Mineralogical classification and crystal water
coloration of beryl from the W-Sn-Be occurrence of
Xuebaoding, Sichuan province, western China

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Abstract

Beryl from Xuebaoding, Sichuan Province, western China is known for its unusual tabular habit and W-Sn-Be paragenesis in a greisen-type deposit. The crystals are typically colorless transparent to pale blue, often with screw dislocations of hexagonal symmetry on the (0001) crystal faces. Combining EMPA and LA-ICP-MS with single crystal XRD, correlated with Raman and micro-IR spectroscopy and imaging, the crystal chemical characteristics are determined. The Na+ (0.24–0.38 apfu) and Li+ up to 0.38 apfu content is at the high end compared to beryl from other localities worldwide. Li+ substitution for Be2+ on the tetrahedral (T2) site is predominantly charge balanced by Na+ on the smaller channel.
(C2) site, with Na\(^+\) ranging from 91.5% to 99.7% (apfu) of the sum of all other alkali elements. Cs\(^+\) and minor Rb\(^+\) and K\(^+\) primarily charge balancing minor M\(^{2+}\) substitution for Al\(^{3+}\) at the A site; all iron at A site is suggested to be trivalent. The \(a\)-axis ranges from 9.2161 to 9.2171 \(\text{Å}\), with unit-cell volume from 678.03 to 678.48 \(\text{Å}^3\). The \(c/a\) ratio of 1.0002–1.0005 is characteristic for T2-type beryl with unit-cell parameters controlled primarily by Be\(^{2+}\) substitution. Transmission micro-IR vibrational spectroscopy and imaging identifies coordination of one or two water molecules to Na\(^+\) (type IIs and type IId, respectively) as well as alkali free water (type I). Based on IR absorption cross section and XRD a C1 site water content of 0.4–0.5 apfu is derived, \textit{i.e.} close to 50 % site occupancy. Secondary crystal phases with a decrease in Fe and Mg, yet increase in Na, suggest early crystallization of aquamarine, with goshenite being late. With similar crystal chemistry to beryl of columnar habit from other localities worldwide, the tabular habit of Xuebaoding beryl seems not causally related to chemical composition and alkali content.

**KEYWORDS:** Beryl, Xuebaoding, crystal chemistry, tabular habit, crystal water, infrared spectroscopy.

**Introduction**

**Background:** Beryl as the most common beryllium mineral is of high geochemical significance in different geologic contexts. Ideally \(\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}\), beryl is a cyclosilicate mineral of hexagonal crystal structure. Six-membered rings of Si tetrahedra are linked by tetrahedrally coordinated Be\(^{2+}\) (T2 site) and octahedrally coordinated Al\(^{3+}\) (A site) in planes parallel to (0001) (Aurisicchio \textit{et al.}, 1988, 1994; Černý, 2002; Groat \textit{et al.}, 2008). The rings form channels parallel to the crystallographic \(c\)-axis which in natural beryl typically contain variable amounts of primarily neutral molecules of water, CO\(_2\), or CH\(_4\), and alkali cations (Ginzburg, 1955; Wood and Nassau, 1968; Hawthorne and Černý, 1977; Aines and Rossman, 1984; Artioli \textit{et al.}, 1993; Charoy \textit{et al.}, 1996; Pankrath and Langer, 2002; Gatta \textit{et al.}, 2006; Groat \textit{et al.}, 2008; Fridrichová \textit{et al.}, 2016). The accommodation of monovalent alkali cations on the two channel vacancy sites charge balances the substitution of divalent or trivalent cations (e.g., Mg\(^{2+}\), Fe\(^{2+/3+}\), or Mn\(^{2+}\)) for Al\(^{3+}\) at the A site, or the substitution of primarily Li\(^+\) for Be\(^{2+}\) at the T2 site (Folinsbee, 1941; Wood and Nassau, 1968; Bakakin \textit{et al.}, 1969; Hawthorne and Černý, 1977; Aurisicchio \textit{et al.}, 1988). The smaller alkali Na\(^+\) occupies the narrower channel site (C2/2b), while the larger K\(^+\), Cs\(^+\), or Rb\(^+\) as well as H\(_2\)O and CO\(_2\), prefer the wider channel site (C1/2a) (Aurisicchio \textit{et al.}, 1994; Łodziński \textit{et al.}, 2005; Fukuda and Shinoda, 2008). While pure beryl is colorless (var. goshenite), the different substitutions give rise to distinct colors of blue (var. aquamarine, Fe), green (var. emerald, Cr/V), yellow (var. heliodor, Fe), or pink (var. morganite, Mn) (Lum \textit{et al.}, 2016; Tempesta \textit{et al.}, 2020).

Following early UV, visible, and IR spectroscopy (Wood and Nassau, 1967, 1968), lattice position, molecular orientation, bonding state, and dynamic behavior of water in natural and
synthetic beryl, and at variable temperature, have been characterized spectroscopically (Kim et al., 1995; Charoy et al., 1996; Kolesov and Geiger, 2000; Łodziński et al., 2005; Fukuda and Shinoda, 2008, 2011). Based on these studies, water on the C1/2a sites has been defined as type I or type II with molecular dipole moment orientated perpendicular or parallel with respect to the c-axis, respectively. Further, the preference for one or the other type is controlled by the channel alkali content.

**Xuebaoding beryl:** One notable occurrence of beryl is the Xuebaoding greisen-type W-Sn-Be deposit in the Songpan-Ganzi (or Songpan-Garzê) orogenic belt in Sichuan Province, western China (Zhang et al., 2014). Explored since the 1950s, the occurrence is known for scheelite, cassiterite, and beryl of exceptional size and gem quality, with quartz, fluorite, and minor apatite formed in a post-magmatic hydrothermal process (Lin et al., 2000; Zhou et al., 2002; Liu et al., 2005). The abundant beryl is typically transparent and colorless to pale blue. In contrast to the common columnar prismatic habit of beryl parallel to the c-axis, Xuebaoding beryl is primarily of tabular habit parallel to the c-axis. Despite the range of studies having addressed the gemology (Qi et al., 2001a, b, c, d) and mineralogy of beryl from Xuebaoding over more than 2 decades (Guo et al., 2000a, b; Lin et al., 2000; Ye et al., 2001; Zhou et al., 2002; Liu et al., 2007, 2012), its crystal chemistry has not yet been well established with several analytical results either inconclusive or in part contradictory, leading to a confusing picture even about elementary questions of composition and structure. Further, contrasting hypothesis were proposed, with crystal growth controlled by defects and dislocations (Qi et al., 2001b) or by high alkali content at the Be and channel sites (Liu et al., 2012) being responsible for the tabular habit.

**This work:** The goal of this work is a systematic chemical, including trace element, and structural classification of beryl from Xuebaoding and comparison to beryl from other localities, notably of comparable tabular habit. Further, water in its different structural states and its vibrational response are quantified by combining single crystal X-ray diffraction correlated with Raman and infrared (IR) micro-spectroscopy and -imaging.

**Geographic and Geologic Setting**

The sample locality is generally referred to as Xuebaoding (Sichuan Province, China) situated northeast of the Longmen Shan range, at the eastern margin of the Tibetan plateau, at an elevation of 3900 - 4200 m. The locality is named after the mountain Xuebaoding (‘Snow Treasure Crown’, Tibetan name: Shar Dung Ri, elevation 5,588 m). However, Xuebaoding mountain itself is 5.3 km to the NW of the locality, and not visible from the locality, separated by several high ridges and the mountain Sigenxiangfeng (5,360 m). Instead, the peak visible to the immediate NW (Fig. 1a, top left), is Little Xuebaoding (5,443 m) and situated above the valley to the western terminus of the locality area. The confusion between the two peaks, including confusion about first ascends of these mountains persisted well into the 1980s, and until today by the local population, as a reflection of the complex topography and extreme relative relief of up to 4000 m between the valley floors and adjacent peaks, with many of similar altitude.
Tectonically, the area is situated in the Songpan-Ganzi orogenic belt to the west of the Sichuan basis near the contact with the Qinling orogenic belt (north) and the western Yangtze block (east and south-east) (Fig. 1b). The Songpan-Ganzi orogenic belt is the result of two stages of tectonic movements. Following the late Indochina tectonic epoch with long-term intracontinental convergence and associated series of magmatic and metamorphic events, the subsequent Himalayan movement starting at ca. 80 Ma resulted in a pronounced twist in the Songpan-Ganzi orogenic belt (Xu et al., 1992; Kirby and Ouimet, 2011). Along the Minshan (or Min Mountains) the active fault system of the N-S trending Huya fault, a steeply west-dipping reverse fault, contributes to the ongoing uplift of the Minshan. The Huya fault separates Precambrian basement and overlying late Proterozoic to Permian rock units to its east, from the Triassic Songpan-Ganzi flysch sequences to its west (Kirby and Ouimet, 2011). The numerous intruded granites in the eastern margin of the Tibetan plateau have been dated at 220 to 188 Ma (Roger et al., 2004, 2010; Xiao et al., 2007).

**Geology of Xuebaoding deposit**

The Xuebaoding mineralization is associated with several Mesozoic leucogranite intrusions, of a few 100 m to 1 km in extent in outcrop (Pankou, Pukou, Wuzhutang etc.), of similar spatial separation, and dated at 194–201 Ma (Fig. 1c) (Ye et al., 2001; Zhou et al., 2002; Cao et al., 2004; Jiang et al., 2007; Li et al., 2007). Whether these different outcrops are of a single intrusion, or represent separate intrusions, and their relationship is yet unknown. However, their similarities in rock type and associated mineralization suggests a at least a close magmatic relationship.

