamict	Leon T. Silver
1232	Wilberforce, Ontario, Canada		pale brown	biref in cracks	partially metamict	Leon T. Silver
1233	Southeast Asia (CIT 10011)A		colorless	no inclusions	crystalline	
1238	Ratnapura, Sri Lanka (Ceylon gem 1-24)	alluvial (granulite peg)	green	no inclusions	metamict	Leon T. Silver
1465	Sigalani Village, Tambani area, Blantyre, Malawi	alluvial	tan-brown	numerous xl and fluid	metamict	Minerals Unlimited
1466	Fredericksberg, Norway	nepheline syenite peg	dark brown	numerous dusty opq	nearly metamict	purchased
1467-1	Henderson Co., North Carolina, U.S.A.	alluvial	tan	numerous cracks/incl	nearly metamict	purchased
1467-2	Henderson Co., North Carolina, U.S.A.	alluvial	tan	numerous cracks/incl	nearly metamict	purchased
1468-1	Sonora, Mexico (CIT 7570)		orange	prismatic inclusions	crystalline	
1468-2	Sonora, Mexico (CIT 7570)		light red	prismatic inclusions	crystalline	
1469	Uralla, New South Wales, Australia		brown	numerous dusty opq	nearly metamict	purchased
1472	Sieland, Norway (CIT 13217)	pegmatite	brown	hi biref in cracks	partially metamict	Anthony Jones
1473	Indiahoma, Oklahoma, U.S.A. (CIT 8506)		brown	numerous xl and dusty	nearly metamict	R.M. Wilke

* Chase and Osmer (1966).

** Özkan et al. (1974).

† Franco and Loewenstein (1948).

line of Nb, of the $M\alpha$ line of Th, and the $M\beta$ line of U were measured using a PET crystal. Intensities of the $K\alpha$ lines of Ti, Mn, and Fe were measured using a LiF crystal. Beam sizes of 20–30 μm were used to avoid damaging the more metamict samples. Probe data were reduced using the program CITZAF1, version 3.03, (Armstrong, 1988) employing the Phi(RhoZ) absorption correction of Armstrong (1982), the fluorescence correction of Reed (1965) as modified by Armstrong (1982), the Love and Scott atomic number correction, the Phi (0) equation, a

backscatter correction (Love et al., 1978), and mean ionization potentials of Berger and Seltzer. Analyses of each sample are listed in Table 3; structural formulas normalized to four O atoms are listed in Table 4.

RESULTS AND DISCUSSION

Spectroscopic features

The portion of the IR spectra from 4000 to 2500 cm^{-1} of the zircon samples studied is remarkably diverse.

TABLE 2. Infrared band intensities for zircon samples

Sample	Combination modes				OH-stretching modes								
	2750	3200	3100	32/31	3420		3385		: ⊥	Other OH-stretching bands observed			
	E _c	E _{⊥c}	E _{⊥c}	Ratio	E _c	posn.	E _{⊥c}	posn.	Ratio	band	posn.	band	posn.
274	0.000	0.000	0.000	—	2.990	3430	2.640	3450	1.13				
339	0.721	1.120	0.398	2.82	0.108	3419	0.036	3387	3.00	0.031	3328		
340	0.000	0.000	0.000	—	6.930	3498	6.930	3498	1.00				
341	0.669	2.925	1.836	1.59	0.866	3420	0.164	3384	5.27	0.036	3560		3350
486	0.767	0.000	0.000	—	0.000	—	0.000	—	—				
576	0.000	0.000	0.000	—	2.381	3424	2.560	3379	0.93	0.267	3618	0.124	3595
1218	0.810	3.408	5.070	0.67	0.001	3422	0.000	—	—				
1222-1	0.791	1.597	0.760	2.10	0.296	3417	0.095	3383	3.13				
1222-2	0.765	1.523	0.902	1.69	0.280	3417	0.088	3383	3.18				
1223	0.772	1.506	1.060	1.42	0.000	—	0.000	—	—	0.022	3325		
1224	0.366	0.000	0.000	—	2.356	3410	2.089	3377	1.13	1.722	3701	0.124	3664
1225a	0.000	0.000	0.000	—	6.906	3436	5.874	3386	1.18				
1255b	0.000	0.000	0.000	—	6.278	3430	5.112	3380	1.23				
1226	0.679	0.000	0.000	—	0.452	3390	0.050	3350	—	0.924	3280		
1228-1	0.357	0.000	0.000	—	12.143	3420	4.167	3385	2.91	0.167	3563	1.333	3510
1228-2	0.363	0.000	0.000	—	17.976	3418	8.690	3386	2.07	0.286	3563	0.690	3510
1229	0.741	0.424	0.200	2.12	2.012	3417	0.859	3384	2.34	0.099	3510		
1230	0.359	0.071	0.089	0.80	3.089	3395	0.893	3385	3.46	4.171	3275		
1231	0.159	0.000	0.000	—	3.723	3432	3.069	3370	1.21				
1232	0.409	0.000	0.000	—	0.727	3390	0.864	3290	0.84				
1233	0.818	1.353	0.776	—	0.000	—	0.000	—	—				
1238	0.000	0.000	0.000	—	1.080	—	1.080	—	1.00				
1465	0.000	0.000	0.000	—	21.188	3358	21.749	3334	0.97	0.573	3695	0.358	3621
1466	0.235	0.000	0.000	—	18.358	3402	15.299	3340	1.20	1.000	3697	0.418	3622
1467-1	0.146	0.000	0.000	—	9.281	3380	8.922	3325	1.04	2.748	3700	2.162	3625
1467-2	0.000	0.000	0.000	—	11.078	3480	10.240	3430	1.08	8.065	3696	4.922	3621
1468-1	0.620	7.843	8.690	0.90	0.161	3425	0.000	—	—	0.200	3890	0.132	3825
1468-2	0.761	2.404	4.247	0.57	0.101	3421	0.022	3384	4.50				
1469	0.058	0.000	0.000	—	20.424	3413	17.857	3340	1.14	0.246	3701		
1472	0.519	0.000	0.000	—	0.746	3420	0.269	3385	2.78	4.819	3539	2.922	3323
1473	0.000	0.000	0.000	—	11.839	3400	9.283	3350	1.28				

Spectra of metamict zircon (Fig. 1), crystalline zircon (Fig. 2), and partially metamict zircon (Fig. 3) show a wide range of OH-stretching features and a strong effect of radiation damage on their appearance. Woodhead et al. (1991) showed that the strength of the combination-mode triplet at $\sim 2750\text{ cm}^{-1}$ in the E_{⊥c} polarization is a measure of crystallinity in the Sri Lanka zircon suite. That band is weak or absent in the zircon spectra shown in Figure 1. These samples are thus metamict or nearly so. Their IR spectra are representative of those of all the highly radiation-damaged samples listed in Table 1. The isotropic, or nearly isotropic, bands with peaks between 3300 and 3500 cm^{-1} (Table 2) result from the stretching mode of OH. Although their broad, asymmetric shapes are reminiscent of bands resulting from unoriented H₂O in some other silicates, no structural H₂O has been detected. H₂O can be distinguished from OH on IR spectra by the presence of the H-O-H bending mode at $\sim 1600\text{ cm}^{-1}$ and the H-O-H combination mode at $\sim 5200\text{ cm}^{-1}$. The absence of those bands from the spectra of inclusion-free zircon indicates that H₂O is below detectability. In the inclusion-free samples with relatively strong OH-stretching mode bands, the OH overtone mode at $\sim 6665\text{ cm}^{-1}$ is readily seen, but the H-O-H combination mode at $\sim 5200\text{ cm}^{-1}$, which is equally intense in H₂O, is not present. This confirms that OH is the only hydrous species present in those samples.

The breadth of the OH-stretching band in the spectra

of metamict zircon is a result of the multitude of OH environments caused by the structural disorder brought about by radiation damage during the metamictization process. Several samples have a maximum intensity of the OH-stretching band of about three times that of Sri Lanka zircon 6500 (no. 340), the most OH-rich sample found in our previous study (Woodhead et al., 1991). Beer's law calculations suggest that the maximum OH content in our samples is about 0.1 wt% expressed as H₂O. These calculations are based on molar absorptivity data for the broad OH-stretching band in glass (Newman et al., 1986; $\epsilon = 100$) because no calibration of the relationship between IR band strength and OH content in zircon is yet available.

