



Article Water Molecules in Channels of Natural Emeralds from Dayakou (China) and Colombia: Spectroscopic, Chemical and Crystal Structural Investigations

Yu-Yu Zheng¹, Xiao-Yan Yu^{1,*}, Bo Xu^{1,2}, Ting-Ya Zhang¹, Ming-Ke Wu¹, Jia-Xin Wan¹, Hong-Shu Guo¹, Zheng-Yu Long¹, Lin-Yan Chen¹ and Li-Jie Qin¹

- ¹ School of Gemology, China University of Geosciences Beijing, Beijing 100083, China; 3009210001@email.cugb.edu.cn (Y.-Y.Z.); bo.xu@cugb.edu.cn (B.X.); 2009190028@cugb.edu.cn (T.-Y.Z.); 2009210033@email.cugb.edu.cn (M.-K.W.); 2009190029@cugb.edu.cn (J.-X.W.); 2009180045@cugb.edu.cn (H.-S.G.); 3001210014@email.cugb.edu.cn (Z.-Y.L.); 2009190026@cugb.edu.cn (L.-Y.C.); 2009200043@cugb.edu.cn (L.-J.Q.)
- ² State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences Beijing, Beijing 100083, China
- Correspondence: yuxy@cugb.edu.cn

Abstract: H_2O molecules in emerald channels have been extensively discussed over the past half century. Recent studies paid attention to their classification and coordination, but have mostly focused on the type related to Na⁺. There are few works on the other types, and the related infrared (IR) absorption bands are rather controversial. This paper investigated natural emeralds from China and Colombia by means of micro-Fourier transform infrared (μ -FTIR) spectroscopy, micro-confocal Raman spectroscopy, and laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS). The results suggested that doubly (IId) and singly (IIs) coordinated H₂O molecules were incorporated in natural emerald channels. Type IId H₂O predominated in those emeralds with relatively low alkali content. As the alkali content increased, the proportion of type IIs H₂O rose, stemming from the decrease of the H₂O^{II}/Na⁺ apfu ratio. Moreover, IR bands of H₂O corresponding to Li⁺ and Cs⁺ were tentatively ascribed here. IR bands for D₂O and HDO in Colombian sample were observed in the range of 2600–2850 cm⁻¹ and preliminarily assigned, which might be a potential tool for emerald origin determination. Our work expanded the existing classification of water molecules in emerald channels and redefined the controversial IR absorption bands.

Keywords: natural emerald; H₂O, D₂O and HDO molecules; spectroscopy; classification; coordination

1. Introduction

An emerald is the green gem variety of the mineral beryl with a general formula of $Be_3Al_2Si_6O_{18}$. The charming color is due to trace amounts of Cr and/or V in the crystal structure. Beryl crystallizes in the space group P6/mcc. Its crystal structure is characterized by the six-membered rings comprised of six [SiO₄] tetrahedras, which are linked together by Al^{3+} at octahedral (O) site and Be^{2+} at tetrahedral (T2) site. These six-membered rings stack along the c-axis, forming large channels that are not identical in diameter. As shown in Figure 1, the cavities of channel are approximately 5.1 Å in diameter, while the "bottlenecks" are 2.8 Å, and the distance between adjacent cavities is about 4.6 Å [1,2]. There are two types of structural positions in the uneven channels: twelve-coordinated 2a position (0 0 1/4) in the center of cavity and eight-coordinated 2b position (0 0 0) in the center of "bottleneck". Large-sized channels are sufficient to incorporate alkali metal cations (Na⁺, K⁺, Li⁺, Rb⁺, Cs⁺), transition metal ions (such as Fe²⁺, Fe³⁺), Ca²⁺, REE³⁺, NH₄⁺, F⁻, Cl⁻ and neutral molecules (H₂O and CO₂), as well as noble gases, such as argon, helium, xenon, and neon [1–14]. The discourse about the positions of these cations and molecules in channel has raged unabated for over half a century [1–3,5,10,15]. To date, it has commonly



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). been assumed that the large cations and molecules, such as K^+ , Cs^+ , Rb^+ , NH_4^+ , H_2O , and CO_2 , occupy the 2a site, whereas the smaller Na⁺, Li⁺, Ca²⁺, Fe²⁺, Fe³⁺ and REE³⁺ are likely to reside in the narrower 2b site.