The granites intruded into upper Triassic Zhuwo series, accompanied by slate, schist, and marble lenticules, as well as layers of marble of shallow metamorphism of late Indosinian orogeny to early Yanshan age (Zhou et al., 2002; Cao et al., 2004; Ottens, 2005; Li et al., 2007). The sequence of layers of sericite-, quartz-, and carbonaceous schist, mudstone, marble, and local skarn, are overturned, with shallow dip to the west, yet steeply dipping to the east of the granite contacts (Fig. 1c).

**Mineral assemblage**

The Xuebaoding locality is a globally significant occurrence of scheelite and cassiterite, in combination with beryl, all of unusual large size, gem color, and crystal quality. It is a greisen-type deposit of quartz and muscovite. Albeit locally variable in relative distribution, the joint mineralization of scheelite, cassiterite, and beryl suggests that it is derived from a highly fractionated and evolved magma in the apical section of the granitic body (Cao et al., 2002, 2004; Li et al., 2007; Zhang et al., 2014; Zhu et al., 2020). Highly enriched in volatiles and metallic elements this gives rise to simple mineralization of large, mostly common, W, Sn, Be, F, and P minerals. The mineralization of muscovite, with fluorite and apatite in addition to the W and Sn mineralization is typical for a S-type granite derived system. The mineralization is fracture-controlled and occurs in sheeted veins and stockwork, emanating from the greisenized granite into the country rock. However, associated post-magmatic alteration of the host rock by
volatiles and solutions derived from the cooling granitic intrusion, as would be typical for greisen, is not very pronounced (Aurisicchio et al., 1994).

Forming interconnected networks of quartz (with muscovite and fluorite), well defined mineralized veins with a N-S trend are primarily found in marble, with a more stockwork type in the surrounding schist. This reflects that the marble is more brittle forming fractures for fluids to circulate and deposit, with the schist more ductile. The different ore veins in granite, marble, and schist as host rock with different generations and conditions with spatial and temporal variations in mineralization exhibit large variations in mineral assemblage - with locally spatial ring fractures, replacement mineral bodies, distal vein emplacement, hydrothermal breccia boiling, and hydrothermal alterations.

**Xuebaoding beryl**

The global occurrence of beryl, especially in large crystals, is typically associated with pegmatites. W and Sn mineralizations often occur simultaneously and associated, but typically without beryl. Mineralization together with W, Sn, and Be is generally uncommon. This combination of W, Sn, and Be mineralization, and that it is not of a pegmatite-type but rather of a hydrothermal/greisen-type, make Xuebaoding unusual.

Despite decades of research since its discovery in the 1950s (Guo et al., 2000a; Qi et al., 2001b; Cao et al., 2002; Zhou et al., 2002; Liu et al., 2012; Zhang et al., 2012), only limited field studies have been performed and the ore forming processes and source of the fluid are not yet clear. Further, despite several ages reported for granite and mineralization, some dates are inconsistent, and unclear if they reflect the mineral formation age.

Xuebaoding beryl is mostly colorless transparent, rarely with a hint of blue. It typically exhibits a simple morphology, yet of characteristic tabular habit shortened in the c-direction, with the most common basal pinacoid (0001), prisms (10̅0), and (11̅21) faces as shown in Fig. 2. The habit is rarely columnar, and if then of low aspect ratio (Fig. 2c).

Numerous studies covering a wide range of techniques have addressed selected aspects of the crystal chemistry of beryl from Xuebaoding (Guo et al., 2000a; Qi et al., 2001b; Cao et al., 2002; Zhou et al., 2002; Liu et al., 2012; Zhang et al., 2012). Specifically, several studies using bulk chemical analysis, electron microprobe analysis (EPMA), and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) identified enrichment in Na⁺ (Na₂O = 0.035–1.66 wt. %) and Li⁺ (Li₂O = 0.63–3.04 wt. %) with variable amounts of Cs⁺ (Cs₂O = 0.11–0.92 wt. %), and minor K⁺ (K₂O = 0.01–1.13 wt. %), Mg²⁺ (MgO = 0.03–0.13 wt. %), Ca²⁺ (CaO = 0.01–0.88 wt. %) and Fe³⁺ (FeO₉ = 0.06–0.54 wt. %) (Liu et al., 2001b, 2005, 2012; Qi et al., 2001b; Zhou et al., 2002) (literature data summarized in Table S1 in Supplement). While some analyses are inconsistent, they confirm the trend which defines Xuebaoding beryl as a lithium-sodium or "tetrahedron" beryl (Aurisicchio et al., 1988, 1994)

A comprehensive EMPA of beryl, whole rock of granite, and fluid inclusions suggested a post-magmatic pneumatolytic-hydrothermal solution as the source of the beryl mineralization
An XRF and LA-ICP-MS trace element analysis, in combination with XRD, and surface textural features, identified Li\(^+\) substitution at the tetrahedral Be\(^{2+}\) site together with divalent cation substitution for Al\(^{3+}\) with associated charge balancing by other alkali on the vacancy site (Liu et al., 2012). The high alkali content (0.255–0.327 apfu, not including Li\(^+\)) was hypothesized to be responsible for the tabular crystal growth (Liu et al., 2012). In contrast, a detailed analysis of surface defects on different crystal phases in combination with a growth rate model as a function of supersaturation (Qi et al., 2001b) suggested interstitial deformation and dislocation sliding responsible for the different growth rate of basal vs. prismatic crystal faces giving rise to the tabular morphology (Zhang et al., 2012).

Several fluid inclusion studies were performed for quartz, beryl and scheelite identifying homogenization temperatures covering a wide range of 214–288 °C (Cao et al., 2002), 158–310 °C (Zhou et al., 2002), 250–292 °C (Chen et al., 2002), 265–315 °C (Lin et al., 2000), 188–373 °C (Zhang et al., 2012), and 266–389 °C (Liu et al., 2005), suggesting a shallow hydrothermal quartz vein type system. These works suggested volatile-rich pneumatolytic-hydrothermal solution derived from post-magmatic fluid as a source of the mineralization (Cao et al., 2002; Zhou et al., 2002). Related work suggests a temperature range of 250–292 °C, at high pressure (about 86 MPa) with high CO\(_2\) density \(d\) (CO\(_2\)) = 0.662 g/cm\(^3\), and low salinity \(w\) (NaCl) = 6.191 wt.% during the formation of beryl (Chen et al., 2002). This is consistent with more recent work (Zhang et al., 2012) suggesting a temperature of beryl formation of ~300 °C.

**Material and analytical methods**

For this study selected single crystals and rock forming beryl were chosen from different veins and collected in situ. The rock forming sample hosted in quartz schist Tzh\(^1\)(1–4) has been extracted from an active mine on the east side of Pankou (thin section 1702B2, for details see Supplement, Fig. S1). Further, from clefts in veins hosted in marble Tzh\(^1\)(5) small single crystals of 0.5–1 cm in size were obtained and cut into thin sections, with 2 samples cut parallel and 4 perpendicular with respect to the \(c\)-axis (1901B1 and 1901B2, for details see Supplement Fig. S1). Lastly several single crystals were collected from open space in veins in the northern area of Pankou (#Q1-Q7, see Supplement, Fig. S1). The different crystal faces were first studied by atomic force microscopy (AFM, AIST Inc., noncontact mode, probe tips from μMasch Inc., spatial resolution better than 10 nm, sample scanner resolution 2 nm), prior the preparation of slabs of 2–3 mm in thickness for EMPA cut along different crystallographic directions perpendicular to (0001), (10\(\overline{1}\)0) and (11\(\overline{2}\)1) (#Q7, #Q3, #Q6), as shown in Fig. 3. Subsequently for IR transmission spectroscopy and imaging, the samples were thinned to about 0.1 mm double sided polished slabs.

Micro-scale compositional mapping and quantitative microanalyses were performed with a JEOL JXA-8230 electron microprobe at the University of Colorado (Department of Geological Sciences). It is a five-spectrometer instrument equipped with argon X-ray detectors (P-10 mixture) on spectrometer 1 and 2, and xenon X-ray detectors on spectrometers 3 to 5. Analytical conditions were 15 kV and 20 nA with a 5 μm beam diameter (samples XBD 19-01-B1 and
Background positions were chosen to avoid interferences. In order to improve precision, a few additional analyses were performed at 50 nA and 10 μm beam diameter (samples #Q7, #Q6 and #Q3). The mean atomic number background correlation was used for all analyses (Donovan et al., 2016). Counting time was optimized to improve detection limit. ZAF matrix correction from (Armstrong, 1988) using the FFAST mass absorption coefficient table (Chantler et al., 2005) was applied throughout. Be-content was recalculated based on stoichiometry, assuming 18 O and 6 Si atoms per formula unit (apfu). Typical detection limits are about 0.01 wt.% for main and minor elements.

Minor and trace elements were measured by LA-ICP-MS at the USGS Denver Federal Center, US. Three beryl crystals with representative primary and secondary crystal phases based on the EMPA were selected. A Photon Machines Analyte G2 LA system (193 nm, 4 ns excimer) was coupled to a PerkinElmer DRC-e ICP-MS. Spot-lined analyses were carried out for known locations, crossing the primary and secondary phase zones. A wavelength of 193 nm was used. Ablation was carried out using an 80-micrometer square spot size at 12 J/cm². Single spot analyses were ablated using 15 pulses/sec (15 Hz). Signals were calibrated using USGS synthetic basalt glass GSE-1g. Silicon (29Si) was used as the internal standard element (using an average Si wt.% content from EMPA data) for concentration calculations (Pauly, 2019).