Some additional sharp OH-stretching bands that occur at ~ 3700 and $\sim 3625\text{ cm}^{-1}$ are quite strong in the IR spectra of a few zircon samples and are detectable in others (Table 2). Weaker bands at ~ 3660 and $\sim 3560\text{ cm}^{-1}$ associated with the other two sometimes also can be discerned. These bands are invariably isotropic, even in partially metamict samples with anisotropic OH-stretching bands at $\sim 3400\text{ cm}^{-1}$. They occur only in samples that contain numerous distributed dusty inclusions or numerous cracks filled with inclusions (Table 1). In a search of IR spectra of minerals, we found that the only matches for these bands are in the spectrum of kaolinite, which matched perfectly, or in the spectra of two other kaolinite-group minerals, halloysite and dickite, which matched

TABLE 2—Continued

OH-stretching modes					
Other OH-stretching bands observed					
band	posn.	band	posn.	band	posn.
0.036	3292				
0.476	3379	0.086	3310		
1.611	3624	0.058	3554		
20.476	3264				
18.952	3261				
0.108	3470	0.301	3229	0.500	3180

TABLE 4. Zircon formulas based on electron microprobe analyses

Sample	Formulas
274	Zr _{0.984} Hf _{0.032} Mn _{0.001} U _{0.004} Si _{0.996} P _{0.002} Al _{0.001} O ₄
339	Zr _{0.986} Hf _{0.013} Ti _{0.001} Fe _{0.001} Si _{1.000} O ₄
340	Zr _{0.935} Hf _{0.055} Y _{0.003} Th _{0.001} U _{0.006} Si _{0.991} P _{0.002} O ₄
341	Zr _{1.000} Hf _{0.020} Si _{0.980} O ₄
485	Zr _{0.998} Si _{1.001} O ₄
576a	Zr _{0.971} Hf _{0.024} Ca _{0.004} Mn _{0.001} Fe _{0.008} Y _{0.003} Th _{0.001} U _{0.003} Si _{0.990} P _{0.003} O ₄
1218	Zr _{1.008} Hf _{0.011} Si _{0.981} O ₄
1222-1	Zr _{0.991} Hf _{0.012} Ca _{0.001} Si _{0.998} O ₄
1222-2	Zr _{0.990} Hf _{0.011} Ca _{0.001} Si _{0.998} O ₄
1223	Zr _{0.989} Hf _{0.020} Si _{0.990} O ₄
1224	Zr _{0.986} Hf _{0.016} Si _{0.987} O ₄
1225a	Zr _{0.979} Hf _{0.021} Ti _{0.001} Mn _{0.001} Si _{0.997} O ₄
1225b	Zr _{0.978} Hf _{0.021} Ti _{0.001} Si _{0.997} O ₄
1228-1	Zr _{0.982} Hf _{0.009} Ca _{0.002} Mn _{0.002} Fe _{0.004} Si _{1.004} O ₄
1228-2	Zr _{0.994} Hf _{0.010} Ca _{0.003} Mn _{0.003} Fe _{0.002} Si _{0.992} O ₄
1229	Zr _{0.985} Hf _{0.016} Si _{0.999} O ₄
1230	Zr _{0.991} Hf _{0.011} Ti _{0.001} Si _{0.997} O ₄
1231	Zr _{0.983} Hf _{0.008} U _{0.001} Si _{0.997} O ₄
1232	Zr _{0.990} Hf _{0.011} Si _{0.999} O ₄
1233	Zr _{0.998} Hf _{0.011} Ti _{0.001} Si _{0.990} O ₄
1238	Zr _{0.936} Hf _{0.058} U _{0.008} Si _{0.983} O ₄
1465	Zr _{0.987} Hf _{0.013} Fe _{0.001} Y _{0.002} U _{0.001} Si _{0.995} Al _{0.003} O ₄
1466a	Zr _{0.978} Hf _{0.018} Fe _{0.005} Y _{0.003} Th _{0.003} U _{0.002} Si _{0.994} Al _{0.001} O ₄
1466b*	Th _{0.805} U _{0.056} Zr _{0.042} Ca _{0.003} Ti _{0.002} Fe _{0.014} Y _{0.024} Si _{0.992} Al _{0.098} O ₄
1467-1	Zr _{0.982} Hf _{0.014} Y _{0.001} Th _{0.002} U _{0.001} Si _{1.001} O ₄
1468-1	Zr _{0.984} Hf _{0.010} Fe _{0.001} Y _{0.007} U _{0.001} Si _{0.998} O ₄
1468-2	Zr _{0.988} Hf _{0.010} Y _{0.002} U _{0.001} Si _{0.999} O ₄
1469	Zr _{0.974} Hf _{0.011} Ca _{0.001} Ti _{0.001} Fe _{0.001} Y _{0.004} Th _{0.003} U _{0.001} Si _{1.005} Al _{0.002} O ₄
1472	Zr _{0.990} Hf _{0.010} Si _{0.999} Al _{0.001} O ₄
1473	Zr _{0.986} Hf _{0.030} Y _{0.005} U _{0.001} Si _{0.990} P _{0.006} O ₄

* Thorite inclusion in zircon from Fredericksberg, Norway.

TABLE 3. Electron microprobe analyses of zircon samples

Sample	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	MnO	FeO	P ₂ O ₅	ZrO ₂	Y ₂ O ₃	HfO ₂	ThO ₂	UO ₂	Total*
274	0.03(3)**	32.47(6)	—†	—	0.03(2)	—	0.08(1)	64.46(13)	—	3.64(3)	—	0.52(5)	101.25
339	—	32.76(7)	—	0.05(2)	—	0.03(1)	—	66.24(13)	—	1.44(2)	—	—	100.56
340	—	31.68(6)	—	—	—	—	0.07(1)	61.36(13)	0.21(1)	6.12(4)	0.09(3)	0.83(5)	100.98
341	—	31.19(6)	—	—	—	—	—	65.25(13)	—	2.23(3)	0.06(3)	—	98.76
485	—	32.64(7)	—	—	—	—	—	66.74(13)	—	—	—	—	99.41
576a	—	31.46(6)	0.12(1)	—	0.05(2)	0.23(1)	0.09(1)	63.22(13)	0.19(1)	2.64(3)	0.15(3)	0.42(5)	98.57
1218	—	31.08(6)	—	—	—	—	—	65.50(13)	—	1.19(2)	—	—	97.80
1222-1	—	32.53(6)	0.02(1)	—	—	—	—	66.33(13)	—	1.40(2)	—	—	100.32
1222-2	—	32.43(7)	0.02(1)	—	—	—	—	65.97(13)	—	1.24(2)	—	—	99.68
1223	—	31.84(6)	—	—	—	0.02(1)	—	65.22(13)	—	2.29(3)	—	—	99.39
1224	—	32.69(7)	0.01(1)	—	—	—	—	66.34(13)	—	1.85(3)	0.05(3)	—	100.98
1225a	—	32.20(6)	—	0.04(2)	0.03(2)	—	—	64.96(13)	—	2.39(3)	—	0.35(5)	99.96
1225b	—	32.27(6)	—	0.04(3)	—	—	—	64.88(13)	—	2.41(3)	—	0.40(5)	100.03
1228-1	—	32.57(7)	0.05(1)	—	0.09(1)	0.16(3)	—	65.33(13)	—	1.02(2)	—	0.05(4)	99.30
1228-2	—	31.99(6)	0.09(1)	—	0.13(2)	0.06(1)	—	65.73(13)	—	1.12(2)	—	—	99.17
1229	—	32.50(7)	—	—	—	—	—	65.72(13)	—	1.81(3)	—	—	100.05
1230	—	32.57(7)	—	0.04(2)	—	—	—	66.36(13)	—	1.26(2)	—	—	100.29
1231	—	32.28(6)	—	—	—	—	—	65.91(13)	—	0.92(2)	—	0.14(4)	99.28
1232	—	32.35(6)	—	—	—	—	—	65.71(13)	—	1.21(2)	—	—	99.29
1233	—	31.89(6)	—	0.06(2)	—	—	—	65.93(13)	—	1.19(2)	—	—	99.08
1238	—	31.17(6)	—	—	—	0.04(1)	—	60.87(13)	—	6.50(4)	0.03(3)	0.81(5)	100.82
1465	0.07(1)	31.89(6)	—	—	—	0.02(1)	—	64.85(13)	0.12(1)	1.46(2)	—	0.10(4)	98.57
1466a	0.04(1)	31.96(6)	—	—	—	0.18(1)	—	64.44(13)	0.19(1)	1.99(3)	0.38(4)	0.25(4)	99.43
1466b‡	1.40(1)	10.22(4)	0.15(1)	0.05(3)	—	0.29(2)	6.51(5)	1.50(03)	0.77(2)	—	61.01(24)	4.37(9)	86.30
1467-1	—	32.04(6)	0.01(1)	—	—	0.01(1)	—	64.42(13)	0.04(1)	1.55(2)	0.22(3)	0.10(4)	98.39
1468-1	—	32.16(6)	—	—	—	0.05(1)	—	65.07(13)	0.43(2)	1.14(2)	0.04(3)	0.09(4)	99.01
1468-2	—	32.35(6)	—	—	—	0.02(1)	—	65.62(13)	0.13(1)	1.18(2)	—	—	99.44
1469	0.06(1)	32.49(6)	0.03(1)	0.04(2)	—	0.03(1)	—	64.60(13)	0.24(1)	1.24(2)	0.38(4)	0.10(4)	99.22
1472	0.03(1)	32.59(7)	—	—	—	—	—	66.22(13)	—	1.09(2)	—	—	99.93
1473	—	31.86(6)	—	—	—	0.02(1)	0.24(2)	63.75(13)	0.29(1)	3.37(3)	—	0.21(4)	99.73