H₂O molecules in emerald channels were preliminarily classified as two types: Type I and II, and commonly recognized by infrared (IR) and Raman spectroscopies [1,11,15–19]. Both types of H₂O have three vibrational modes, which are symmetric stretching (v_1), antisymmetric stretching (v_3), and bending (v_2) modes. Type I H₂O exists at 2a site with the twofold axis perpendicular to c-axis (Figure 1a). Type II H₂O exists near an alkali ion (Figure 1b,c), and its orientation is changed from perpendicular to parallel to c-axis due to the electrostatic attraction between the charged cation and the oxygen of H₂O molecule. Recently, there have been some more detailed studies on the subtypes of type II H₂O. For example, [4] firstly proposed singly (IIs) and doubly (IId) coordinated type II water molecules related to Na on the basis of the IR bands of v_1 and v_2 modes. This classification was further updated by [20–22]. Since Na⁺ is the dominant alkali ions in the channel of natural emerald and the other cations such as Li⁺ and Cs⁺ are comparably subordinate, the coordination of H₂O molecules with Li⁺ or Cs⁺ has not been carried out yet.



Figure 1. Channel configurations of type I H₂O (**a**), type IIs H₂O (**b**), and type IId H₂O (**c**). Modified after [2,16,22].

Infrared spectroscopy is a widely used method to characterize the vibrational frequencies of water molecules in the emerald channel. The difference in frequencies between type I and type II H₂O might be due to the coupling cations [4,8]. Furthermore, the difference in bond lengths between Na⁺ and oxygen atoms of water molecules results in the different IR absorption bands of type IIs and IId H₂O. Extensive research has recorded the IR bands corresponding to the three vibration modes of type I, IIs and IId H₂O [1,2,4,7,9,11,14,16–35]. However, there are currently no consensuses on the v₁ band of type I H₂O and the v₃ band of type IIs H₂O. Additionally, the IR bands of H₂O related to Li⁺ or Cs⁺ have not been determined.

Aside from OH groups, vibration of OD groups in natural emeralds from Brazil and Colombia was firstly observed by [29]. Additionally, then [35] reported two bands at 2640 and 2671 cm⁻¹ [14] synthesized a unique type of H₂O, D₂O, and HDO bearing beryl, and put forward the assignments of corresponding IR bands [31] synthesized D₂Ocontaining beryl crystals, investigated the distribution of type I and type II D₂O in the channel, and concluded the coordination of Li⁺ with two type II D₂O molecules based on the calculated contents. Currently, –OD related IR bands in the range of 2600–2800 cm⁻¹ tend to be a potential tool for emerald origin determination since its common occurrence in emeralds from a few deposits such as Colombia. However, a systematic investigation on D₂O and HDO molecules in natural emeralds is still lacking.

This paper investigates the chemical composition and spectroscopy of natural emeralds from Dayakou (China), and explores the coordination of alkali ions with H_2O in the channel. We here aim to expand the existing classification of channel water, to redefine the controversial IR absorption bands, and to quantitatively express the relationship between

type II H_2O and Na content. We also investigate the spectroscopy of emerald from Colombia to systematically assign the IR absorption bands of D_2O and HDO in natural emerald.

2. Materials and Methods

2.1. Materials

Fifteen rough emeralds from Dayakou (China) and one emerald crystal from Colombia (col-022) were collected for this study (Figure 2). Dayakou samples consist of crystal fractions and euhedral columnar single crystals. Sized from 2 to 13 mm, these crystals are translucent to opaque and their colors cover various shades of green. All the Dayakou emeralds were cut into thin sections parallel to c-axis with the thickness of 1 mm and polished with double parallel sides. The Colombian sample is a polished crystal cut parallel to the c axis with a weight of 0.82 ct.



Figure 2. Fifteen rough emeralds from Dayakou (China) and one emerald crystal from Colombia (col-022).

2.2. Methods

2.2.1. Micro-Fourier Transform Infrared (µ-FTIR) Spectroscopy

Unpolarized μ -FTIR spectra in the range of 600–6000 cm⁻¹ were measured at room temperature using a Bruker LUMOS FTIR spectrometer equipped with a MCT (mercury-cadmium-telluride) detector cooled at 77 K, housed at the Gem Research Center, the School of Gemology, China University of Geosciences, Beijing (CUGB). Due to the limitation of transparency of crystal, the reflectance mode was used for Dayakou samples, while transmission mode for Colombia sample to measure a FTIR spectrum in range of 400–4000 cm⁻¹. The spectral resolution was 2 cm⁻¹, and each spectrum was averaged from 512 scans. All the measurements were conducted with same crystal orientation. Peak analysis was performed using an Origin 2018 professional software package, and the peaks were fitted using Gauss–Lorentz function.