For X-ray diffraction and structure refinement, fragments were cut from crystal #Q3, #Q6 and #Q7. Single-crystal X-ray diffraction data were acquired on a Brucker P4 four-circle diffractometer (University of Colorado) equipped with a point detector, an APEX II CCD detector, and a rotating Mo-anode generator operating at 50 kV and 250 mA. Unit-cell parameters were refined using the point-detector. The program SHELXL-97 (Sheldrick, 2008) was used to analyze the site occupancies.

Micro-Raman spectroscopy on polished sections and oriented crystals was performed on a setup (XploRA Nano, Horiba Jobin Yvon) based on a confocal Raman microscope, using 532 nm excitation, a 50× objective (NA = 0.5, focus size ~1 μm diameter), with power on sample of about 3 mW. Spectra are acquired using a grating of 1,800 grooves/mm providing for a spectral resolution of 0.5 cm⁻¹, with a thermoelectrically cooled CCD camera. The phonon response of silicon at 520.7 cm⁻¹ was used to calibrate the spectrometer.

Unpolarized micro-IR spectroscopy and imaging was performed in transmission, reflection, and attenuated-total reflection mode (FTIR microscope LUMOS, Bruker Inc.). Background spectra were recorded before the sample measurements in air and subtracted to obtain absorbance spectra of the samples. Measurements were performed in transmission on the double-sided polished crystal slabs of 120 μm thickness or less, with 50 μm spatial resolution, and 2 cm⁻¹ spectral resolution from 800 cm⁻¹ to 6000 cm⁻¹. Point spectra, line scans, and images were acquired after EMPA and LA-ICP-MS and in areas of close proximity to correlate the CO₂ and H₂O IR spectra with the elemental crystal composition. For infrared peak frequencies and mode assignment see Table S2.

Results
1) Surface texture

Optical microscopy and AFM have been used to study the beryl surface texture notably of the (0001), (10\(\bar{1}0\)) and (11\(\bar{2}1\)) crystal faces. As established previously (Qi et al., 2001b), the (0001) face shows hexagonal protrusions representing screw dislocations (Fig. 4a, e). Most of the hexagonal screw dislocations in (0001) display finely spaced growth steps. The (10\(\bar{1}0\)) faces are dominated by left-handed or right-handed screw dislocations of nearly rhombohedral shape with long axis approximately parallel with respect to (0001) (Fig. 4b, f). The screw dislocations grow from the nucleation site in spirals outwards (Qi et al., 2001b). The lower density of the screw steps and kinks on (10\(\bar{1}0\)) compared to (0001) indicates a more rapid crystal growth in the (10\(\bar{1}0\)) lattice plane compared to (0001) leading to the tabular crystal habit (Qi et al., 2001b). In some (11\(\bar{2}1\)) lattice planes of beryl (Fig. 4c, g), the stacking fault defects grow layer-by-layer, until they cover the entire crystal face. Eventually, a step source that no longer disappears is formed at the protrusion of the stacking fault. The stacking fault also acts as the nucleus of the contract twin (Fig. 4k) (Qi et al., 2001b). Occasionally, dispersed heart-shaped step bunching is observed. The dislocation step spirals outwards from the protrusion and forms a closed spiral (Fig. 4d, h). A detailed future study of defects, dislocations, and other structural bulk and surface features may possibly relate these features to crystal morphology and growth environment (Sunagawa, 1984; Scandale et al., 1990; Scandale and Lucchesi, 2000; Tempesta et al., 2011).

2) Chemical composition

Fig. 5 shows optical and EMPA of the narrow vein (thin section 1702B2) containing scheelite at schist contact and beryl in muscovite (Fig. 5a plain light, Fig. 5b UV with scheelite grain fluorescence). The beryl exhibits complex zoning as seen in the example of Fig. 5c (corresponding BSE image Fig. 5d). Quantitative compositional element mapping of Al, Na, Fe, and Cs (Fig. 5e–h, in oxide wt. %) indicates the anticorrelation of Al and Fe, representing the substitution of Al\(^{3+}\) for M\(^{2+}/3+\) cations, and the corresponding positive correlated of Al\(^{3+}\) with Na\(^+\) and Cs\(^+\) for charge balance.

Results of EMPA of 7 representative zones averaged over 3 points of 1702B2 (low Na\(^+\), circles; high Na\(^+\), squares; intermediate Na\(^+\) in beryl in the green area in (a), for details see Fig. 6), as well as analyses of samples 1901B and #Q7 (see analysis points in Figs S2, S3) are summarized in Table 1 and cover the range of compositional variations observed. SiO\(_2\) values range from 64.22 to 65.04 wt. % (ideal 67.07 wt.%) and Al\(_2\)O\(_3\) values range from 17.81 to 18.55 wt. % (ideal 18.97 wt. %). Of the minor elements, Na\(_2\)O dominates ranging from 1.23 wt. % up to 2.01 wt. % and CaO up to 0.49 wt. %. Iron as FeO\(_T\) (total Fe reported as FeO) ranges up to 0.50 wt. %, and MgO up to 0.19 wt. %. Traces of K\(^+\), Ca\(^{2+}\), Ti\(^{4+}\), Mn\(^{2+}\) are close to detection limit of around 0.01 wt. %.

The EMPA calculations (Table 1) are based on 18 O apfu and 3 [Be + Li]. LA-ICP-MS revealed a close correlation between Li\(^+\) and Na\(^+\), allowing for the use of Na\(^+\) as a proxy for Li\(^+\) to a good approximation. Be\(^{2+}\) is thus assumed to be 3 -- Li\(^+\). For comparison, calculation based on the
assumptions of either 18 O and 3 Be, or 6 Si are shown in Table S3 and S4, respectively (Groat et al., 2008; Fridrichová et al., 2016; Lum et al., 2016).

With Si$^{4+}$ ranging from 5.978 to 5.994 apfu this indicates almost full 6 Si T1 site occupation without Si-Al substitution. Na$^+$ ranges from 0.20 to 0.36 apfu, which is much higher than Mg$^{2+}$ (up to 0.027), K$^+$ (0.001-0.004), Cs$^+$ (0.004-0.019), Ca$^{2+}$ (< 0.002), Ti$^{4+}$ (< 0.002), Fe$^{3+}$ (up to 0.034), and Mn$^{2+}$ (< 0.002). Na$^+$ typically occupies the channel site to balance the charge difference by coupled substitution.

LA-ICP-MS is used to determine Li$^+$ and other minor and trace elements. Fig. 7 shows representative results of LA-ICP-MS line scans in samples #Q7, #Q6, and #Q3, selecting regions of primary concentric zoning dissected by secondary veinlets (#Q7, Fig. 7a), typical primary concentric zoning (#Q6, Fig. 7b), or irregular but zoned regions near a crystal surface (#Q3, Fig. 7c), with corresponding LA-ICP-MS transects (Fig. 7d–f) as indicated. A characteristic and correlated increase in Na$^+$ and Li$^+$ is observed in the secondary phases, with corresponding depletion in K$^+$, Rb$^+$, Cs$^+$, Mg$^{2+}$, Mn$^{2+}$, and Fe$^{3+}$. This effect is reflected in the BSE contrast in primary as well as secondary growth darker areas corresponding to higher light element content of Li$^+$ and Na$^+$, with depletion in the heavy elements.

Representative quantitative LA-ICP-MS results are listed in Table 2, with calculated apfu values based on assuming 6 Si. Consistent with EMPA result, Na$^+$ ranges from 0.25 to 0.37 apfu, compared to minor Cs$^+$ (0.0035-0.016), Mg$^{2+}$ (0.000-0.017), Fe$^{3+}$ (0.000-0.015), and only traces of other elements. In the primary zones, Na$^+$ (0.246-0.268) is considerably less than in the secondary zones with Na$^+$ (0.354-0.371) yet closely correlated with the amount of Li$^+$ in primary (0.254–0.272) and secondary beryl (0.347–0.368).

In summary, these results show the presence of an only weak Al$^{3+}$ A-site for 2+ cations substitution vector, but a dominating Li$^+$ T2-site for Be$^{2+}$ substitution vectors (see discussion below).

3) Crystallography and structure refinement

The refined crystal-structure parameters as well as data collection parameters, are summarized in Table 3. The unit-cell parameters were refined from centering angles of 60 strong reflections with 2 between 10 and 28° using a point detector system on a Bruker P4 diffractometer. The a-axis values of the lattice range from 9.2161 to 9.2171 Å, while c-axis values range from 9.2178 to 9.2219 Å, and the unit-cell volume ranges from 678.03 to 678.48 Å$^3$. The c/a ratio ranges from 1.0002 to 1.0005 and is consistent with T2 type beryl, with unit-cell controlled primarily by Be$^{2+}$ substitution (Aurisicchio et al., 1988, 1994). Intensity data were measured using a Bruker APEX II CCD detector out to a two-theta angle of about 80° (Table 3). Atom position, displacement parameters, and cation occupancies were refined using SHELXL (Sheldrick, 2008) based on ionized atom scattering factors for cations (Cromer and Mann, 1968) and O$^2-$ (Azavant and Lichanot, 1993). Atom position, displacement and occupancy parameters are given in Supplement Table S5.
Selected bond distances derived from refinements using ionized-atom scattering factors are shown in Table 4 (Liu et al., 2007; Robinson et al., 1971) (further details and atomic position coordinates and anisotropic displacement parameters are listed in Supplement, Table S5). Here, O1 indicates oxygen linked with Si, while O2 indicates the oxygen shared by Si, Al, and Be. Si-O has the shortest (1.61 Å) while Al-O has the longest bond length (1.91 Å).