* Nb analyzed for in all samples, but not present.

** Units in parentheses represent one standard deviation counting error on least units cited.

† Dash: not detected or counting statistics error >75%.

‡ Thorite inclusion in zircon from Fredericksberg, Norway.

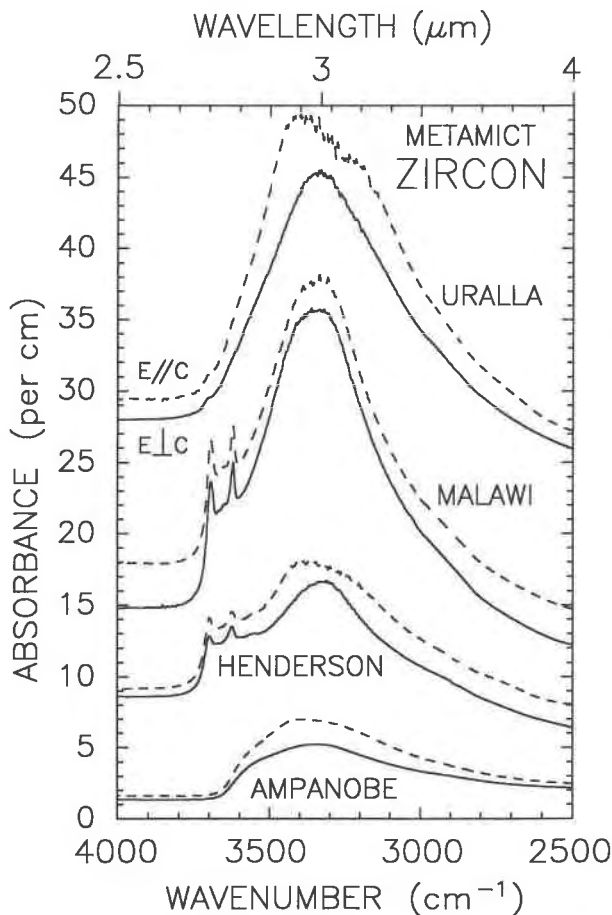


Fig. 1. Polarized infrared spectra of four samples of metamict zircon: Uralla, New South Wales, Australia (no. 1469); Sigwani Village, Malawi (no. 1465); Henderson, North Carolina (no. 1467); and Ampanobe (black), Madagascar (no. 1225). In this and the following figures spectra have been vertically offset for clarity.

less well. The sharp bands in the 3550–3700 cm^{-1} range thus are not related to hydrous species directly incorporated into the zircon structure.

The Uralla and Malawi samples both contain numerous fluid inclusions. The presence of the H-O-H bending-mode overtone at 5185 cm^{-1} in their IR spectra confirms that H_2O is present in the fluid inclusions. The combination of H_2O in fluid inclusions and OH in kaolinite inclusions probably accounts for at least two-thirds of the OH present in these two samples. Thus, even the estimate of 0.1 wt% is probably too high by a factor of 3.

The IR spectra of crystalline zircon (Fig. 2) bear little resemblance to those of metamict zircon. In the representative spectra shown, the combination-mode band at $\sim 2750 \text{ cm}^{-1}$ ($\text{E} \parallel \text{c}$) has an intensity of at least 0.6 per cm, indicating a lack of radiation damage. Other bands in the spectra at $\sim 3510 \text{ cm}^{-1}$ ($\text{E} \parallel \text{c} > \text{E} \perp \text{c}$), $\sim 3420 \text{ cm}^{-1}$ ($\text{E} \parallel \text{c}$), $\sim 3385 \text{ cm}^{-1}$ ($\text{E} \perp \text{c}$), $\sim 3200 \text{ cm}^{-1}$ ($\text{E} \perp \text{c}$), $\sim 3180 \text{ cm}^{-1}$ ($\text{E} \perp \text{c}$), and $\sim 3100 \text{ cm}^{-1}$ ($\text{E} \perp \text{c}$) exhibit considerable vari-

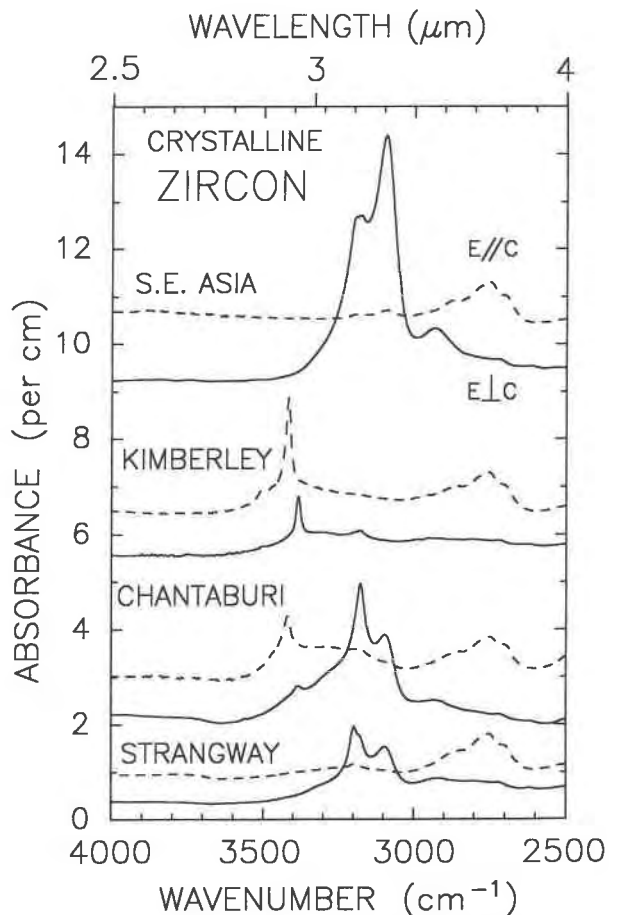


Fig. 2. Polarized infrared spectra of four samples of crystalline zircon: southeast Asia (no. 1218); Kimberley (no. 1229); Chantaburi, Thailand (no. 341); and Strangway, Northern Territory, Australia (no. 1223).

ability. The pair of sharp bands at $\sim 3420 \text{ cm}^{-1}$ ($\text{E} \parallel \text{c}$) and $\sim 3385 \text{ cm}^{-1}$ ($\text{E} \perp \text{c}$) are OH bands resulting from trace amounts of oriented OH. They indicate the presence of a hydrous component in several of the natural crystalline zircon samples. Their absence in the spectra of other samples shows them to be anhydrous.

The Kimberley zircon exhibits the strongest OH-stretching mode band of any crystalline zircon studied. Because the Beer's law calculation used above for the metamict samples cannot be applied to the sharp bands in crystalline zircon spectra, another means of estimating OH content is needed. Robinson et al. (1971) showed that the crystal structure of zircon is similar to that of garnet in many ways. Rossman and Aines (1991) calibrated IR spectra and OH content in grossular. Using their integrated absorbance calibration factor (3746 per mol/L OH per cm) as an approximation for crystalline zircon yields an OH content of 0.007 wt%, expressed as H_2O .