2.2.2. Micro-Confocal Raman Spectroscopy

Raman spectra of Dayakou emerald sections were collected at room temperature using Horiba HR Evolution micro-confocal Raman spectrometer at the Gem Research Center, the School of Gemology, CUGB. The system was equipped with $50 \times$ magnification objectives and a Peltier-cooled Si-based CCD detector. The Raman spectra (100–4000 cm⁻¹) were recorded using 532 nm solid stage laser with the resolution of 4 cm⁻¹. The grating, acquisition time, and accumulation were 600 slots/mm, 3 s, and 1, respectively. Data analysis was performed using Labspec6 and Origin 2018 professional software, and the peaks were fitted using the Gauss–Lorentz function.

2.2.3. Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

In situ chemical composition measurements were carried out in the same area where the spectroscopic measurements were performed using a Thermo X-Series ICP-MS fitted with a J-100 343 nm femto-second laser ablation system, housed at the National Research Center for Geoanalysis (CAGS). The parameter settings are the same as those of [36]. The radiofrequency power of ICP-MS was 1300 W. Helium gas carrying the ablated sample aerosol from the chamber was mixed with argon gas and nitrogen as an additional diatomic gas to enhance sensitivity. A baffled-type smoothing device in front of the ICP-MS was used to reduce fluctuation effects induced by laser-ablation pulses and to improve the analytic quality. Samples were ablated for 60 s at a repetition rate of 8 Hz at 8 J/cm^2 , and ablation pits were ~50 µm in diameter. Each analysis incorporated an approximate 20 s background acquisition (gas blank) followed by 50 s data acquisition from the sample. Every twelve analyses were followed by a calibration process with two analyses of NIST 610 and one analysis of NIST 612 in order to correct the time-dependent drift of sensitivity and mass discrimination. All elemental concentrations were calculated by applying ²⁹Si as an internal standard. Data reduction was carried out with the commercial software ICPMSDataCal 10.8, and the analytical procedures and calibration methods were similar to those described by [37]. The precision and accuracy are about 10% rel. at ppm level.

3. Results

3.1. Chemical Analyses of Dayakou (China) Emerald

The results of the concentrations of alkali elements in Dayakou emeralds are presented in Table 1. The results suggest that the total concentration of alkali elements in Dayakou emerald ranges from 7164 to 14,685 ppm, with the Na concentration from 5612 to 11,864 ppm, the Li concentration from 278 to 654 ppm, and the Cs concentration from 771 to 3123 ppm. The content of Rb is generally below 40 ppm. Although the average Cs content of Dayakou samples is the highest ever reported among that of worldwide emeralds [36,38], the calculated Cs⁺ atoms per formula unit (apfu) are negligible. The main alkali ions in channel are Na⁺ (0.131–0.287 apfu) and Li⁺ (0.022–0.051 apfu). The proportions are in the order: Na⁺ (79.66–89.30%) > Li⁺ (7.93–18.96%) > Cs⁺ (1.34–4.45%). The water content (0.634–0.806 apfu) was calculated using the equation relating Na⁺ to H₂O molecules, which was proposed by [39]. In Table 1, the sample YEW-33 shows the lowest content of alkali elements, whereas samples YEW-22 and YEW-19 display relatively high alkali contents.

Sample No.	YEW-1	YEW-5	YEW-6	YEW-10	YEW-11	YEW-12	YEW-14	YEW-19	YEW-22	YEW-24	YEW-25	YEW-28	YEW-29	YEW-32	YEW-33
SiO ₂ (wt.%)	64.85	65.39	65.83	64.05	65.45	65.06	66.33	64.86	66.93	65.25	65.51	66.59	67.05	66.46	66.98
BeO (wt.%)	14.23	14.08	13.90	13.79	13.70	14.16	13.25	14.18	12.86	14.37	14.42	13.75	13.89	14.12	13.88
Al ₂ O ₃ (wt.%)	18.13	15.38	15.90	16.04	16.33	16.76	16.67	16.45	15.86	15.75	15.74	16.88	15.96	17.06	16.56
Li (ppm)	445	303	343	438	373	507	569	379	654	345	290	311	278	343	294
Na (ppm)	7648	8975	10,409	10,099	10,339	11,112	7916	11,864	10,548	9977	10,814	6274	6402	5748	5612
K (ppm)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Rb (ppm)	8.0	33.0	25.4	23.2	37.3	16.4	14.0	25.2	13.9	24.2	21.9	22.9	23.7	23.0	16.4
Cs (ppm)	990	2508	1944	1798	3123	1044	771	2417	2254	2101	1904	1515	1878	1504	1242
Alkali elements total (ppm)	9091	11,819	12,721	12,358	13,872	12,679	9270	14,685	13,469	12,448	13,029	8123	8582	7618	7164
Li ⁺ (apfu)	0.036	0.024	0.027	0.036	0.030	0.040	0.045	0.030	0.051	0.027	0.023	0.024	0.022	0.027	0.023
Na ⁺	0.185	0.215	0.248	0.247	0.248	0.268	0.187	0.287	0.247	0.240	0.259	0.148	0.150	0.136	0.131
Rb ⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cs^+	0.004	0.010	0.008	0.008	0.013	0.004	0.003	0.010	0.009	0.009	0.008	0.006	0.008	0.006	0.005
H ₂ O *	0.693	0.726	0.763	0.762	0.762	0.785	0.695	0.806	0.762	0.754	0.775	0.652	0.654	0.638	0.634
Alkali ions total	0.225	0.250	0.283	0.291	0.290	0.313	0.235	0.327	0.307	0.276	0.290	0.178	0.179	0.169	0.159
Na ⁺ /Alkali ions	82.27%	86.12%	87.56%	85.09%	85.28%	85.64%	79.66%	87.60%	80.47%	86.83%	89.30%	82.85%	83.63%	80.38%	82.46%
Li ⁺ /Alkali ions	15.87%	9.63%	9.55%	12.23%	10.19%	12.94%	18.96%	9.26%	16.53%	9.95%	7.93%	13.60%	12.05%	15.89%	14.31%
Cs ⁺ /Alkali ions	1.84%	4.16%	2.83%	2.62%	4.45%	1.39%	1.34%	3.09%	2.97%	3.16%	2.72%	3.46%	4.24%	3.64%	3.16%

