AQUAMARINE FROM THE THUONG XUAN DISTRICT, THANH HOA PROVINCE, VIETNAM

Le Thi-Thu Huong, Wolfgang Hofmeister, Tobias Häger, Nguyen Ngoc Khoi,
Nguy Tuyet Nhung, Wilawan Atichat, and Visut Pisutha-Arnond

Vietnamese aquamarine is notable for its attractive color and well-formed crystals. Commercially significant deposits are known only from the Thuong Xuan District in Thanh Hoa Province, where the aquamarine (as well as topaz) have been mined from granitic pegmatites and associated eluvial deposits. Rough and cut samples were investigated by standard gemological methods, Raman and IR spectroscopy, and electron microprobe and LA-ICP-MS chemical analysis. The samples were characterized by a low concentration of alkalis and relatively high amounts of iron and cesium. Raman and IR spectroscopy showed the presence of CO_2 and type I H_2O in the beryl structural channels.

Gem-quality aquamarine has been produced mainly from Brazil and Africa (Bank et al. 2001; Webster, 2002), as well as Pakistan, Russia, Myanmar, China, India, Ukraine, and the United States (Shigley et al., 2010). Aquamarine was discovered in Vietnam in 1985 at the village of Xuan Le (Thuong Xuan District in Thanh Hoa Province) during geological mapping by the government. While known for more than 25 years, this attractive aquamarine has been described in only a few brief reports (Pham Van et al., 2004; Huong et al., 2008; Atichat et al., 2010; Laurs, 2010). According to local dealers, ~100–150 kg of gem material were recovered by local people annually during the past decade, and in 2010 some 300–400 kg were produced. A limited number of gemstones have been faceted so far (e.g., figure 1), and sold mainly into the Vietnamese market. This article describes the geologic setting, gemological properties, and spectroscopic characteristics of Thuong Xuan aquamarine.

LOCATION, GEOLOGY, AND MINING

The Thuong Xuan aquamarine deposits lie ~70 km west of the provincial capital, Thanh Hoa City (figure 2). While Thuong Xuan is the only commercially significant aquamarine locality in the country, the adjacent Que Phong District in Nghe An Province has produced small amounts of aquamarine from eluvial deposits.

The Thuong Xuan region is cross-cut by a group of mainly northwest-trending faults. The aquamarine is hosted by pegmatites distributed mostly within the Ban Chieng and Ban Muong granite complexes, which together cover an area of 100 km^2 (figure 3). The pegmatite bodies typically form lenses or veins, ranging from 10 to 30 cm thick and a few meters in length to 4–5 m thick and tens of meters long. According to unpublished research by one of the authors (NNK), the pegmatites consist of quartz (38–48%), K-feldspar (~35%), plagioclase (18–24%), muscovite (2.3–3.5%), and biotite (0–2%). Quartz, feldspar, aquamarine, topaz, tourmaline, fluorite, and (rarely) zircon are found in miarolitic cavities. Although the topaz is of gem quality, it is not hosted by the same pegmatites as the aquamarine.

Many eluvial occurrences of aquamarine are known, of which four—Ban Pang, Lang Ben, Non Na

---

See end of article for About the Authors and Acknowledgments.

GEMS & GEMOLOGY, Vol. 47, No. 1, pp. 42–48.

Figure 1. These faceted aquamarines (2.40–7.65 ct) from Vietnam's Thuong Xuan District were studied for this report. Photo by L. T.-T. Huong.

Ca, and Ban Tuc—are the most productive; all are derived from pegmatites intruding the Ban Chieng granite. Most of the recent production has come from these deposits, which typically contain aquamarine of very good gem quality together with quartz, topaz, and cassiterite. So far there has been no organized mining; the crystals are simply gathered by hand from the eluvial deposits or recovered from shallow workings in the pegmatites using rudimentary tools. The crystals have a prismatic hexagonal shape, variable hue and saturation, and are transparent to translucent. They typically range from 5 to 20 cm long and 1–6 cm in diameter.