The derived crystal structure is shown in Fig. 8a (projected onto (0001)) and Fig. 8b with its edge-linked distorted tetrahedrally coordinated T2 (Be) and octahedrally coordinated A (Al) sites. Crystal channels are characterized by the wide C1/2a site between the rings and narrow C2/2b site of the interior of the tetrahedral \([\text{Si}_6\text{O}_{18}]^{12-}\) ring with diameters \(~5.2\ \text{Å}\) and \(~2.6\ \text{Å}\), respectively. Fig. 8c shows C2 site occupation with Na\(^+\) and associated type IIId, IIs, and I water configurations, with the distinct coordination of two water molecules to Na\(^+\) (type IIId), one water molecule and optionally C1 site occupation with CO\(_2\) (type IIs), or the alkali cation free water configuration (type I) (Fridrichová et al., 2016).

Generally similar site occupancy values for the different lattice sites are found for all three crystals analyzed. The A, T1, and T2 sites are almost fully occupied. The site population calculation is in good agreement with the EMPA and LA-ICP-MS analyses with a significant Li\(^+\) substitution for Be\(^{2+}\) (T2), minor M\(^{2+}\) substitution for Al\(^{3+}\) (A), charge balanced predominantly by Na\(^+\) as the only alkali occupying the small C2 site, and the larger alkali (K\(^+,\) Cs\(^+,\) Rb\(^+)\) and Fe\(^{2+}/3+\) together with water and minor CO\(_2\) on the C1.

4) Raman spectroscopy

Representative polarization resolved Raman spectra reflecting the different crystal orientations and type I and II water orientation are shown in Fig. 9. Here, E\(_{\text{inc}}\) and E\(_R\) represent incident fundamental pump polarization, and Raman scattered polarization, respectively. All spectra of different sample locations have negligible background indicating high structural integrity and overall low defect/inclusion density. The peaks below 1400 cm\(^{-1}\) are associated with beryl lattice phonon modes (For Raman peak frequencies and mode assignment see Table S6 (Kim et al., 1995; Qi et al., 2001b). The strong peaks at 685 cm\(^{-1}\) and 1066 cm\(^{-1}\) are due to Si-O vibrations. The modes at 322 cm\(^{-1}\) and 396 cm\(^{-1}\) are Al-O bands. The two bands at 524 cm\(^{-1}\) and 1009 cm\(^{-1}\) represent Be-O vibrations. In the water stretch region the two and only partially resolved peaks are due to type II (3594 cm\(^{-1}\)) and type I (3604 cm\(^{-1}\)) water.

Fig. 9a and 9b shows the non-degenerate symmetry modes (A\(_{1g}\)) which have the strongest Raman response. Fig. 9c and 9d present the doubly degenerates symmetry modes E\(_{1g}\). Water Raman emission polarized perpendicular with respect to the c-axis of beryl is weak when incident field is polarized parallel with respect to the c-axis as expected and shown in Fig. 9d. Fig. 9e and 9f present the doubly degenerate symmetric modes E\(_{2g}\) in which 398 cm\(^{-1}\) and 684 cm\(^{-1}\) are due to Si-O and Al-O vibrations, respectively, and with corresponding water peak (Kim et al., 1995; Hagemann et al., 1990). The combination of Fig. 9b and 9f confirm the expected molecular orientation of type I and type IIs water (Hagemann et al., 1990). Type I is expected to be more polarizable along the c-axis, and thus stronger in Fig. 9b, while type II is expected to be
more polarizable perpendicular with respect to the c-axis and thus stronger in the polarization combination of Fig. 9f as observed. Polarized Raman spectra with incident wave vector perpendicular with respect to the (1010) face and unpolarized Raman spectra are shown in Fig. S4.

5) Micro-IR spectroscopy and mapping of water content

Fig. 10 shows a representative IR point spectrum (a) from transect #Q3-7 (b) acquired parallel with respect to the LA-ICP-MS line on #Q3 in Fig. 7 (see also inset Fig. 10b). Infrared peak frequencies and mode assignment are listed in Table S2 (Charoy et al., 1996; Qi et al., 2001d; Łodziński et al., 2005; Adamo et al., 2008; Della Ventura et al., 2015; Mashkovtsev et al., 2016). The spectrally narrow bending ($v_2^I$) and asymmetric stretch ($v_3^I$) of type I (1600 and 3694 cm$^{-1}$), bending ($v_2^{II}$) and symmetric stretch ($v_4^{II}$) of type II's water (1637 and 3588 cm$^{-1}$), and asymmetric CO$_2$ stretch (2358 cm$^{-1}$) modes can be discerned. The broad peak at ~1950 cm$^{-1}$ has been assigned to the overtone absorption of a lattice phonon mode (Charoy et al., 1996). The zoomed in transect to the type I and II stretch modes in Fig. 10b shows an inversion in relative type I and II water content at the transition from primary to secondary beryl. Further, the type II peak is split as seen in the zoomed in region of Fig. 10c, with the main peak $v_4^{II}$ at ~3588 cm$^{-1}$ corresponding to type II's water and the shoulder at ~3630 cm$^{-1}$ corresponding likely to a combination of the symmetric stretches of type I ($v_4^I$) and type II water ($v_4^{II}$). The minor peak at about 3651 cm$^{-1}$ is due to the antisymmetric stretch of type II's water ($v_3^{II}$).

To determine relative peak intensities, the spectra are fit using simple Lorentzian lineshapes, with 5-6 peaks (dashed lines in Fig. 10c, see also supplement Fig. S5), with center frequencies of $v_4^{II}$ and $v_3^I$ of 3588 cm$^{-1}$ and 3694 cm$^{-1}$, respectively. The frequencies vary by less than ±1 cm$^{-1}$ between primary and secondary crystal phases.

Fig. 11a shows the spatial variation of the relative IR peak absorption for type I and II's water and CO$_2$ across the primary and secondary phase. The increase in spectral intensity of $v_4^{II}$ (orange) is observed in the secondary phase (1.0 to 1.7 mm), while $v_3^I$ (brown) decreases. The mixed shoulder at ~3605 cm$^{-1}$ (black) correlates with the $v_3^I$ intensity, suggesting that it is primarily associated with $v_3^I$. Additionally, the CO$_2$ stretch (purple) slightly decreases in the secondary phase.

The corresponding absolute amount of water can be estimated based on the Lambert-Beer law $A = \varepsilon \cdot c \cdot d$, where $A$ is the absorbance, $\varepsilon$ the molar absorption coefficient (L/mol·cm), $c$ the water concentration (mol/L), and $d$ the sample thickness (cm) (Fukuda et al., 2009). In our case, the sample thickness of #Q3 is ~120 μm. We use reported molar absorption coefficients of type I (3696 cm$^{-1}$) and type II's (3588 cm$^{-1}$) water modes of $\varepsilon_1 = 197$ (L/mol·cm) (Charoy et al., 1996), and $\varepsilon^{II} = 256$ (L/mol·cm), respectively, (Goldman et al., 1977) While the value for $\varepsilon^{II}$ is for cordierite, we expect it to equally apply for beryl to a good approximation given the similarity in water structure and index of refraction in the IR. Absorption peak intensity $A$ for each mode is approximated by the ratio of fitted peak area and line width. Using a density value of beryl
calculated from XRD of $\rho = 2.75 \text{ g/cm}^3$, with its variation with $\text{Na}^+$ content negligible for our case, the amount of water can be obtained as $\text{H}_2\text{O}_{\text{tot}} \text{ (wt. \%)} = c \times \text{M} \times 10^{-1}/ \rho$ where M is the molar mass of water. An ideal and maximum 1 apfu water on C1 corresponds to 3.24 wt. % for an ideal beryl with $M = 537.47 \text{ g/mol}$ (Hawthorne and Černý, 1977; Pankrath and Langer, 2002).

The resulting apfu values based on the Lambert-Beer law for $v_{1}^{\text{II}}$ and $v_{3}^{\text{I}}$ from Fig. 11a and their sum are shown in Fig. 11b. Type IIIs water (orange) increases from 0.20 apfu in the primary phase to 0.38 apfu in the secondary phase, and positively correlates with $\text{Na}^+$ (red), and anticorrelates with $\text{Fe}^{3+}$ (green) based on the co-localized LA-ICP-MS transect. Meanwhile, type I water (brown) decreases from 0.21 apfu in the primary apfu to 0.12 apfu in the secondary phase. It appears that the ~50% decrease of type I water in the secondary zone is more than compensated by a corresponding increase in type IIIs water, with the total water content ($v_{1}^{\text{II}}+v_{3}^{\text{I}}$) (blue) increasing from 0.42 apfu in the primary phase to 0.50 apfu in secondary beryl.

The amount of water of 0.42 apfu determined for the primary phase by IR absorption is in good agreement with the value of 0.40 apfu derived from XRD (Table 5). The XRD result further suggests that the C1 site is almost half occupied with combination of the trace amount of alkali K$^+$, Cs$^+$, and Rb$^+$, and water (see Table 5). The approximately equal total amount of water in primary and secondary beryl is interesting to note, with primarily a change in ratio of type I to type II water, which is controlled by the different $\text{Na}^+$ content (occupying the C2 site).