Table 1. Concentrations of alkali elements (in ppm), major elements (oxide, in wt.%), and H₂O (apfu) in Dayakou emeralds.

Note: Compositions were recalculated on the basis of Si = 6. Apfu = atoms per formula unit. bdl = below detection limit. * Calculated using $[1.1061 * Na^+ (apfu) + 0.4884 = H_2O (apfu)]$ proposed by [39].

3.2. Micro-Confocal Raman Spectra of Channel Water Molecules

In the region of 3500–3700 cm⁻¹, the Raman shifts of v_1 modes of type I and II H₂O can be observed at 3605 cm⁻¹ (P1) and 3596 cm⁻¹ (P2), respectively. Three distinct spectral patterns of channel water molecules in Dayakou emeralds are displayed in Figure 3. These are: "alkali-poor" (Figure 3a), "medium alkali" (Figure 3b), and "alkali-rich" (Figure 3c) patterns, among which the "alkali-rich" pattern is most common.



Figure 3. Raman spectra of Dayakou emeralds. (**a**) "Alkali-poor" pattern of sample YEW-33 shows that the 3605 cm⁻¹ peak (P1) is more intense than the 3596 cm⁻¹ peak (P2). (**b**) "Medium alkali" pattern of YEW-29 shows the similar intensity of both peaks. (**c**) "Alkali-rich" pattern of YEW-22 shows that the intensity of P2 exceeds that of P1. (**d**) Waterfall plots of the Raman spectra of all Dayakou samples.

The waterfall plots of Raman spectra of all Dayakou samples (Figure 3d) suggest that there is no absolute negative correlation between P1 and P2. The intensity of P1 even rises simultaneously with P2, indicating that the overall content of channel water increases. After peak fitting, the intensity, full width at half maxima (FWHM) and peak area of P1 and P2 were collected. As shown in Table 2, the peak intensity ratio of P2 to P1 ranges from 0.40 to 1.99. The FWHM of P1 is in the range of 9.3–14.8 cm⁻¹, while that of P2 in 3.5–7.2 cm⁻¹. In addition, the peak area of P2 (8912–34,385 cm⁻¹) is much larger than P1 (4413–12,981 cm⁻¹) and the ratios are generally greater than 1, revealing the content of type II water precedes type I water.

	Sample No.	YEW-1	YEW-5	YEW-6	YEW-10	YEW-11	YEW-12	YEW-14	YEW-19	YEW-22	YEW-24	YEW-25	YEW-28	YEW-33	Range
PI (a.u.)	3596 cm^{-1}	2063	1108	687	865	942	1176	2398	1348	1300	1587	769	1980	1725	767-2061
	3605 cm^{-1}	1113	1648	1366	1699	1814	1446	1112	2061	1849	1860	1408	802	767	687-2398
	$3596 \text{ cm}^{-1}/3605 \text{ cm}^{-1}$	0.54	1.49	1.99	1.96	1.93	1.23	0.46	1.53	1.42	1.17	1.83	0.40	0.44	0.40 - 1.99
FWHM (cm ⁻¹)	3596 cm^{-1}	11.7	13.2	14.8	9.3	14.5	13.2	9.5	14.2	14.7	14.8	14.6	11.4	10.4	9.3-14.8
	3605 cm^{-1}	4.7	6.7	4.9	5.5	4.8	4.9	3.5	6.7	6.9	6.3	7.2	4.7	3.8	3.5-7.2
	$3596 \text{ cm}^{-1}/3605 \text{ cm}^{-1}$	2.47	1.97	3.01	1.67	3.00	2.69	2.71	2.10	2.14	2.37	2.02	2.44	2.77	1.67-3.01
PA (cm ⁻¹)	3596 cm^{-1}	16,829	27,995	23,478	20,463	31,305	22,475	13,747	34,385	31,871	33,385	23,950	9732	8912	8912-34,385
	3605 cm^{-1}	12,763	9668	4413	6267	5952	7529	8901	11,852	11,667	12,981	7217	12,112	6896	4413-12,981
	$3596 \text{ cm}^{-1}/3605 \text{ cm}^{-1}$	1.32	2.90	5.32	3.27	5.26	2.99	1.54	2.90	2.73	2.57	3.32	0.80	1.29	0.80-5.32