The weak, sharp absorption bands at 3510 cm^{-1} ($\text{E} \parallel \text{c}$) and 3504 cm^{-1} ($\text{E} \perp \text{c}$) in the IR spectrum of the Kimberley zircon (Table 2) are at essentially the same position

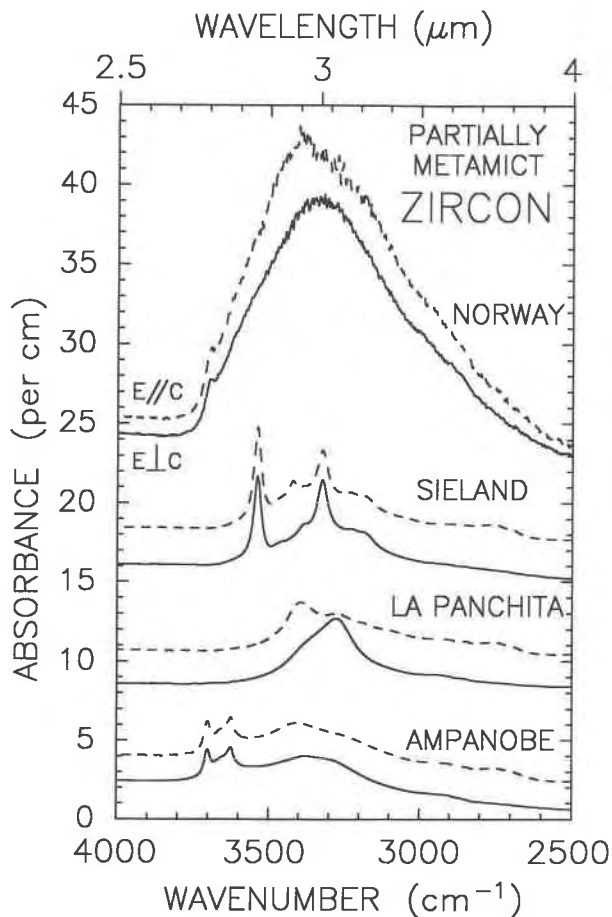


Fig. 3. Polarized infrared spectra of four samples of partially metamict zircon: Fredericksberg, Norway (no. 1466); Sieland pegmatite, Norway (no. 1472); La Panchita pegmatite, Mexico (no. 1230); Ampanobe (brown), Madagascar (no. 1224).

as the OH-stretching band detected by Caruba et al. (1985) in their unpolarized IR spectra of synthetic hydroxylated zircon. Those bands are considerably less intense than the prominent OH bands at 3417 cm^{-1} ($E\parallel c$) and 3384 cm^{-1} ($E\perp c$), however. If this is in fact the same band as reported by Caruba et al., then the hydrogrossular substitution $[4(\text{OH})^-] \leftrightarrow [(\text{SiO}_4)^{4-}]$ does occur in natural crystalline zircon, but is not the most important OH site.

The highly variable bands at ~ 3200 , ~ 3180 , and $\sim 3100\text{ cm}^{-1}$ are in an unusually low-energy range for OH-stretching modes and are more likely to be the result of lattice vibration combination modes. However, the tail of the broad OH band in the metamict zircon extends to even lower wavenumbers, and OH bands with similarly low energies are known to occur in other orthosilicates such as sillimanite (3248 cm^{-1} ; Beran et al., 1989) and phenakite (3120 cm^{-1} ; Beran, 1990). It is thus possible that the bands result from the presence of OH in an orientation where the O-H...O bond distance is unusually short. We conducted the crystalline zircon heating exper-

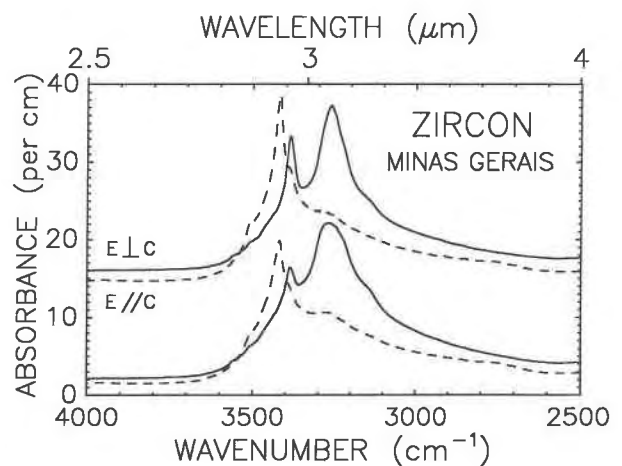


Fig. 4. Polarized infrared spectra of two samples of partially metamict zircon from Poças de Caldas, Minas Gerais, Brazil (1228-1 and 1228-2).

iment discussed below to determine the identity of these bands.

The IR spectra of partially metamict zircon (Fig. 3) are characterized by weak combination-mode bands at ~ 2750 ($E\perp c$) and exhibit features intermediate between the spectra of metamict and crystalline zircon. The zircon samples shown have a wide range of crystallinities. Their IR spectra are noticeably anisotropic in the OH-stretching region. The OH band at about 3400 cm^{-1} is much like similar bands in metamict zircon, but its breadth depends on the degree of metamictization of the sample. Its position and strength depend on the polarization of the incident IR beam. This indicates a tendency for the OH to be crystallographically aligned in the partially radiation-damaged structure. The maximum OH content is again calculated to be approximately 0.1 wt%.

Sharp, isotropic kaolinite bands can be seen in the spectrum from Ampanobe (brown) (no. 1224) and probably result from the myriad of dusty, birefringent inclusions in numerous cracks [in contrast to the cleaner, but more radiation-damaged, Ampanobe sample (black) (no. 1225) specimen of Fig. 1]. The La Panchita zircon sample exhibits a strong band at 3275 cm^{-1} ($E\perp c$), and some indication of the same band can be seen in the Ampanobe (brown) zircon spectrum. As both samples contain numerous inclusions in cracks, these bands cannot be assigned unambiguously to structural OH in zircon without further confirmation. The slightly radiation-damaged Sieland pegmatite zircon has a particularly complex spectrum. The weak, relatively sharp anisotropic bands at 3420 cm^{-1} ($E\parallel c$) and 3385 cm^{-1} ($E\perp c$) are the same OH bands observed in OH-bearing nonmetamict zircon. The isotropic bands at 3539 , 3470 , 3323 , 3230 , and 3180 cm^{-1} are probably the result of inclusions in the numerous cracks in the specimen.

The zircon samples from Minas Gerais, Brazil, (no. 1228) (Fig. 4) are partially metamict grains from within

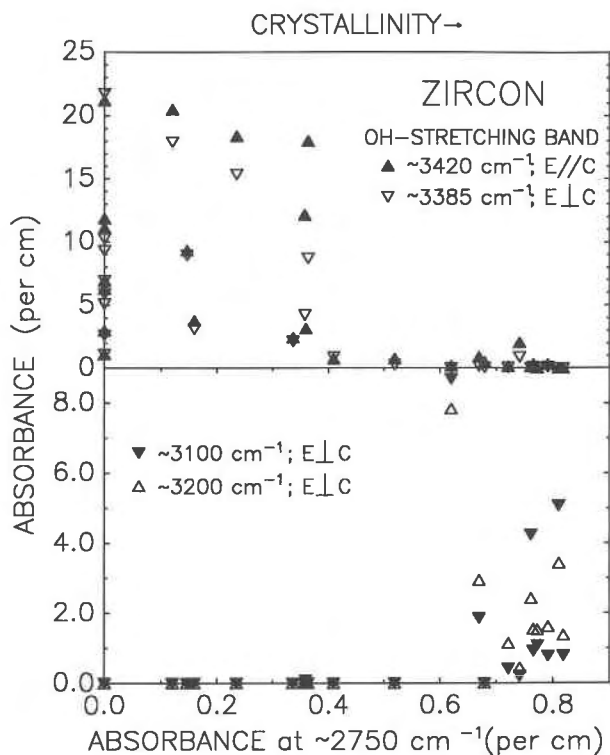


Fig. 5. Plots of infrared band intensities as functions of crystallinity for the zircon samples studied (Table 2): (top) OH-stretching band intensities in two polarizations vs. intensity at $\sim 2750 \text{ cm}^{-1}$ (E//c). (bottom) IR band intensities at ~ 3100 and $\sim 3200 \text{ cm}^{-1}$ (E⊥c) vs. intensity at $\sim 2750 \text{ cm}^{-1}$ (E//c).