Fig. 12 shows corresponding spatial images of type I water (a, d), type II water (b, e), and CO$_2$ (c, f) peak integrated values for the two crystal regions #Q3-2 (a-c) and #Q3-9 (d-f) as indicated in Fig. 3c and acquired in proximity and an either side of the LA-ICP-MS trace (images of minor band centered at 3605 cm$^{-1}$ is shown in Fig. S6 and full width at half maximum of type I in S7). Akin to the IR line trace analysis above, the same anticorrelation of type I and type II water, and correlation of type I water with CO$_2$ stand out.

Discussion

1) Coupled Substitution

In the following we analyze the role of the two primary substitution vectors for the octahedrally-coordinated A and tetrahedrally-coordinated T2 site for our study (Belov, 1958; Wood and Nassau, 1968; Bakakin et al., 1969; Hawthorne and Černý, 1977; Aurisicchio et al., 1988; Sherriff et al., 1991) with

$$3^{\text{T2}}\text{Be}^{2+} + \square \rightarrow (3-n)\text{Be}^{2+} + n^{\text{T2}}\text{Li}^+ + n^{\text{CR}}^+$$

(1)

and

$$2^{\text{A}}\text{Al}^{3+} + \square \rightarrow (2-k)\text{Al}^{3+} + g\text{X}^{2+} + (k-g)\text{Y}^{3+} + g^{\text{CR}}^+$$

(2)

where $\text{R}^+$ represent alkali ions, $\text{X}^{2+}$ the divalent cations, $\text{Y}^{3+}$ trivalent cations, with respective coefficients $n$, $k$, and $g$. 

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Summarizing the data from all EMPA and LA-ICP-MS analyses in Fig. 13 shows the corresponding correlations for A and T2 site substitution and indicates an only weak coupling between the two substitution vectors.

Fig. 13a shows the anticorrelation of $2^+/3^+$ cations with $\text{Al}^{3+}$ content based on sets of EMPA values from different samples (#Q3, #Q6, and #Q7), in comparison with the theoretical behavior based on eq. 2 with slope -1. Here we assume that all $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions occupy the A site. The small deviation of the data from the ideal behavior is likely due to slightly too high Al EMPA values, as supported by XRD suggesting $\text{Al} < 2$ apfu, or that Fe is dominated by $\text{Fe}^{3+}$ (see also below). But overall, the role of A-site substitution is small, with the sum of divalent trace elements ranging from as low as $\sim 0.001$ apfu to a maximum value not exceeding $\sim 0.06$ apfu.

Fig. 13b shows the positive correlation of Na$^+$ with Li$^+$ closely following the ideal behavior with slope 1. This shows that the substitution vector eq. 1 is dominated by Na$^+$ alone, which ranges from 91.5%–99.7% (apfu) of the sum of all alkali elements, and charge balancing for Li$^+$ as it substitutes for $\text{Be}^{2+}$. This suggests that the remaining alkalis K$^+$, Rb$^+$, and Cs$^+$ are primarily charge balancing the $\text{Al}^{3+}$ substitution for divalent cations at the A site. Note the bimodal distribution with lower Li$^+$ and Na$^+$ content in the primary, and higher Li$^+$ and Na$^+$ values in the secondary phases. Correspondingly this behavior is to first order inverse for the other alkalis vs. X$^{2+}$ cations (Fig. 13d). This suggests that in the secondary phase the role of the T2 substitution vector (eq. 1) increases, whereas the A substitution vector (eq. 2) diminishes. The deviations of certain data groups (green and red) in Fig. 13d with anticorrelation in Fig. 13b suggests a weak coupling between the two substitution vectors through the alkali R$^+$ mixing.

Combining both substitutions of eq. 1 and 2 Fig. 13c shows the sum of the vector Li$^+$ for $\text{Be}^{2+}$ at the T2 site, and the sum of all divalent cations to replace for $\text{Al}^{3+}$ at the A site, i.e., the combination of both substitution vectors and their charge balance by the sum of all alkali cations. The good agreement with the theoretical slope 1 of all data, in contrast to (b) or (d) suggests that all iron at the A site is trivalent, i.e., not necessitating charge balancing with alkali (Fe with other divalent cations vs. alkali elements see Supplement Fig. S8).

The combined results can then be expressed by the empirical formula:

$$T_2(\text{Be}_{2.62-2.75}\text{Li}_{0.25-0.38}\text{Al}_{2.00}^3)[\text{Al}_{1.94-2.00}\text{(Mg,Fe}^{3+},\text{Ca,Mn,Ti)}_{-0.06}]_{\text{2.00}}^2\text{Si}_6\text{O}_{18}^{2+}[(\text{Na}_{0.25-0.36}\text{(K,Rb,Cs)_0.06})_{\text{2.06}}^2\text{C}_2(\text{H}_2\text{O}_{0.4-0.5}\text{(CO}_2)^{-0.01})]$$

In accordance with the IMA-CNMNC rules (Bosi et al., 2019), this formula leads to the end-member composition $T_2\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ (beryl). In summary, the studied sample can be classified as (Li, Na) beryl.

2) Crystal structure

The Si value close to ideal 6 apfu by EMPA indicates the negligible Si-Al substitution. The tetrahedral volumes are 2.133, 2.133, and 2.136 Å$^3$ for #Q7, #Q6, and #Q3 (Table 4), respectively, values typical for pure Si tetrahedral sites.
The distinct coordination of water with Na\(^{+}\) features a shorter bond length of H-O1 for type IIs compared to type IId (Fukuda and Shinoda, 2008, 2011). This results in a correspondingly larger bond strength giving rise to a higher frequency of the IR bending mode. Our type IIs bending mode value of 1637 cm\(^{-1}\) agrees with the range of theoretical peak positions of 1637–1639 cm\(^{-1}\) for type IIs water rather than 1624–1627 cm\(^{-1}\) for type IId water (Fridrichová et al., 2016).

Theoretical Na-O bond lengths of type IIs and IId are 2.227 Å and 2.483 Å, and Na-O1 bond lengths of IIs and IId are 2.558 Å and 2.540 Å, respectively (Fridrichová et al., 2016). The IIs values are in good agreement with our measured values of the average Na-O and Na-O1 band lengths of 2.305 Å and 2.556 Å, respectively. This indicates the Na bound water is primarily type IIs.

3) Water content

The water estimates based on the absolute IR absorbed intensity, consistent with the results from XRD informed by LA-ICP-MS, indicate that the water occupancy ranges from 0.4 apfu to 0.5 apfu in #Q7, which is close to half of the maximum water occupation with an approximate stoichiometry of Be\(_2\)Al\(_2\)Si\(_6\)O\(_{18}\) \(\cdot\) 0.5 H\(_2\)O. Similarly, from XRD, the water occupation is close to 0.5 apfu for #Q6 (0.46), yet slightly low for #Q7 (0.37) and #Q3 (0.40). The Na\(^{+}\) content (C2 site/2b-site) controls the dipole orientation and types of water on the channel site in the center of the Si rings (C1/2a-site) with type II water correlated with Na\(^{+}\) content as expected.

Few other studies have yet addressed the water content in Xuebaoding beryl. Only (Guo et al., 2000b; Lin et al., 2000) have estimated the water content using a wet chemical method and obtained values of 1.97 wt.% to 3.56 wt.% corresponding to apfu values ranging from 0.61 to 1.13, with the later value exceeding the maximum possible value of 1 apfu.

From other localities, water content in beryl was determined by wet-chemical analyses (Charoy et al., 1996; Guo et al., 2000b; Lin et al., 2000), thermogravimetric analyses (Artioli et al., 1993; Pankrath and Langer, 2002; Gatta et al., 2006; Fridrichová et al., 2016), or based on the empirical equation H\(_2\)O (in wt%) =\([0.84958 \times \text{Na}_2\text{O} \text{ (in wt%)}] + 0.8373\) (Giuliani et al., 1997; Groat et al., 2008; Fridrichová et al., 2016), with values ranging from less than 1 wt% to more than 3 wt%. However, these methods structure sensitivity to the type of water, or may overestimate including fluid inclusions or water on grain boundaries. This highlights the value of quantitative micro-IR spectroscopy with spatial resolution and site specificity.

4) Comparison with previous Xuebaoding beryl studies

The results of EMPA and LA-ICP-MS are in agreement with some but not all prior studies of beryl from Xuebaoding which are summarized in Table S1 and S7 in the supplement. In general good agreement is found with (Guo et al., 2000b; Qi et al., 2001b; Zhou et al., 2002). Yet results from (Liu et al., 2001b), with identical results in (Liu et al., 2005) are inconsistent, reporting too high SiO\(_2\) (66.04–67.25 wt%) and too low Na\(_2\)O (0.42–0.83 wt%). A bulk wet chemical analysis (Liu et al., 2001a; Qi et al., 2001c) with same data in (Liu et al., 2005) and again in (Liu et al., 2007) is in general agreement, except their third set of data with too low Na\(_2\)O (0.27 wt%) and
too high FeO\(^{1}\) (0.76 wt%) (bolded data in Table S7). However, a later analysis by the same authors using LA-ICP-MS and XRF (Liu et al., 2012) is again inconsistent with implausibly high Li\(^{+}\) (Li\(_2\)O 2.60-3.04 wt%) that cannot be charge balanced by the other alkali as quantified. A single wet chemical analysis (Lin et al., 2000) reports exceptionally high Fe (0.67 wt%) and Ca (0.88 wt%).