Table 2. Raman peak information of water molecule in Dayakou emeralds.

Note: PI = peak intensity, FWHM = full width at half maxima, PA = peak area.

3.3. μ -FTIR Spectra of H₂O in Dayakou Samples

The infrared spectra of Dayakou and Colombian samples are displayed in Figure 4, and the specific infrared absorption bands are presented in Table 3. It can be found that the IR bands of natural emeralds slightly shift to higher wavenumbers than those of beryls. In this work, IR bands caused by different modes of H₂O molecular vibration were observed in three regions: (1) 1500–1700 cm⁻¹ (ν_2); (2) 3500–3800 cm⁻¹ (ν_1 and ν_3); and (3) 5000–5500 cm⁻¹ (combination mode). To shorten the expression, an abbreviation like H₂O^I ν_1 is used to symbolize the ν_1 mode of type I H₂O.



Figure 4. (a) IR spectra of Dayakou samples in the range of 6000–600 cm⁻¹; (b) IR spectrum of Colombian sample in the region of 4000–400 cm⁻¹.

As shown in Figure 5, IR bands at 1603 and 1637 cm⁻¹ can be ascribed to $H_2O^I\nu_2$ and $H_2O^{II}\nu_2$, respectively. Besides, the 1558 cm⁻¹ and 1651 cm⁻¹ bands commonly appear in all Dayakou samples, while the 1645 cm⁻¹ band is more obvious in samples with high alkali content. These bands were referred to as the ν_2 -related modes of type I water [25].

Figure 6 displays the IR bands of four representative Dayakou samples in the region of $3500-3800 \text{ cm}^{-1}$. The most significant absorption at ~3603 cm⁻¹ and ~3704 cm⁻¹ could be assigned to $H_2O^{II}v_1$ and $H_2O^{I}v_3$, respectively. In Figure 6d, two bands related to $H_2O^{II}v_1$ at 3593 and 3604 cm⁻¹ could be observed after peak fitting. Bands in 3650–3690 cm⁻¹ are mainly caused by $H_2O^{II}v_3$, which include the 3661/3663 cm⁻¹ and 3675/3676 cm⁻¹ bands in low alkali content samples (Figure 6a,b), and the 3650, 3666 and 3683 cm⁻¹ bands in medium and high alkali content samples (Figure 6c,d). The assignments of these bands and the weak band at ~3633 cm⁻¹ are discussed in a later section.

IR band at 5273 cm⁻¹ is likely to be the combined frequency of v_2 and v_3 modes. As shown in Figure 7, there is a significant positive correlation between the alkali content and the peak intensity. In previous studies, the 5273 cm⁻¹ band was commonly ascribed to type I H₂O according to the orientation of measurement [14,23,29], but occasionally related to type II H₂O [24,34]. Since the obvious positive correlation observed in Figure 7, this band is assigned to H₂O^{II} v_2 + v_3 here.