Figure 2. The Thuong Xuan aquamarine deposit is located in north-central Vietnam, not far from the border with Laos.

MATERIALS AND METHODS

Six aquamarine crystals from eluvial deposits (up to 4.5 cm long; figure 4) and four faceted stones (2.40–7.65 ct; again, see figure 1) representative of the current production from Thuong Xuan were examined using standard gemological techniques. These samples were purchased from local dealers, except for one crystal that was found in an eluvial deposit by one of the authors (NTN). All samples were tested with a dichroscope, Schneider refractometer, hydrostatic Shimadzu balance, UV lamp, and Schneider immersion microscope with Zeiss optics.

Raman spectroscopy was used to investigate H_2O and CO_2 molecules in the beryl structural channels, as these can show differences between aquamarine from different sources, and to identify inclusions in selected samples. The spectra were collected with a Jobin Yvon LabRam HR 800 spectrometer coupled with an Olympus BX41 optical microscope and an Si-based CCD (charge-coupled device) detector; samples were excited by a 514 nm green Ar^+ ion laser. Raman microspectroscopy of inclusions was performed in confocal mode, facilitating analysis at the micron scale (2–5 µm).

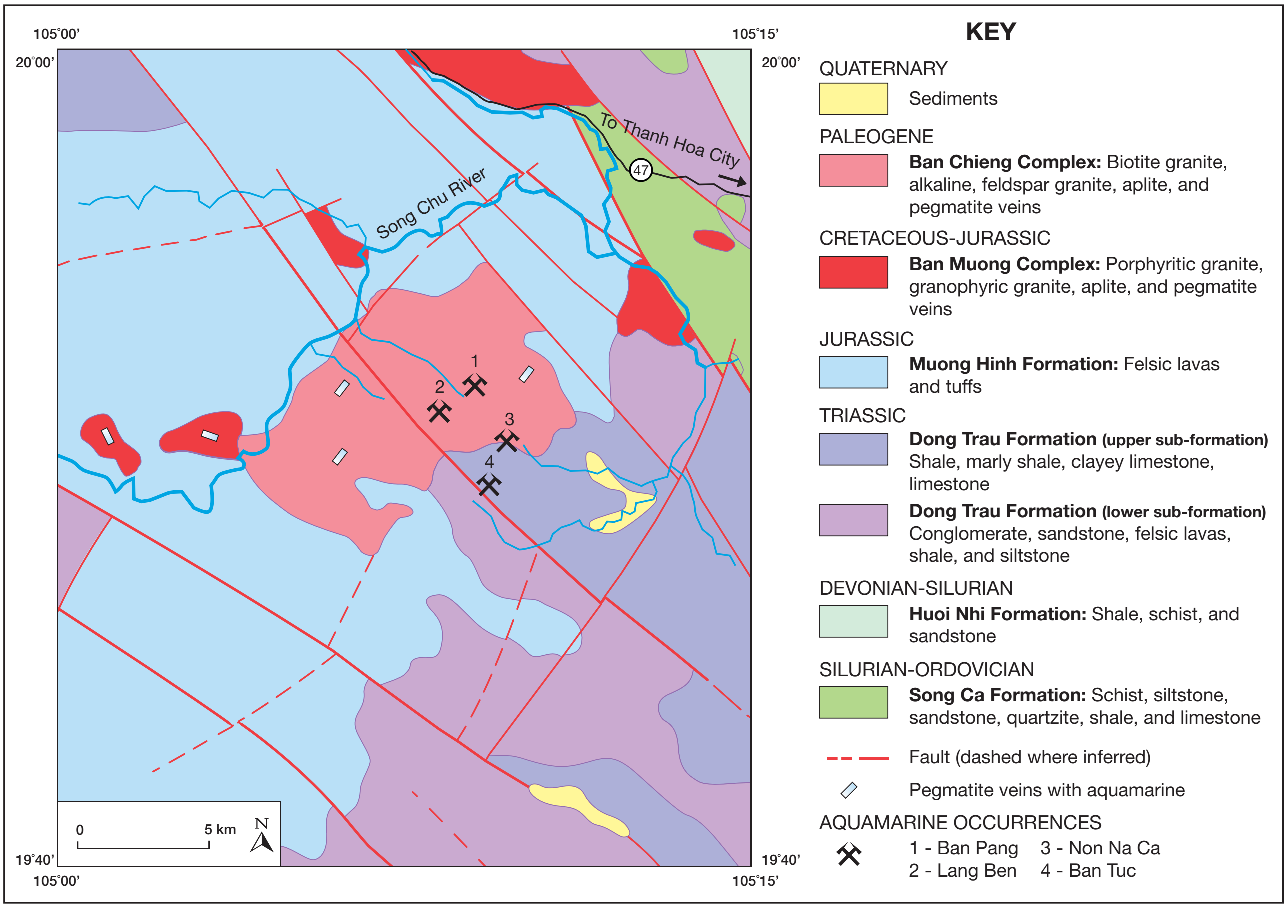


Figure 3. The primary and eluvial occurrences of aquamarine in the Thuong Xuan area are associated with granitic rocks. Modified after Bach and Quan (1995).

To study the characteristics of H_2O in the beryl channels, we recorded IR spectra from portions of two crystals using the KBr pellet method (2 mg of powdered sample mixed with 200 mg of KBr) in the range of 4000–500 cm^{-1} with a Perkin Elmer FTIR 1725X spectrometer.

Three of the crystals were partially polished for chemical analysis by electron microprobe and by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS). Microprobe analyses were performed with a JEOL JXA 8900RL instrument equipped with wavelength-dispersive spectrometers, using 20 kV acceleration voltage and 20 nA filament current. Silicon was analyzed by microprobe, and wollastonite was used as the standard. LA-ICP-MS data for all elements except Si were obtained using an

Figure 4. These aquamarine crystals (up to 4.5 cm long) were characterized for this study. Photo by L. T.-T. Huong.