Our XRD unit-cell parameter derived are in good agreement with an earlier analysis of (Guo et al., 2000a) with \(a = 9.209(2) \, \text{Å}\) and \(c = 9.2221(9) \, \text{Å}\) with \(c/a = 1.0001\). However, our results are in disagreement with (Liu et al., 2007) that reports implausibly short a and b values based on small number of reflections and poor R value. Instead, our results are in better agreement with earlier (Liu et al., 2005) and later work (Liu et al., 2012) by the same authors.

5) Comparison with beryl from other localities

The Xuebaoding beryl is overall characterized by a simple chemistry with minor octahedral (A) site substitution with Fe\(^{3+}\) and Mg\(^{2+}\) and negligible Ti\(^{4+}\), Zn\(^{2+}\), or Ca\(^{2+}\) with charge balance through Cs\(^{+}\) and minor Rb\(^{+}\) and K\(^{+}\). Fe as Fe\(^{3+}\) is suggested to substitute for Al\(^{3+}\) on the A site (Aurisicchio et al., 1988; Neiva and Neiva, 2005; Groat et al., 2008, 2010). The low Fe\(^{3+}\) content is consistent with a only light color trend towards blue (aquamarine) (Mihalynuk and Lett, 2003; Fridrichová et al., 2015; Lum et al., 2016). Appreciable Li\(^{+}\) substitution for Be\(^{2+}\) on the tetrahedral (T2) site with Li\(^{+}\) up to 0.38 is on the high end compared to other localities worldwide (Aurisicchio et al., 1988) and charge balanced by Na\(^{+}\) incorporation on the channel site. This classifies the Xuebaoding beryl as “(Na, Li) beryl” (Černý, 1975) as typically associated with Li-rich pegmatites, and of the crystallographic ‘tetrahedral’ variety, i.e., the dominance of the T2 site Li substitution as opposed to A-site substitution (Aurisicchio et al., 1988).

Compared to beryl from other localities worldwide, the chemical composition and structure of beryl from Xuebaoding do not stand out in any particular way (Hawthorne and Černý, 1977; Aurisicchio et al., 1988, 1994; Sherriff et al., 1991; Artioli et al., 1993; Černý et al., 2003; Groat et al., 2008; Lum et al., 2016). The Si\(^{4+}\) content of most beryl is close to 6. Al\(^{3+}\) apfu values generally range from as low as 1.2 in few cases, to 2, with majority of data above 1.5 apfu, compared to Xuebaoding beryl with Al\(^{3+}\) close to 2 apfu. Be\(^{2+}\) ranges from 2.5 to 3.0 apfu (Hawthorne and Černý, 1977; Aurisicchio et al., 1988, 1994; Sherriff et al., 1991; Artioli et al., 1993; Černý et al., 2003), similar to Xuebaoding beryl varying between 2.62 and 2.75. Be\(^{2+}\) substitution for Li\(^{+}\) and correlated with Na\(^{+}\) is observed frequently with Li\(^{+}\) ranging from 0 to 0.5 (with Xuebaoding Li\(^{+}\) of 0.25 to 0.4 in the middle of that range).

With site substitution controlling the unit-cell parameters (Pankrath and Langer, 2002), the values for the a-axis range from 9.202 to 9.228 Å and c-axis from 9.185 to 9.240 Å (Hawthorne and Černý, 1977; Aurisicchio et al., 1988; Sherriff et al., 1991; Artioli et al., 1993; Černý et al., 2003). Corresponding values for Xuebaoding beryl fall within the middle of that range. Notably similar in composition and unit-cell parameter to Xuebaoding beryl #Q7 is beryl from the Mount Bity region, Madagascar (pale pink sample #18) (Aurisicchio et al., 1988), with Si\(^{4+}\) = 6, and
Al$^{3+} = 2$, Li$^+ = 0.27$ substituting Be$^{2+}$ at T2 site, and Na$^+ = 0.18$ and Cs$^+ = 0.02$ occupy the channel to charge balance, resulting the $a = 9.215$ Å, $c = 9.218$ Å, closely resembling the Xuebaoding beryl values of $a = 9.2161$ Å and $c = 9.2178$ Å. The beryl from Pala, California, USA (pale pink sample #28) (Aurisicchio et al., 1988) with $a = 9.213$ Å and $c = 9.212$ Å, and with similar composition of Si$^{4+} = 5.996$, Al$^{3+} = 2.004$, but lower Li$^+$ = 0.17 and Na$^+$ = 0.14 matches closely Xuebaoding sample #Q7.

6) Comparison with tabular beryl worldwide

A particular feature of Xuebaoding beryl is the tabular habit. Similar tabular habits are observed, e.g., in morganite (pink beryl) (Cook, 2011) from San Diego County, yet exhibit dominance of A-site substitution (Mn$^{2+}$) with charge balanced by Cs$^+$ (on C1) and low water content. Clear beryl (goshinite) from lithium-rich microcline-albite pegmatites from Minas Gerais, Brazil (Cook, 2011) sometimes occur as tabular crystals, with high Li$^+$ and Na$^+$ content and are water rich (Fukuda and Shinoda, 2011). Similarly, tabular beryl from the Bikita rare-element granitic pegmatite (Zimbabwe) exhibits high Li$^+$ content and T2-site substitution (Černý et al., 2003) with alkali charge balancing, and only minor A-site substitution. The beryl group member pezzottaite with maximum lithium substitution on T2 (ideally Cs(Be$_2$Li)Al$_2$Si$_6$O$_{18}$) (Yakubovich et al., 2009) also exhibits tabular habit. However, based on our study the major and trace element characteristics and site occupancies of Xuebaoding beryl does not stand out in any distinct way compared to beryl from other localities worldwide of the usual columnar habit.

The crystal chemistry of the Xuebaoding beryl, while not deterministic with regards to the crystal habit, may give some insight into the evolution of the ore forming fluids (Černý, 2002; Černý et al., 2003; Uher et al., 2010; Sardi and Heimann, 2014). The alkali and ferromagnesian content can reflect the evolution and composition of the host fluid to some degree (Černý, 1975).

Summary and Implications

Overall, the Xuebaoding beryl exhibit very similar tabular habit throughout the deposit, only rarely columnar, or etched. This suggests generally similar and stable conditions during the crystallization of the veins. The low Fe$^{3+}$ and Mg$^{2+}$ content is consistent with the low degree of Fe$^{3+}$ mineralization in general (minor pyrite). The secondary phases in crystal sections or metasomatic replacement with decrease in Fe$^{3+}$ and Mg$^{2+}$, yet increase in Na$^+$, indicate a further evolution and fractionation of the fluid in its late stage. This would support the hypothesis of early crystallization of aquamarine with goshenite being late. These observations relate to the suggestion that goshenite is associated with highly evolved fluids, e.g., in pegmatites (Černý et al., 2003; Neiva and Neiva, 2005; Wang et al., 2009) and with the limited Fe$^{3+}$ and A-site substitution not being of magmatic origin. These results are further consistent with the understanding that the Xuebaoding W-Sn-Be-F-P mineralization is primarily hydrothermal in origin and derived from a highly evolved fluid emerging from the Pankou and Pukouling albite leucogranites that are highly fractionated, alkali, peraluminous, Li-F-enriched (Zhu et al., 2020) giving rise to the beryl, cassiterite, scheelite, fluorite, and apatite mineral assemblage.
The tabular habit is thus likely not causally related to chemical composition and alkali content. However, the factors that control crystal habit in this and other localities remain unknown. More plausible than a chemical effect is the role of pressure and temperature, giving rise to anisotropy in lattice compressibility and thermal expansion. That may control not only the size of lattice sites affecting substitution, but also the free energy of and preferential growth along particular crystallographic directions. Understanding the relationship of crystal habit to chemical, pressure, and temperature conditions of the source fluid would be a subject of considerable general importance.

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Fig. 1. (a) Xuebaoding locality, with Little Xuebaoding (5,443 m, left) in background, and mineralized zones along marble band with white mine tailings, further along and below both sides of ridge to the right (mining camp at bottom right); (b) Generalized geological map of eastern margin of Tibetan plateau with Xuebaoding (XBD) mountain west of the Huya fault and to NE of the Longmen Shan range and uplift zone defined by Yingxiu-Beichuan (Y-B) and Wenchuan-Maixian (W-M) faults; major peaks of Siguniangshan (4G) and Xuebaoding (XBD) indicated (modified with permission after Kirby and Ouimet, 2011); (c) Geologic map of the main locality area (pink rectangle in (b)) associated with outcropping granite bodies Pukoupo, Pankou, and Caodi (defining the cirques in (a)). Legend: 1: normal fault, 2: highly mineralized quartz vein containing beryl, scheelite, and cassiterite, 3: overturned dip and strike (modified after Zhou et al., 2002). Rock units: Tzh\(^{1-4}\) quartz schist, marble, biotite-quartz schist; Tzh\(^{1-5}\) ore-bearing strata, marble; Tzh\(^{1-6,8}\) calcareous quartz schist, sericite quartz schist; \(\gamma_{A-C}\) granite margin through transition to core zone. The W-Sn-Be mineralization is concentrated throughout schist and marble within < 100 m from the granite intrusions.
Fig. 2. Examples of representative Xuebaoding beryl habits: (a) cluster of tabular beryl with muscovite (largest crystal 25 mm in width); (b) individual clear tabular crystal (40 mm in width); (c) rare columnar habit (on albite, 25 mm in width), light blue, with typical dislocation texture on (0001); (d) schematic of tabular habit.