This Wo (cm ⁻¹ , Unpo	ork larized)	Refs. [1,2,4,7,9,11,14,16–35] (cm ⁻¹)	Assignments	Polarization Relative to c Axis		
Davakou	Colombia					
		7143/7144	$H_2O^{I}(v_1 + v_3)/HDO^{I}$			
		7044/7102	$H_2 O^{II} (\nu_1 + \nu_3)$	unpolarized		
		5297	$D_2 O^{I} (v_1 + v_3)$	1		
5273		5274/5276	H_2O^{I} or H_2O^{II} ($v_2 + v_3$)?	Ü		
		5038	$HDO^{I}(d + v_{OH})$	Ï		
		4076	$HDO^{I} (d + v_{OD})$	Ü.		
		3825/3979/4057/4060	$H_2O^{II}(v_3 + v_{libr})$	Ü.		
		3914	$D_2 O^{I} (v_2 + v_3)$	Ï		
		3747/3850/3863/3880	H_2O^{I} or H_2O^{II} ($v_3 + v_{libr}$)?	\perp		
3703-3705		3690/3693/3696-3700	$H_2O^{I}(\gamma_3)$			
		3653/3660/3661/				
3674/3683		3666//3670/3671	$H_2O^{II}(v_3)$ (unclassified)	\perp		
3661/3666		3661/3662/3664/3665	$H_2O^{IId}(v_3)$	\perp		
3650-3652		3643/3651	$H_2O^{IIs}(v_3)$	\perp		
		3655	$HDO^{I}(\gamma_{OH})$			
		3636	$HDO^{II}(v_{OH})$	 		
		3602-3610		Ш		
3628/3634/3637		3630–3635	$H_2O^{I}(v_1)$	\perp		
		3647/3649/3650	2 (1)			
		3587-3599	$H_2O^{II}(v_1)$ (unclassified)			
3602-3604		3596/3597/3600/3602	$H_2O^{IId}(v_1)$	Ï		
3593		3586–3589	$H_2O^{IIs}(\gamma_1)$	 		
		3222/3230/3236	$H_2 O^{II} (2v_2) \text{ or}$	"		
		2010 (2056	$\Gamma e_2(OH)_4$	II		
	2012	3019/2938	$D_2O^2(v_3 + v_{libr})$			
	2813	2876	$D_2O^{-}(v_3 + v_{libr})$	1		
	2730	2743	$D_2O^2(v_3)$			
	2/24/2/30	2726/2729	$D_2 O^{-} (v_3)$	⊥ ∥		
	2684	2007	$HDO^{-}(v_{OD})$			
	2675	2075/2075/2070	$DO^{-}(v_{OD})$			
	2640	2033	$D_2O^{-}(v_1)$	⊥ ∥		
	2029	2031/2034/2041 1632/1632/1630/	$D_2 O^{-1}(v_1)$	ll		
1637		1622/1623/1630/	$H_2O^{II}(v_2)$ (unclassified)			
		1631/1633/163/	$\mathbf{H}_{\mathbf{A}}$			
		1017/1020/102//1628	$\Pi_2 O^{-1} (v_2)$			
1602		1031/1033/103//1038	$\Pi_2 \cup (V_2)$	ll		
[1558, 1651]		1599–1607 [1546, 1645]	$H_2O^I(v_2)$	\perp		

Table 3. Assignments of the IR absorption bands (cm^{-1}) of H₂O, HDO, and D₂O molecules in beryls and emeralds.







Figure 6. IR spectra of four representative Dayakou samples in the region of $3500-3800 \text{ cm}^{-1}$. (a) and (b): IR spectra "alkali-poor" samples (YEW-33 and YEW-32); (c): IR spectrum of YEW-1 with medium alkali content; (d): IR spectrum of "alkali-rich" sample (YEW-22); experimental spectrum = black solid line, fitted peaks = cyan solid line, cumulative fit = red dash line.



Figure 7. Comparisons between IR spectra of Dayakou samples with distinct alkali contents.

3.4. μ -FTIR Spectra of D₂O and HDO in Colombian Sample

Figure 8 illustrates the IR spectra of D_2O and HDO molecules in Colombian emerald sample. In Figure 8, a series of intense IR bands of sample col-022 locate at 2640, 2673, ~2740 and 2813 cm⁻¹. After peak fitting, the intense shoulder absorption band at ~2740 cm⁻¹ is split into three bands located at 2724, 2736, and 2750 cm⁻¹. Additionally, weak bands at 2629 and 2684 cm⁻¹ are separated.



Figure 8. IR spectra of D_2O and HDO molecules in Colombian sample in the region of 2600–2850 cm⁻¹. Experimental spectrum = black solid line, fitted peaks = cyan solid line, cumulative fit = red dash line.

4. Discussion

It is a widely held view that type I H₂O predominate in alkali-poor emeralds with the frequencies of 1599–1607 cm⁻¹ for H₂O^I ν_2 and 3690–3700 cm⁻¹ for H₂O^I ν_3 . In this work, the bands corresponding to these two vibrations are at ~1603 cm⁻¹ and ~3704 cm⁻¹ (Figure 9a). What is controversial is the H₂O^I ν_1 related band, which was generally reported in the range of 3602–3610 cm⁻¹ [14,21,23,25,30] and occasionally observed at 3630–3635 cm⁻¹ [16,22] and 3647–3650 cm⁻¹ [22,32]. Additionally, 3602–3610 cm⁻¹ is

thought to be a reliable range for the frequency of $H_2O^Iv_1$ band, but this band is not determined in our work as a result of overlapping the strong $H_2O^{II}v_1$ absorption.