a few centimeters of each other in a single hydrothermal vug (Franco and Loewenstein, 1948). Hydrothermal zircon is not common, but one might expect it to be enriched in OH if zircon really can take up OH during growth. The OH-stretching bands at 3420 cm^{-1} (E//c) and 3385 cm^{-1} (E⊥c) are sharp and among the strongest observed in all the samples studied. They probably represent primary OH incorporated during the crystallization of the zircon in an environment with high H_2O activity. The high OH content may be zoned or only metastable, however, as these two samples of identical paragenesis exhibit band strengths that differ by approximately 50% (Fig. 4). The OH content of the grain with the most OH is about 0.05 wt% (as H_2O) based on the grossular calibration of Rossman and Aines (1991), modified to account for the lower wavenumber of the zircon OH absorption band using the intensity vs. wavenumber correlation of Paterson (1982).

The strong bands at 3263 cm^{-1} (E⊥c > E//c) also differ in both strength and breadth among spectra for grains. Because the Minas Gerais zircon samples are virtually free of inclusions, the band at 3263 cm^{-1} probably results from an additional OH orientation. The band's similarity in position and polarization to the unassigned bands in the La Panchita and Ampanobe (brown) zircon spectra

suggests that they, too, are genuine zircon hydroxyl bands in partially metamict samples.

The sharp bands at 3508 cm^{-1} (E//c) and 3510 cm^{-1} (E⊥c) in the Minas Gerais spectra coincide with the OH band of Caruba's hydroxylated zircon (Caruba et al., 1985). They are an order of magnitude stronger than in the Kimberley zircon, but the hydrogrossular substitution $[4(\text{OH})^-] \leftrightarrow [(\text{SiO}_4)^{4-}]$ is still not the dominant OH site.

The systematic relationship between OH and degree of metamictization is of particular interest in zircon. A plot of band strengths at $\sim 3420 \text{ cm}^{-1}$ (E//c) and $\sim 3385 \text{ cm}^{-1}$ (E⊥c) vs. $\sim 2750 \text{ cm}^{-1}$ (Fig. 5) shows relative OH content as a function of crystallinity. The zircon spectra fall approximately into three crystallinity groups: crystalline, with $\sim 2750 \text{ cm}^{-1}$ intensities greater than 0.6; metamict, with intensities of zero; and partially metamict, with intermediate intensities. Although OH-stretching bands are evident in the IR-absorption patterns of several of the crystalline zircon samples, their OH contents are apparently restricted to very low values. The crystalline zircon with the highest OH content is the Kimberley sample (no. 1229), a mantle-derived zircon sample from a kimberlite pipe. This suggests a considerably higher activity of OH in zircon-forming environments in the mantle than in the majority of such crustal environments, consistent with results from other minerals such as olivine (Miller et al., 1987) and pyroxene (Skogby et al., 1990). We have little information about the parageneses of the rest of the crystalline zircon samples.

The OH contents of the metamict and partially metamict samples exhibit about an order of magnitude more variability than the crystalline samples. Some are nearly as anhydrous as their crystalline analogues, while others contain much more OH. This pattern contrasts with the situation in the Sri Lanka zircon suite (Woodhead et al., 1991), in which only totally metamict samples exhibited OH-stretching bands of greater than 1 absorbance unit per cm. If the structural OH in radiation-damaged zircon represents a primary hydrous species, there should be a correlation between the amount of OH detected and the expected activity of H_2O in their growth environments. However, pegmatitic zircon samples have OH amounts that span the entire range of the OH contents we observed. Similarly, if alluvial metamict zircon took up secondary OH readily during transport, their OH contents should be higher than other samples. However, the highest and lowest OH content samples are both alluvial. Such variability prevents us from establishing clear correlations between OH content and postcrystallization history. We do note that none of the partially metamict zircon samples in this survey are as anhydrous as those in the Sri Lanka suite.

The bands at $\sim 3200 \text{ cm}^{-1}$ (E⊥c) and $\sim 3100 \text{ cm}^{-1}$ (E⊥c) are absent in metamict and partially metamict zircon, whether high or low in OH content (Fig. 5). They are present only in crystalline zircon but with variable intensities. These data suggest that the bands are not OH-

stretching bands, but may be some extremely sensitive measure of zircon crystallinity.

Chemical analyses

Electron microprobe analyses (Tables 3 and 4) yielded nearly stoichiometric formulas for all the crystalline zircon samples. Within the error of the analyses, other compounds such as ZrO_2 or SiO_2 are not intermixed with the zircon. In most of the crystalline samples, the only significant substituent for Zr is Hf. The Sonora zircon contains considerable Y and about 1000 ppm U. Its crystallinity suggests that it is relatively young or has been annealed. There is no relation between Hf content and $\sim 2750\text{ cm}^{-1}$ band strength in the crystalline samples, confirming that the intensity of that band is a valid measure of crystallinity in other suites as well as that from Sri Lanka and not a function of composition. There is no unambiguous correlation between Hf content and band strength at ~ 3200 and $\sim 3100\text{ cm}^{-1}$ either. Although the natural samples with the lowest Hf contents (nos. 1218 and 1468) exhibited the strongest bands, the pure synthetic zircon (no. 485), with no Hf, exhibited no signs of them at all.

If the OH content of crystalline zircon results from the hydrogrossular substitution $[4(OH)^-] \leftrightarrow [(SiO_4)^{4-}]$, there should be a Si deficiency in the microprobe analyses that matches the OH content inferred from the IR spectra. However, the calculated OH content of the crystalline samples is far below the standard deviation of Si content based on counting statistics, so no OH-Si deficiency correlation could be established.

If the OH content of crystalline zircon results from a charge-balance substitution of the form $[M^{3+} + H^+] \leftrightarrow [Zr^{4+}]$, there should be a net deficit of charge in the structural formulas that matches their OH contents. Taking both Mn and Fe to have valencies of +3, the net charge imbalance of the Kimberley zircon from the probe analyses (-0.0006) virtually matches the approximate mole fraction of H present (0.0005). This cannot be considered positive evidence that the charge-balance substitution takes place, however, because analyses of most of the rest of the crystalline zircon samples indicate similar or greater apparent charge deficiencies even though they contain considerably less OH.

Electron microprobe analyses of metamict and partially metamict samples also yielded nearly stoichiometric structural formulas. A number of samples contain several cations substituting for Zr. Some contain P substituting for Si. The Minas Gerais zircon samples have an unusually high Mn content as well as considerable Fe. Their net charge imbalance (-0.01) is twice the fraction of H present (0.005) in the more hydrated sample and about three times that of the other. These data do not necessarily contradict the $[M^{3+} + H^+] \leftrightarrow [Zr^{4+}]$ substitution scheme; the analyses are simply not precise enough to solve the problem. The Fredericksberg, Norway, sample hosts trace inclusions of euhedral thorite up to a few tens