Fig. 3. Beryl samples as cut and studied from larger single crystal specimens: (a) #Q7, (0001) faces; (b) #Q6, (1121) faces; (c) #Q3, (1010) faces. Indicated are positions of LA-ICP-MS transects (white arrows, Fig. 7), BSE imaging (white rectangles, Fig. 7), micro-IR transects and mapping (red dashed line and rectangles, Figs. 10-12), XRD (chips cut at dashed green triangles), and EMPA (blue dots).
Fig. 4. Surface texture of different crystal faces of Xuebaoding beryl. (a-d) unpolarized optical microscope images of #Q7, #Q3, #Q6 and #Q5, respectively. (e-f) AFM images of areas indicated in (a-d) (red square). (i-l) differential interference microscope images of similar defects on corresponding faces [modified after (Qi et al., 2001a)]. (a, e, i) are (0001) faces, (b, f, j) are (10̅0) faces, and (c, d, g, h, k, l) are (11̅21) faces.

Fig. 5. Narrow vein of muscovite in schist with scheelite and beryl (thin section 1702B2): (a) plane light; (b) UV
light; (c) beryl under crossed polarized light (red area from a); (d) corresponding BSE image. Quantitative EMPA mapping (scale bar oxide wt. %) of Al₂O₃ (e), Na₂O (f), FeO (g), and Cs₂O (h) of yellow region indicated in (c) with zoning and coupled substitution. Data for EMPA point analyses (open circles and squares in (f)) in Table 1. For BSE and EMPA data of second area (green rectangles in (a) and (b)) see Fig. 6.

**Fig. 6.** Concentric zoning of beryl of thin section sample 1702B2 (green box in Fig. 5a and 5b). (a) optical microscope image under crossed polarization, (b) BSE image with EMP transect (red dots), Δ indicate the selected measured points listed in Table 1. (c-f) quantitative mapping of selected area for Na₂O, Cs₂O, Al₂O₃ and FeO in wt. %, respectively.
Fig. 7. Representative BSE images of single crystal samples #Q7 (a), #Q6 (b), and #Q3 (c), with LA-ICP-MS transects (d-f, dashed lines in (a) and (c)): Transect (d) location is ~0.3 mm just left of field of view in (a) at extension of meandering secondary feature. Transect (e) is not related to (b) with location indicated in Fig. 3b. Transect (f) shown in (c) as indicated, the full position is shown in inset of Fig. 10b. The LA-ICP-MS elemental pattern reflects primary and secondary beryl phases, with characteristic correlation of Na and Li, both anticorrelated with all other trace elements. Area in (c) (red dashed rectangle) indicates micro-IR mapping #Q3-2 as shown in Fig. 12.
Fig. 8. Crystal structure of beryl: (a) along orientation parallel with respect to c-axis, and (b) perpendicular with respect to c-axis, with octahedral A (Al), tetrahedral T2 (Be), Si, and two channel sites at the C1/2a (H₂O, large alkali) and C2/2b (Na) positions; (c) type Ild, type IIs, and type I H₂O molecule configuration, with corresponding Na⁺ and CO₂ positions on channel sites after (Fridrichová et al., 2016).
Fig. 9. Polarized Raman spectra of beryl. (a-b) $k \perp c$-axis and $E_{inc} // c$-axis and $E_R // c$-axis, (c-d) $k \perp c$-axis and $E_{inc} // c$-axis and $E_R \perp c$-axis, (e-f) $k \perp c$-axis and $E_{inc} \perp c$-axis and $E_R \perp c$-axis. $k$ is the incident wave-vector, $E_{inc}$ and $E_R$ are the polarization directions of the fundamental and Raman light, respectively. The crystallographic $z$-axis is parallel to optical $c$-axis. $A_{1g}$ indicate the non-degenerate symmetric modes, $E_{1g} / E_{2g}$ indicate the doubly degenerate symmetric modes. Peak assignments are listed in Table S6.
Fig. 10. IR point spectrum and micro-IR transect #Q3-7 (for location see Fig. 3c): (a) Peak assignment with type I water (1600 and 3694 cm\(^{-1}\)), type II water (1637 and 3584 cm\(^{-1}\)), and CO\(_2\) (2358 cm\(^{-1}\)); (b) IR spectral transect with spectra centered on the water stretch region crossing secondary beryl zone (red) with primary beryl on either side (black). (inset: optical micrograph, with IR transect in red and LA-ICP-MS line in black); (c) representative spectra from primary (blue) and secondary (red) zone with intensity anticorrelation of type I and type II water, with Lorentzian line fits (dashed) for type IIs (3588 cm\(^{-1}\)), mixed type IId/I (3605 cm\(^{-1}\)), and type I (3694 cm\(^{-1}\)) (for details see also Fig. S5).

Fig. 11. IR and ICPMS transect analysis of #Q3-7 (see Fig. 3c and Fig. 7c): (a) IR-absorbance from Lorentzian peak fits showing qualitative correlated and anti-correlated variations of CO\(_2\), type I and IIs water across primary and secondary zones; (b) Quantitative comparison of type I and type IIs (type IId negligible) water (apfu) derived from absolute IR absorption cross sections, in relation to Na and Fe content from LA-ICP-MS.
Fig. 12. Micro-IR imaging on primary and secondary beryl of #Q3-2 (a–c) and #Q3-9 (d–f) (area indicated in Figs. 3c, 7c), based on peak intensities of (a and d) type I water (3694 cm⁻¹), (b and e) type IIs water (3584 cm⁻¹), and (c and f) CO₂ (2358 cm⁻¹). Type I water is less (blue area in (a and d)), while type IIs water is more in the secondary phases (red area in (b and e)). CO₂ (c and f) correlates with type I water.
Fig. 13. Correlations and trends in major element variations: (a) Linear correlation between A-site Al and corresponding $X^{2+}$ (divalent ions at A-site) substituents; (b) Correlation between T2 $Li^+$ substitution for $Be^{2+}$ with $Na^+$ charge balancing on the C2 site; (c) combined A and T2 substitution expressed as $R^+$ (monovalent alkali ions in channel) vs. $Li^+ + X^{2+} - Fe^{3+}$ with linear correlation; (d) $R^+ - Na^+$ vs. $X^{2+}$ with inversely correlated deviations of some data groups compared to (b), indicating weak coupling between the two substitution vectors. (a) based on microprobe data, (b-d) LA-ICP-MS data. Black lines represent the ideal substitution or charge balance relationship, $Al^{3+} + X^{2+} = 2$ (a); $Li^+ = Na^+$ (b); $R^+ = Li^+ + X^{2+} - Fe^{3+}$ (c) and $R^+ - Na^+ = X^{2+}$ (d).
| Sample number | #1702B2 | #1702B2 | #1702B2 | #1901 | #1901 | #Q7 | #Q7 |
|---------------|---------|---------|---------|-------|-------|-----|-----|
| Wt % oxide    | TS      | TS      | TS      | TS    | TS    | SC  | SC  |
| Ideal crystal | Low-Na  | High-Na | Int.-Na | High-Na| Low-Na | Low-Na | Low-Na | High-Na |
| Na2O          | 1.231   | 1.690   | 1.338   | 2.005 | 1.130 | 1.422 | 1.719 |
| MgO           | 0.193   | 0.026   | 0.025   | 0.033 | 0.064 | 0.179 | 0.001 |
| K2O           | 0.020   | 0.029   | 0.018   | 0.005 | 0.010 | 0.035 | 0.007 |
| Cs2O          | 0.416   | 0.481   | 0.315   | 0.152 | 0.389 | 0.486 | 0.093 |
| CaO           | 0.004   | 0.016   | 0.005   | -     | 0.001 | -    | -   |
| TiO2          | 0.032   | -       | 0.005   | -     | 0.010 | -    | 0.004 |
| FeO           | 0.495   | 0.067   | 0.139   | 0.013 | 0.235 | 0.170 | -   |
| MnO           | 0.026   | -       | 0.005   | 0.000 | 0.021 | -    | -   |
| SiO2          | 67.07   | 64.668  | 64.479  | 64.507| 64.360| 64.841| 64.705| 64.914 |
| Al2O3         | 18.97   | 17.810  | 18.307  | 18.210| 18.481| 18.366| 18.079| 18.516 |
| Li2O<sub>cal</sub> | 0.594 | 0.815 | 0.645 | 0.967 | 0.545 | 0.685 | 0.829 |
| BeO<sub>cal</sub> | 13.96 | 12.481 | 12.088 | 12.365| 11.827| 12.628| 12.336| 12.150 |
| Total         | 100.00  | 97.969  | 97.999  | 97.578| 97.843| 98.243| 98.098| 98.234 |

Every value represents the average of three analyses. The measured points for ○ and □ are shown in Fig. 4f. The measured points for other symbols are shown in Figs S3–5.

cal: calculated value, Be = 3 - Li.

fixed: Li set to Na value based on correlation derived from LA-ICP-MS.