Two subtypes of type II H₂O proposed by Fukuda and Shinoda [4] were also supported by our results. Among the alkali ions of Dayakou samples, the proportion of Na⁺ exceeds 80%, which indicates that the type II H₂O related to Na is dominant. In samples YEW-33 and YEW-32 with relatively low Na content, IR bands corresponding to $H_2O^{II}v_3$ locate at 3661 and 3663 cm^{-1} (Figure 6a,b). Furthermore, in samples YEW-1 and YEW-22 with higher Na content, aside from the above peaks, an obvious band at 3650/3652 cm⁻¹ can be observed (Figure 6c,d). In Figure 6d, two types of $H_2O^{II}v_1$ band are observed at 3593 and 3604 cm⁻¹. These results suggest that type IId (Figure 9b) and IIs H₂O (Figure 9c) molecules also exist in natural emerald channels, and are controlled by the content of sodium. Their IR absorption features are distinguished by the correlation between bond length of Na-O and vibration frequency of H₂O molecules. As shown in Figure 9b, the doubly coordinated Na⁺ is shared by two hydroxyl oxygen (^WO). The bond valence and length are 0.14 vu and 2.483 Å, whereas those of singly coordinated Na⁺ are 0.28 vu and 2.227 Å, respectively [3,22]. With the increasing number of coordinated water molecules, the bond length of Na^+-WO rise together with the H–O–H angle [4,21]. Accordingly, both the frequencies of v_1 and v_3 stretching modes of type IId H₂O shift to higher wavenumbers, which suggesting that the bands at \sim 3603 and \sim 3661 cm⁻¹ are likely to be assigned to $H_2O^{IId}v_1$ and $H_2O^{IId}v_3$, respectively. This is consistent with the results of [21,22]. The ~3593 cm⁻¹ band is related to $H_2O^{IIs}v_1$, and the controversial ~3651 cm⁻¹ band should be ascribed to $H_2O^{IIs}v_3$ rather than $H_2O^{I}v_1$ based on the almost constant frequency difference between v_1 and v_3 modes.

Figure 6a, b indicate that type II water mainly exists as type IId with the v_3 band at ~3661 cm⁻¹ in the channels of emeralds with low sodium content. The emergence of the ~3651 cm⁻¹ band in the IR spectra of relatively high sodium content samples suggests that the H₂O^{II}/Na⁺ apfu ratio drops below 2 as a consequence of the increase of Na content, implicating a higher proportion of type IIs H₂O.

Figure 3a–c reveal that the Raman spectrum patterns of the channel water molecules in emeralds are controlled by the alkali content, especially the dominant Na content. At present, many researchers quantitatively linked alkali cations with water, and various empirical equations using Na content to evaluate the total channel water content have been proposed [39–41], and the preferred equations are:

$$0.6097 \operatorname{Na_2O}(\text{wt.\%}) + 1.6290 = H_2O(\text{wt.\%})$$
(1)

$$Na^{+} + 0.5 = H_2O (apfu)$$
 (2)

However, what is noteworthy is that only type II H_2O is directly related to alkali elements, especially Na. Additionally, the content of type I water is not constant as shown in Figure 3d. Thus, it is more accurate to use the Na⁺ apfu and peak area of P2 Raman peak to explore the quantitative relationship between alkali content and type II water. The data was fitted to a trendline which can be described with the equation:

$$Na^{+} = -0.2190 + 0.0471 \ln (PA_{3596} - 7286)$$
(3)

Shown in Figure 10 as a black solid line. The fitted curve shows the logarithmic relationship between type II water and the Na content, indicating a positive but not linear correlation. The curve slope suggests that the type II water content increases uniformly with the Na content. A possible explanation is that the proportion of type IIs H_2O rises with the increase of Na⁺ apfu, which means that more [Na(H_2O)]⁺ complexes are formed with the same number of water molecules. The specific theory of how the Na content controls the proportion of type IIs and IId H_2O demands further study.



Figure 10. Logarithmic relationship between PA_{3596} (cm⁻¹) and Na⁺ (apfu). PA_{3596} = peak area of 3596 cm⁻¹ band, apfu = atoms per formula unit, fitted curve = black solid line.

Water molecules related to Li⁺ and Cs⁺ were once defined as type III H₂O by [16]. Li⁺ and Cs⁺ therein were set at position 2a while OH⁻ at position 2b. The symmetry axis of Cs(OH) was perpendicular to the c-axis. This configuration is questionable, because the bond length between the eight-coordinated Li⁺ and ring oxygen (^RO) was calculated to be 2.397 Å [3], which is even shorter than Na⁺–^RO (2.568 Å) and also less than the average 2b–O distance with the value of 2.480 Å. Therefore, Li⁺ should occupy the 2b position in the channel rather than the 2a position where Cs⁺ locates.