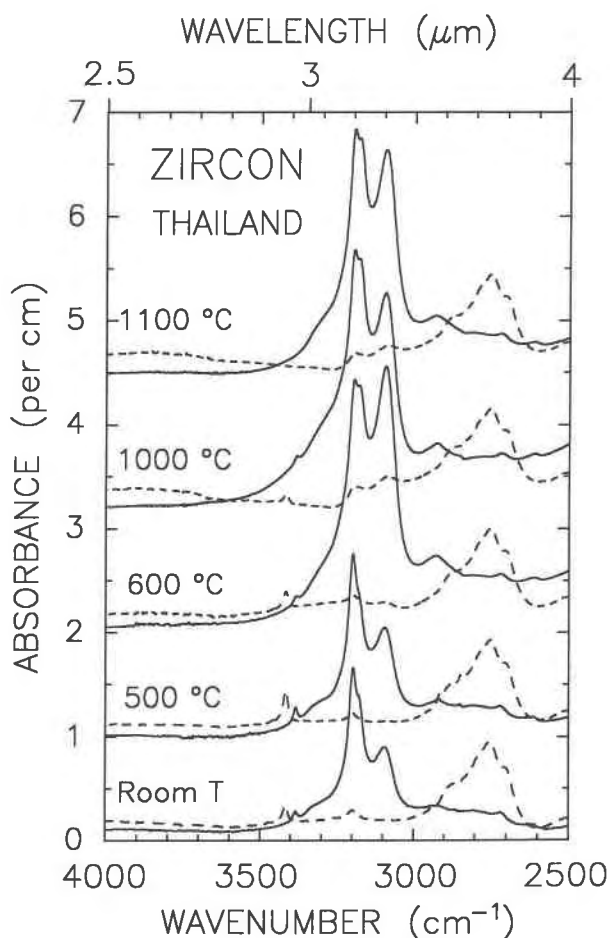


Fig. 6. Selected polarized infrared spectra obtained at room temperature of a crystalline zircon from Thailand (Siam M21-30, no. 1222) subjected to 1-h heating periods at 100°C intervals from 500 to 1100°C .

of micrometers across that are easily visualized using backscattered electron imaging. The analysis of the thorite is considerably Si deficient. The Bedford "cyrtolite" is an intergrowth of zircon, quartz, and monazite. The monazite appears to be zoned and recrystallized as viewed in backscattered electron images.

Heating experiments

To verify that the bands at ~ 3200 and $\sim 3100\text{ cm}^{-1}$ are not OH bands, we performed a stepwise heating experiment on a crystalline zircon sample (Thailand, no. 1222-2) exhibiting a strong combination-mode band at 2752 cm^{-1} ($E\parallel c$); small, sharp, OH-stretching mode bands at 3417 cm^{-1} ($E\parallel c$) and 3383 cm^{-1} ($E\perp c$); and the enigmatic bands at 3198 , ~ 3180 , and 3096 cm^{-1} ($E\perp c$) (Figs. 6 and 7, Table 5).

There was essentially no change in the crystallinity of the sample on annealing as indicated by the nearly constant strength of the combination-mode band at 2752 cm^{-1} (Figs. 6 and 7). The growth of the bands at 3198

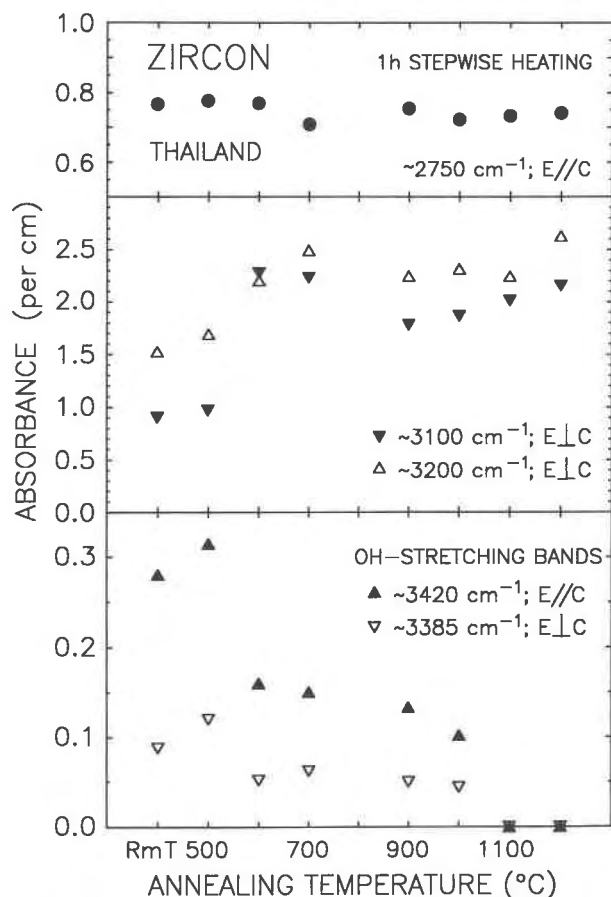


Fig. 7. Plots of infrared band intensities for the Thailand zircon (no. 1222) vs. temperature of annealing: (top) IR band intensity at $\sim 2750\text{ cm}^{-1}$ ($E//C$). (middle) IR band intensities at ~ 3100 and $\sim 3200\text{ cm}^{-1}$ ($E\perp C$). (bottom) OH-stretching band intensities in two polarizations.

and 3096 cm^{-1} at higher annealing temperatures contrasts sharply with the progressive loss of the anisotropic OH-stretching mode bands at 3417 cm^{-1} ($E//C$) and 3383 cm^{-1} ($E\perp C$), suggesting that the former are not OH bands. The large change in the absolute and relative intensities of the two bands at $600\text{ }^{\circ}\text{C}$ suggests that healing of crystal de-

fects (possibly related to the loss of OH) may be the cause of the effect.

The strengths of the anisotropic OH-stretching bands at 3417 and 3383 cm^{-1} increased during the first annealing at $500\text{ }^{\circ}\text{C}$ and decreased dramatically at $600\text{ }^{\circ}\text{C}$, the same temperature at which the reorganization of the 3198 and 3096 cm^{-1} bands occurs. They decreased progressively at higher temperatures, becoming undetectable at $1100\text{ }^{\circ}\text{C}$. The growth of the OH-stretching bands in the first annealing may be the result of the migration of disordered H ions into ordered sites, sharpening and strengthening the OH bands. Subsequent migration of the OH out of the structure results in the loss of the bands at higher temperatures.

To examine the stability of OH in metamict zircon and its relationship with OH in crystalline zircon, we performed a stepwise heating experiment on a nearly metamict zircon sample (Reinbolt Hills, no. 274) (Figs. 8 and 9, Table 6). The sample was oriented for IR study by its external morphology and cut parallel to the (100) face. Although the structure of the highly radiation-damaged zircon was considerably disordered prior to the heating experiment, the polarized IR spectra obtained after high-temperature heating show that the structure recovered its original orientation on annealing. Based on the $\sim 2750\text{ cm}^{-1}$ band, recrystallization did not begin until $1200\text{ }^{\circ}\text{C}$ (Figs. 8 and 9). By $1500\text{ }^{\circ}\text{C}$ the band reached a strength of 0.594 absorbance units per cm, still somewhat less than the 0.7–0.8 values for the same band in the most crystalline samples. The IR spectra in the silicate overtone region of 2100 to 1400 cm^{-1} gave similar results. The spectra remained essentially isotropic (metamict) through the $729\text{ }^{\circ}\text{C}$ heating period. They were anisotropic but broad banded (partially metamict) from 800 to $1100\text{ }^{\circ}\text{C}$ and started to become sharp banded at $1200\text{ }^{\circ}\text{C}$. A weak band at $\sim 3200\text{ cm}^{-1}$ appeared in the $1400\text{ }^{\circ}\text{C}$ heating period spectrum.

The general shape of the OH-stretching mode band (Figs. 8 and 9) was similar to the unpolarized spectra of the Sri Lanka 6500 metamict zircon sample obtained at temperatures up to $800\text{ }^{\circ}\text{C}$ by Aines and Rossman (1985, 1986). Band intensity decreased progressively up to $419\text{ }^{\circ}\text{C}$ while remaining broad and nearly isotropic. At $532\text{ }^{\circ}\text{C}$ the band started to become more anisotropic and sepa-

TABLE 5. Stepwise heating of a crystalline zircon sample from Thailand, GRR 1222

T (°C)	Combination modes				OH-stretching modes				
	2750	3200	3100	32/31	3420		3385		: ⊥
	E//c	E⊥c	E⊥c	Ratio	E//c	posn.	E⊥c	posn.	Ratio
Rm T	0.765	1.523	0.902	1.69	0.280	3417	0.088	3383	3.18
500	0.775	1.695	0.970	1.75	0.315	3416	0.120	3383	2.63
600	0.768	2.204	2.282	0.97	0.160	3416	0.052	3382	3.05
700	0.708	2.490	2.230	1.12	0.150	3416	0.062	3382	2.42
800	800 °C data lost								
900	0.753	2.246	1.780	1.26	0.133	3417	0.050	3381	2.65
1000	0.721	2.315	1.864	1.24	0.102	3417	0.044	3381	2.32
1100	0.732	2.244	2.012	1.12	0.000	—	0.000	—	—
1100 (18 h)	0.740	2.625	2.154	1.22	0.000	—	0.000	—	—