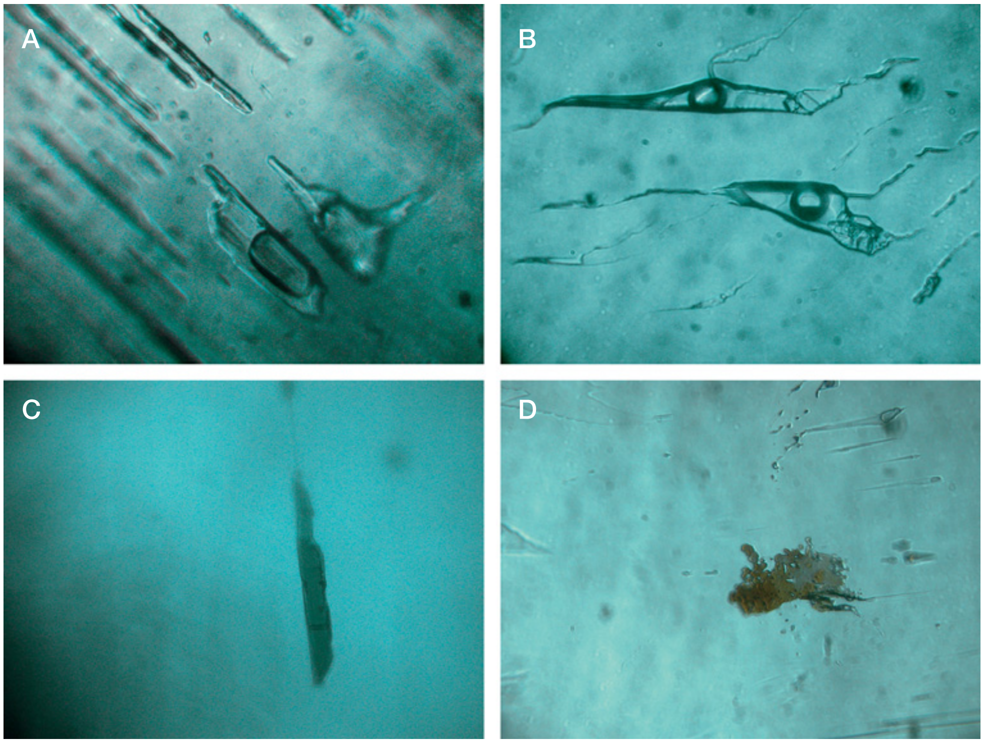


Figure 5. Inclusions documented in the Thuong Xuan aquamarine included growth tubes and two-phase inclusions (A), three-phase inclusions with calcite and albite (B), and mineral inclusions of hematite (C) and biotite (D). Photomicrographs by L. T.-T. Huong; magnified 50×.

Agilent 7500ce ICP-MS in pulse counting mode, and ablation was achieved with a New Wave Research UP-213 Nd:YAG laser ablation system, using a pulse repetition rate of 10 Hz, an ablation time of 60 seconds, a dwell time of 10 milliseconds per isotope, a 100 μm crater diameter, and five laser spots averaged for each sample. Be was calibrated using the NIST 612 glass standard, and BCR2G glass was also analyzed as a reference material.

RESULTS AND DISCUSSION

Visual Appearance and Gemological Properties. The six crystals were translucent to transparent, and light to medium blue. They consisted of well-formed hexagonal prisms $\{10\bar{1}0\}$, $\{01\bar{1}0\}$, and $\{\bar{1}100\}$, while the basal pinacoids {0001} were typically broken or rounded. The four cut samples were fairly clean to the naked eye, with fractures visible in some samples. They were light to medium blue with moderate saturation, and showed obvious pleochroism when viewed with the dichroscope. The refractive indices were n_o = 1.572–1.579 and n_e = 1.569–1.573. SG values varied between 2.66 and 2.70. All samples were inert to long- and short-wave UV radiation.

Internal Features. Microscopic observation revealed growth tubes and angular or elongated two-phase (liquid and gas, figure 5A) fluid inclusions in all the samples. Multiphase (liquid, gas, and crystal) inclusions were seen less frequently. The liquid and gas phases were identified by Raman spectroscopy as H_2O and CO_2. Transparent crystals in the multiphase inclusions within one sample were identified as calcite and albite (figure 5B). Hematite and biotite were found as mineral inclusions in one sample (figures 5C,D).

NEED TO KNOW

- North-central Vietnam is a source of well-formed crystals of attractive blue aquamarine.
- Local people mine the aquamarine from granitic pegmatites and associated eluvial deposits.
- The aquamarine contains low alkalis and relatively high iron and cesium.
- Carbon dioxide and type I water are present in the beryl-structure channels.

Chemical Composition. The chemical composition of the three analyzed samples is presented in table 1. The Thuong Xuan aquamarines were characterized by a relatively high concentration of Fe (up to 1.50 wt.% Fe_2O_3; compare to Adamo et al. [2008] and Viana et al. [2002]) and low amounts of Na (up to 0.048 wt.% Na_2O) and K (up to 0.007 wt.% K_2O).

TABLE 1. Chemical composition of aquamarine from Thuong Xuan, Vietnam.[a]