-: close or below the detection limit.
Table 2. Representative minor and trace element composition of beryl determined by LA-ICP-MS.

| ppm   | #Q7-3 S | #Q7-3 P | #Q6-1 S | #Q6-1 P | #Q3-1 S | #Q3-1 P |
|-------|---------|---------|---------|---------|---------|---------|
| Li    | 4611.20 | 3498.59 | 4462.00 | 3433.05 | 4732.43 | 3264.07 |
| Na    | 15179.02| 11414.04| 15069.01| 11269.89| 15795.65| 10484.95|
| Mg    | 145.29  | 750.37  | 327.22  | 720.82  | 25.57   | 293.78  |
| P     | 27.76   | 16.01   | 28.83   | 11.66   | 14.79   | 15.90   |
| S     | 73.57   | 66.73   | 50.84   | 54.80   | 44.67   | 47.49   |
| K     | 22.02   | 260.59  | 37.25   | 194.15  | 14.09   | 183.23  |
| Ca    | 18.60   | 53.72   | 16.46   | 70.35   | 21.92   | 75.41   |
| Ti    | 35.68   | 20.70   | 20.02   | 3.36    | 5.92    | 11.15   |
| Mn    | 6.02    | 71.22   | 0.21    | 66.12   | 0.23    | 39.11   |
| Fe    | 165.55  | 1157.46 | 40.43   | 1550.04 | 45.93   | 1167.36 |
| Zn    | 6.74    | 54.53   | 1.17    | 49.13   | 13.28   | 58.39   |
| Ga    | 11.82   | 29.84   | 15.52   | 14.90   | 29.69   | 10.88   |
| Rb    | 10.92   | 67.63   | 11.16   | 49.83   | 11.96   | 37.98   |
| Cs    | 1520.71 | 4019.28 | 870.63  | 3170.35 | 958.81  | 2080.47 |

| apfu  |         |         |         |         |         |         |
|-------|---------|---------|---------|---------|---------|---------|
| Li    | 0.3589  | 0.2723  | 0.3473  | 0.2672  | 0.3683  | 0.2540  |
| Na    | 0.3566  | 0.2682  | 0.3540  | 0.2648  | 0.3711  | 0.2463  |
| Mg    | 0.0032  | 0.0167  | 0.0073  | 0.0160  | 0.0006  | 0.0065  |
| P     | 0.0005  | 0.0003  | 0.0005  | 0.0002  | 0.0003  | 0.0003  |
| S     | 0.0012  | 0.0011  | 0.0009  | 0.0009  | 0.0008  | 0.0008  |
| K     | 0.0003  | 0.0036  | 0.0005  | 0.0027  | 0.0002  | 0.0025  |
| Ca    | 0.0003  | 0.0007  | 0.0002  | 0.0009  | 0.0003  | 0.0010  |
| Ti    | 0.0004  | 0.0002  | 0.0002  | 0.0000  | 0.0001  | 0.0001  |
| Mn    | 0.0001  | 0.0007  | 0.0000  | 0.0007  | 0.0000  | 0.0004  |
| Fe    | 0.0016  | 0.0112  | 0.0004  | 0.0150  | 0.0004  | 0.0113  |
| Zn    | 0.0001  | 0.0005  | 0.0000  | 0.0004  | 0.0001  | 0.0005  |
| Ga    | 0.0001  | 0.0002  | 0.0001  | 0.0003  | 0.0002  | 0.0001  |
| Rb    | 0.0001  | 0.0004  | 0.0001  | 0.0003  | 0.0001  | 0.0002  |
| Cs    | 0.0062  | 0.0163  | 0.0035  | 0.0129  | 0.0039  | 0.0085  |

S indicates the secondary phase of beryl while P indicates the primary phase.
**Table 3.** Crystal structure refinement parameters for beryl from Xuebaoding (#Q7, #Q6, and #Q3) compared to reported data

|                  | #Q7   | #Q6   | #Q3   | Reported data |
|------------------|-------|-------|-------|---------------|
| a(Å)             | 9.2161 b | 9.2162 b | 9.2171 b | 9.1961 |
| c(Å)             | 9.2178 b | 9.2182 b | 9.2219 b | 9.1969 |
| V(Å³)            | 678.03 | 678.08 | 678.48 | 673.57 |
| Space group      | P6/mcc | P6/mcc | P6/mcc | P6/mcc |
| Z                | 2      | 2      | 2      | 2         |
| Radiation        | MoKα   | MoKα   | MoKα   | MoKα       |
| 2θ range         | 0-80.77° | 0-80.59° | 0-80.76° | 5.12-66.68° |
| Reflections measured | 41515 | 77872 | 77620 | 5597 |
| Unique reflections | 767    | 762    | 767    | -          |
| R(σ)             | 0.0104 b | 0.0099 b | 0.0130 b | -          |
| R_int            | 0.0384 | 0.0350 | 0.0395 | -          |
| R₁                | 0.0249 c | 0.0268 c | 0.0295 c | 0.046 |

a Liu et al., 2007
b Unit cell refinement obtained from point detector data.
C Using ionized atom scattering factors for cations (Cromer and Mann, 1968) and for O²⁻ (Azavant and Lichanot, 1993).

**Table 4.** Selected interatomic distances (Å) for beryl from Xuebaoding in comparison to reported data.

|                  | #Q7   | #Q6   | #Q3   | Reported data |
|------------------|-------|-------|-------|---------------|
| Be- Tetrahedron (T2) |       |       |       |               |
| Be – O2 (4)      | 1.6656 (6) | 1.6659 (8) | 1.6655 (7) | 1.665 (1) |
| Polyhedral Volume (Å³) | 2.0811 | 2.0825 | 2.0790 | -            |
| Quadratic Elongation b | 1.0909 | 1.0908 | 1.0915 | -            |
| Al-Octahedron (A) |       |       |       |               |
| Al – O2 (6)      | 1.9094 (6) | 1.9097 (7) | 1.9095 (6) | 1.904 (1) |
| Polyhedral Volume (Å³) | 9.0066 | 9.0111 | 9.0092 | -            |
| Quadratic Elongation | 1.0202 | 1.0202 | 1.0202 | -            |
| Si-Tetrahedron (T1) |       |       |       |               |
| Si – O1          | 1.6017 (8) | 1.6021 (10) | 1.6010 (9) | 1.597 (1) |
| Si – O1          | 1.6044 (8) | 1.6046 (10) | 1.6049 (9) | 1.602 (1) |
| Si – O2 (2)      | 1.6153 (6) | 1.6149 (7) | 1.6164 (7) | 1.611 (1) |
| Average Si -O    | 1.6092 | 1.6092 | 1.6097 | 1.603 |
| Polyhedral Volume (Å³) | 2.1337 | 2.1334 | 2.1359 | -            |
| Quadratic Elongation | 1.0015 | 1.0016 | 1.0015 | -            |

Na Channel (C2)
| Crystal sample | Site | Site scattering (epfu) | Site population (apfu) | Site population (from average chemical composition) | Predicted site scattering from chemical composition (epfu) |
|----------------|------|------------------------|------------------------|------------------------------------------------------|------------------------------------------------------|
|                |      |                        |                        |                                                      |                                                      |
| #Q7            | T2   | 5.90(12)               | 2.95(6) Be^{2+}        | 0.289 Li^{+} + 2.711 Be^{2+}                         | 6                                                   |
|                | A    | 19.94(11)              | 1.994(1) Al^{3+}       | 1.973 Al^{3+} + 0.022 Mg^{2+} + 0.008 Fe^{3+}        | 20.13                                               |
|                | T1   | 59.64(2)               | 5.964(2) Si^{4+}       | 5.998 Si^{4+}                                        | 59.98                                               |
|                | C2   | 3.096(2)               | 0.3096(2) Na^{+}       | 0.293 Na^{+}                                         | 2.93                                                |
|                | C1   | 4.56(2)                | 0.456(2) H_{2}O         | 0.003 K^{+} + 0.015 Cs^{+} + 0.368 H_{2}O^{*}        | 4.56                                                |
| #Q6            | T2   | 5.81(12)               | 2.905(6) Be^{2+}       | 0.284 Li^{+} + 2.716 Be^{2+}                         | 6                                                   |
|                | A    | 19.86(13)              | 1.986(1) Al^{3+}       | 2.020 Al^{3+} + 0.010 Mg^{2+} + 0.009 Fe^{3+}        | 20.51                                               |
|                | T1   | 60.00(4)               | 6.0(4) Si^{4+}         | 5.969 Si^{4+}                                        | 59.69                                               |
|                | C2   | 3.2244(2)              | 0.32244(2) Na^{+}      | 0.358 Na^{+}                                         | 3.58                                                |
|                | C1   | 4.86(2)                | 0.486(2) H_{2}O        | 0.004 Cs^{+} + 0.464 H_{2}O^{*}                      | 4.86                                                |
| #Q3            | T2   | 5.83(12)               | 2.915(6) Be^{2+}       | 0.249 Li^{+} + 2.751 Be^{2+}                         | 6                                                   |
|                | A    | 19.89(12)              | 1.989(1) Al^{3+}       | 2.008 Al^{3+} + 0.003 Mg^{2+} + 0.009 Fe^{3+}        | 20.32                                               |
|                | T1   | 59.88(2)               | 5.988(2) Si^{4+}       | 5.982 Si^{4+}                                        | 59.82                                               |
|                | C2   | 2.928(2)               | 0.2928(2) Na^{+}       | 0.252 Na^{+}                                         | 2.52                                                |
|                | C1   | 4.56(2)                | 0.456(2) H_{2}O        | 0.003 K^{+} + 0.009 Cs^{+} + 0.401 H_{2}O^{*}        | 4.56                                                |

H_{2}O^{*} is estimated by site scattering (epfu) except sum of K^{+}, Cs^{+} and Rb^{+}.  

Table 5. Site-scattering refinement with site scattering (epfu) and site population assignment from single crystal #Q7, #Q6 and #Q3, compared to the result of EMPA and LA-ICP-MS analysis.