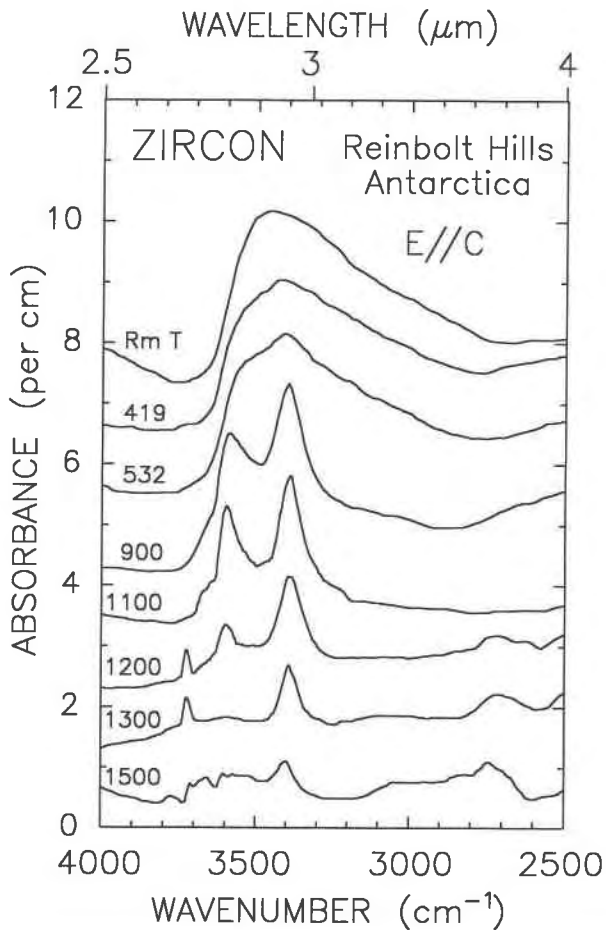


Fig. 8. Selected polarized E||c infrared spectra taken at room temperature of a nearly metamict zircon from Reinbolt Hills, Amery Ice Shelf, Antarctica, (no. 274) subjected to 1-h heating periods at 100 °C intervals from 200 to 1500 °C.

rate into two peaks at ~ 3400 and ~ 3600 cm^{-1} . Over the range of 532–1000 °C the strength of both OH peaks in the E||c polarization increased even though their integrated intensities decreased. This probably resulted from the migration of disordered H into ordered sites at the same time much of the OH migrated out of the zircon. A third OH band at ~ 3725 cm^{-1} appeared at 1200 °C, increased in intensity at 1300 °C, and then decreased along with the band at ~ 3600 cm^{-1} . The broad, weak, irregular anisotropic peaks between approximately 3500 and 3800 cm^{-1} in the 1500 °C spectrum suggest the presence of trace amounts of OH in a number of disordered sites at the highest annealing temperature. Unfortunately the sample was lost before it could be heated further.

The bands near 3400 cm^{-1} in both polarizations correspond to the dominant OH-stretching mode band observed in several crystalline zircon samples. Neither of the new bands at ~ 3600 or ~ 3725 cm^{-1} definitely corresponds to any structural OH bands observed in crystalline zircon. Although they are close to the positions of the isotropic OH bands resulting from hydrous inclu-

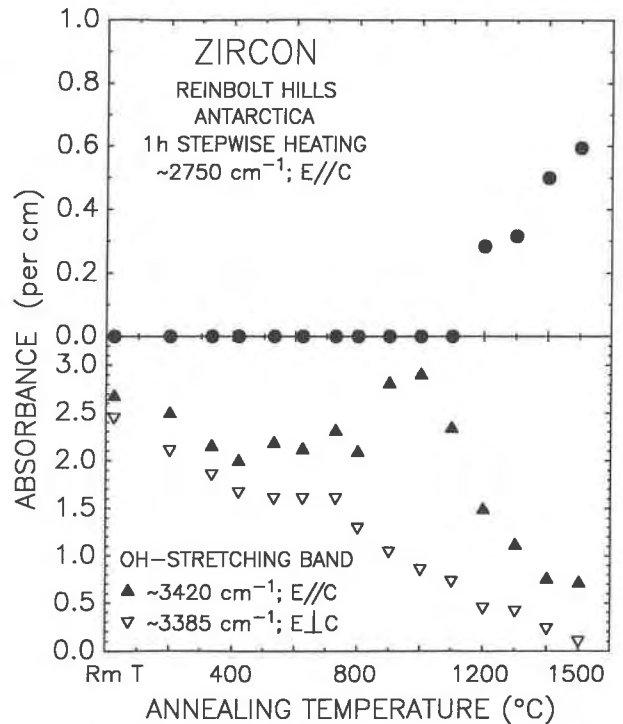


Fig. 9. Plots of infrared band intensities for the Reinbolt Hills, Antarctica, zircon (no. 274) vs. temperature of annealing: (top) IR band intensity at ~ 2750 cm^{-1} (E||c). (bottom) OH-stretching band intensities in two polarizations.

sions, their strong polarization E||c indicates that they represent structurally oriented OH.

OH sites and orientations

In Si-deficient zircon, H is bonded to O atoms at the vertices of the vacant tetrahedron, using the hydrogrossular substitution $[4(\text{OH})^-] \leftrightarrow [(\text{SiO}_4)^+]$. This substitution has been assigned to the band at 3515 cm^{-1} in the IR spectra of synthetic hydroxylated zircon by Caruba et al. (1985) and appears to correspond to the bands at 3510 cm^{-1} in the Kimberley and Minas Gerais zircon samples. The energy of this band is significantly lower than those of the OH bands in members of the grossular-hydrogrossular series (Rossman and Aines, 1991), suggesting a significantly shorter length for the O-H...O H bond of zircon.

The structure of anhydrous, crystalline zircon provides only one unique site for each ion, Zr, Si, and O (Robinson et al., 1971). Thus for zircon with no Si deficiency, there is no question of the O site to which the H will bond. The O is at a vertex of a Si-occupied tetrahedron, bonded to one tetrahedrally coordinated Si and two eightfold coordinated cations on the Zr site. It is quite possible that the H is associated with a lower valency substituent for Zr^{4+} by a coupled substitution of the form $[\text{M}^{3+} + \text{H}^+] \leftrightarrow [\text{Zr}^{4+}]$, but the minute fraction of such substitutions necessary to account for the trace OH contents in natural

TABLE 6. Stepwise heating of a metamict zircon sample, Reinbolt Hills, Amery Ice Shelf, Antarctica

T (°C)	Combination modes				OH-stretching modes								
	2750	3200	3100	32/31	3420		3385		: ⊥	Other OH-stretching bands			
	E c	E⊥c	E⊥c	Ratio	E c	posn.	E⊥c	posn.	Ratio	E c	posn.	E c	posn.
Rm T	0.000	0.000	0.000	—	2.688	3440	2.438	3440	1.10				
200	0.000	0.000	0.000	—	2.500	3440	2.094	3475	1.19				
333	0.000	0.000	0.000	—	2.156	3430	1.844	3480	1.17				
419	0.000	0.000	0.000	—	2.000	3430	1.656	3440	1.21				
532	0.000	0.000	0.000	—	2.188	3407	1.594	3500	1.37	1.781	3560		
624	0.000	0.000	0.000	—	2.125	3408	1.594	3480	1.33	1.875	3540		
729	0.000	0.000	0.000	—	2.313	3410	1.594	3510	1.45	1.750	3577		
800	0.000	0.000	0.000	—	2.094	3408	1.281	3500	1.63	1.750	3560		
900	0.000	0.000	0.000	—	2.813	3399	1.031	3390	2.73	2.094	3591		
1000	0.000	0.000	0.000	—	2.906	3397	0.844	3390	3.44	2.344	3598		
1100	0.000	0.000	0.000	—	2.350	3398	0.719	3390	3.27	1.969	3602		
1200	0.281	0.000	0.000	—	1.500	3398	0.438	3388	3.43	0.750	3607	0.531	3732
1300	0.313	0.000	0.000	—	1.119	3400	0.406	3387	2.75	0.306	3605	0.675	3728
1400	0.500	0.219	0.000	—	0.762	3403	0.219	3400	3.49	0.256	3620	0.200	3718
1500	0.594	0.000	0.000	—	0.719	3403	0.094	3450	7.67	0.212	3608	0.225	3710

crystalline zircon is well below the level confirmable by our microprobe analyses. Because we are unable to correlate OH band strengths with minor element concentrations, we can only speculate on the assignment of the rest of the bands. It is likely that the bands at ~ 3420 cm^{-1} (E||c) and ~ 3385 cm^{-1} (E⊥c) correspond to OH at Si-occupied tetrahedral sites. These are the only OH-stretching bands that occur in several of the crystalline zircon samples. Additional OH-stretching bands at ~ 3270 cm^{-1} (E⊥c > E||c) occur in a few partially metamict zircon samples and may represent differently oriented OH at the vertices of occupied tetrahedra.