The chemical analyses of Dayakou samples show the proportion of Li⁺ among the channel alkali ions ranges from 7.57–17.03%, indicating high possibility of the presence of $[\text{Li}(\text{H}_2\text{O})_n]^+$ complex in which the H₂O molecules are defined as Li-related type II (H₂O^{II-Li}) here (Figure 11a). According to the calculated frequencies of OH vibration of the [M(H₂O)]⁺ complexes by [8] and the variation of the bond strength of M⁺–O, the frequencies of ν_1 and

 v_3 stretching modes of type II-Li should be lower than that of type II-Na. Accordingly, we attempt to assign the weak ~3633 cm⁻¹ band to H₂O^{II-Li}v₃. This band was occasionally assigned to H₂O^Iv₁ in previous work [16,22], because both H₂O^Iv₁ and H₂O^{II-Li}v₃ are IR active when the electric vector (E) is perpendicular to the c-axis. However, in the results of samples BLS and DUV measured by [22], the bands at ~3650, ~3637 and ~3605 cm⁻¹ were simultaneously detected under E⊥c, which supports that these three bands should be ascribed to different vibration modes and is also the evidence of our assignments.



Figure 11. IR absorption features and possible configurations of type II-Li (a) and type III (b) H₂O molecules in natural emeralds.

Research on the coordination of Cs⁺ with H₂O in natural emerald is limited as a result of the negligible Cs content. It is possible to hypothesize a configuration of type III H₂O that the Cs⁺ at position 2a coordinates with OH⁻ at position 2b (Figure 11b). The proportion of Cs⁺ among the alkali ions in Dayakou emerald channels ranges from 1.63–4.24%, indicating possible Cs(OH) complexes. According to the relationship between frequencies of OH vibration and the bond length of M+–O [8], the ~3675 cm⁻¹ band of higher wavenumber than the frequency of H₂O^{IId}v₃ is tentatively assigned to the OH vibration of Cs (OH).

OD vibrations of D₂O and HDO molecules in natural emeralds were once reported [29,35], but not systematically assigned. According to IR absorption features of free D₂O and HDO molecules [42] and the H₂O, D₂O, and HDO bearing beryl [14], two principles of the assignment of OD vibration are obeyed in this work: (1) the D₂O-related vibrational features are similar to those of H₂O molecules; (2) the vibrations of OD group in HDO molecule is independent without intramolecular OD–OD coupling. Additionally, the OD vibration bands are consequently assumed to be about halfway between frequencies of the v₁ and v₃ modes of D₂O [14,29]. Hence, the systematic assignments of IR bands of Colombian emerald are as follows: v₁ and v₃ bands of type I D₂O at 2640 and 2750 cm⁻¹; v₁ and v₃ bands of type II D₂O at 2629 and 2724/2736 cm⁻¹; v_{OD} of type I and type II HDO at 2684 and 2673 cm⁻¹, respectively. A satellite at 2813 cm⁻¹ with a separation of approximately 63 cm⁻¹ from the D₂O I v₃ mode is ascribed to the combination band related to the libration mode. The coordination of D₂O and HDO in the channel of emerald is similar to H₂O (Figure 12).



Figure 12. Configurations and IR absorption features of $D_2O(a)$ and HDO (b) molecules in Colombian emerald.

5. Conclusions

- Two subtypes (IId and IIs) of type II H_2O were detected in Dayakou emerald. IR absorption bands related to v_1 and v_3 modes of H_2O^{IId} are determined to locate at ~3603 and ~3661 cm⁻¹, respectively, while those of H_2O^{IIs} at ~3593 and 3651 cm⁻¹, respectively. Type IId H_2O predominates in those emeralds with relatively low alkali content. As the alkali content increases, the proportion of type IIs H_2O rises as a result of the decrease of the H_2O^{II}/Na^+ apfu ratio. The equation (3) derived from Na⁺ apfu and peak area of the 3596 cm⁻¹ Raman peak is used to express the relationship between the Na content and type II H_2O .
- H_2O corresponding to Li⁺ is defined as type II-Li H_2O , of which the v_3 mode frequency is ascertained to be ~3633 cm⁻¹. A tentative assignment of ~3675 cm⁻¹ band is the OH vibration of Cs(OH) which is classified as type III H_2O here.
- IR absorption bands for D₂O and HDO molecules in Colombian emerald are observed in the range of 2600–2850 cm⁻¹ and preliminarily assigned.

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