The wavenumber and polarization of the OH-stretching bands in crystalline zircon can be used to determine the general environment of the OH groups. In silicate crystals, the H ion of the OH group is usually H bonded to a next nearest neighbor O in the structure. Nakamoto et al. (1955) and Novak (1974) have determined the correlation of OH-stretching band position and O-H...O distance. For H atoms that lie along a linear O-H...O bond, the O...O distance can be estimated. In general, shorter O...O distances produce bands at lower wavenumbers. A fit to Nakamoto's data yields the following approximate O-H...O distances for the zircon OH-stretching mode bands discussed: 3420 cm^{-1} (E||c), 2.87 Å; 3385 cm^{-1} (E⊥c), 2.85 Å; 3510 cm^{-1} (E||c > E⊥c), 2.95 Å; and 3270 cm^{-1} (E⊥c > E||c), 2.78 Å.

There are two unique O...O edge distances (two at 2.430 Å and four at 2.752 Å; Robinson et al., 1971) in the SiO₄ tetrahedron of zircon. Both are shorter than the inferred O-H...O distances for any of the OH-stretching bands. Because the edges of Si-occupied tetrahedra are too short for the band positions observed, it appears that the H of the OH group may extend outward from the tetrahedron rather than along its edges. This is consistent with the expectation that electrostatic repulsion between Si and H would push the H ion out of the tetrahedron. Electrostatic repulsion would not be a factor at vacant tetrahedral sites, but the inferred O-H...O distance is even greater for the hydrogrossular-type band at 3510

cm^{-1} . The discrepancy may decrease if the vacant tetrahedral site expands when Si is not present to counteract the mutual repulsion of the O atoms.

There are two other general environments possible for the H ion outside the silica tetrahedron. One is along the edges of the [ZrO₈] coordination polyhedron, a triangular dodecahedron (Robinson et al., 1971). Again, one would expect electrostatic repulsion to prevent the H from occurring along a polyhedral edge. The second possible location for the H ion is between O atoms that do not share an edge of any occupied polyhedron. There is a vacant sixfold site in the zircon structure with the form of a distorted octahedron that shares faces and edges with both ZrO₈ dodecahedra and other vacant octahedra (Robinson et al., 1971). An O-H...O bond between the O atoms that lie on opposite sides of the vacant octahedron would be aligned nearly perpendicular to the c axis, approximately correct for the ~ 3270 cm^{-1} band. An O-H...O bond between the O atoms that lie along the edge shared by two vacant octahedra would be nearly parallel to the c axis, approximately correct for either the 3420 or ~ 3510 cm^{-1} bands. Electrostatic repulsion would probably favor such locations because the H ion would point away from the nearest high-valency cations. However, the O...O distance across the vacant octahedron is 3.368 Å, and the shared edge is even longer, much too long to account for the positions of the OH bands observed. Thus, assignment of the OH-stretching modes to particular orientations of the OH group is not straightforward. Perhaps, if the presence of the H ion is the result of a $[\text{M}^{3+} + \text{H}^+] \leftrightarrow [\text{Zr}^{4+}]$ coupled substitution, local distortions of the vacant site caused by the trivalent metal cation's lower charge and (usually) larger ionic radius could affect the O...O distances in a way not accounted for by the average structure determined by X-ray analysis. The ion Y³⁺, for instance, has a radius of 1.02 Å in eightfold coordination (compared to 0.84 Å for Zr) and could cause an adjacent vacant octahedral site to have distances to anions that are smaller than average.

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cations in the normally vacant sixfold site coupled with partial hydroxylation of vacant tetrahedral sites may be another means of incorporating OH into the zircon structure. Our microprobe analyses are not accurate enough to detect such an effect. Finally, metamictization must have a very strong disordering effect on the local environments of OH groups, causing a multitude of sites with a wide range of H-bond strengths and thus broadening the OH bands considerably. Aines and Rossman (1986) have proposed that OH groups act to stabilize the metamict state by terminating broken Zr-O and Si-O bonds. However, our estimates of the amounts of OH in metamict zircon suggest that there is not enough to have a significant effect.

CONCLUSIONS

The only structurally incorporated hydrous species found in zircon is OH. It can be found in zircon of all degrees of crystallinity. Crystalline zircon samples contain 0 to <0.01 wt% OH, expressed as H₂O. The highest OH content of any crystalline zircon is in one from the mantle. Metamict and partially metamict zircon samples show a wide range of OH contents, from 0.01 to 0.1 wt%. (Such estimates are subject to revision when accurate calibration of IR data becomes available.) The highest OH content of any partially metamict zircon is in a zircon sample from a hydrothermal vug. The maximum OH content of any of the zircon samples is approximately 2 orders of magnitude less than H₂O contents of radiation-damaged zircon reported in the literature, which were determined by weight loss on heating. It is likely that the greatest fraction of such H₂O was not in fact incorporated in the zircon structure but occurred in cracks and inclusions. All the zircon samples we studied were intergrowths of zircon with other minerals or zircon with abundant secondary inclusions.

The OH-bearing crystalline zircon samples exhibit anisotropic OH bands at ~3420 cm⁻¹ (E||c) and ~3385 cm⁻¹ (E⊥c) resulting from crystallographically oriented OH, possibly at Si-occupied tetrahedra. Such OH may be introduced into the growing crystal by a coupled substitution of the form [M³⁺ + H⁺] ↔ [Zr⁴⁺]. OH bands at ~3510 cm⁻¹ in a few of the crystalline zircon samples result from OH at vacant tetrahedra. This is a much less important OH site in natural zircon than the Si-occupied tetrahedral site. OH may be introduced into that site by the hydrogrossular substitution of the form [4(OH)⁻] ↔ [(SiO₄)⁴⁻]. Additional OH bands are found at ~3270 cm⁻¹. Heating experiments suggest the presence of other stable or metastable OH orientations and demonstrate that labile H can migrate among such sites at elevated temperature.

The various other isotropic bands observed appear to be caused by the presence of randomly oriented hydrous-silicate inclusions distributed throughout the zircon grains or contained in cracks; most notable are the common bands at ~3700 and ~3625 cm⁻¹ resulting from the presence of kaolinite.

Partially metamict zircon retains some anisotropy in the OH-stretching region of their spectra. Their OH bands become progressively broader and more asymmetric as metamictization proceeds. The anisotropic band at ~3720 cm⁻¹ (E⊥c) is found in the spectra of only a few partially metamict zircon samples.

Metamict zircon exhibits broad, asymmetric, isotropic OH bands near 3400 cm⁻¹. The appearance of such bands results from the multitude of OH sites produced by intense disturbance of the original crystal structure. The highest levels of OH in zircon are found in metamict and partially metamict samples. The actual OH content of some of these samples may be overestimated by a factor of 3 as a result of the presence of kaolinite and fluid inclusions. The sample with the highest primary OH content is a zircon sample from a hydrothermal vug. It is the only crustal zircon with more OH than the kimberlite zircon from the mantle. No other relation to paragenesis can be discerned from our study. Exposure to H₂O during transport may not be an important source of the hydrous species present in alluvial zircon. The discovery of OH-bearing crystalline and partially metamict zircon in this survey indicates that the OH behavior in the widely studied Sri Lanka suite is not representative of all zircon suites.

Further work on additional suites of zircon with known geologic histories and well-characterized U-Th-Pb systematics is required to understand the dependence of OH on paragenesis, metamictization, alteration, annealing, weathering, and alluvial transport. Additional heating, hydrothermal, and deuteration experiments are needed to determine the stability of the OH sites and orientations identified in this study.

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