Chemical composition	Sample 1	Sample 2	Sample 3
Oxides (wt.%)			
SiO_2	65.42	65.87	66.41
Al_2O_3	18.13	17.80	18.55
Fe_2O_3	1.50	1.42	1.37
Sc_2O_3	0.005	0.005	0.005
BeO	13.40	13.52	12.59
MnO	0.012	0.009	0.011
MgO	0.046	0.058	nd[b]
CaO	0.046	0.030	0.027
Na_2O	0.025	0.048	0.037
K_2O	0.007	0.003	0.006
Li_2O	0.009	0.001	0.002
Cs_2O	0.193	0.126	0.132
Total	98.79	98.89	99.14
Trace elements (ppm)			
B	1.87	2.82	2.33
P	49.5	17.6	40.2
Ti	6.18	3.07	2.24
V	0.525	0.477	0.198
Cr	2.06	1.52	2.53
Co	0.247	0.134	0.082
Ni	1.9	5.0	0.8
Ga	71.4	71.2	70.0
Ge	0.850	0.630	1.06
Rb	58.1	54.9	55.7
Sr	0.047	0.125	0.510
Y	0.042	0.018	0.046
Zn	0.130	0.123	0.060
Nb	0.027	0.027	0.037
Mo	0.082	0.103	0.223
Ba	0.178	0.152	0.780
La	0.024	0.033	0.019
Ta	0.022	0.011	0.030

[a] *Si was analyzed by electron microprobe, and the others by LA-ICP-MS. Elements typically reported in beryl analyses were converted to oxides for ease of comparison with the published literature.*
[b] *Abbreviation: nd = not detected.*

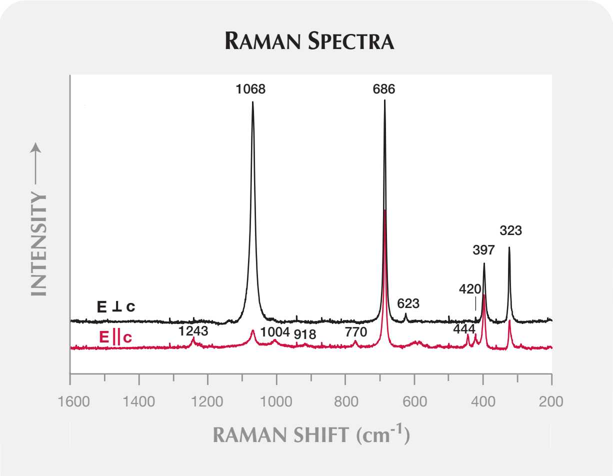
The Cs contents were very high compared to aquamarine from other sources (Adamo et al., 2008; Viana et al., 2002), with up to 0.193 wt.% Cs_2O. Also present were small but significant amounts of Mg, Mn, Ca, Sc, Li, Ga, Rb, and P, as well as traces of several other elements (again, see table 1).

Spectroscopic Investigation. *Raman.* The main Raman bands of the beryl group, shown in figure 6, are due to ring vibrations (e.g., Kim et al., 1995; Charoy et al., 1996) and Si-O stretching vibrations (Adams and Gardner, 1974; Huong, 2008). In addition, a band at 1243 cm^{-1} present in all samples is related to the vibration of CO_2 molecules in the beryl structural channels (Charoy et al., 1996). It was seen only in the E||c orientation, because the only possible orientation of CO_2 molecules in the channel is with the symmetry axis parallel to the c-axis. While CO_2 has been previously documented as a channel constituent in beryl (e.g., Aines and Rossman, 1984), to our knowledge it has not been ascribed to aquamarine from a particular locality.

Figure 7 shows a representative Raman spectrum of Thuong Xuan aquamarine in the 3700–3500 cm^{-1} range, which corresponds to the energy of H_2O vibrations in beryl. A band at 3608 cm^{-1}—related to type I H_2O and not associated with alkalis (e.g., Huong et al., 2010)—was observed in all samples. Conversely, a band at 3598 cm^{-1}—related to type II H_2O and associated with alkalis—was almost undetectable. This is consistent with the chemical data showing low contents of alkalis (sodium and potassium), which are associated with type II H_2O in the structural channels of beryl.

Infrared. Various bands consistent with those typically seen in aquamarine were observed in the IR spectra of the Thuong Xuan aquamarines (figure 8). Those recorded in the range 1300–800 cm^{-1} have

Figure 6. In addition to typical Raman features for beryl, the aquamarine showed a peak at 1243 cm^{-1} in the E||c orientation that is due to CO_2.



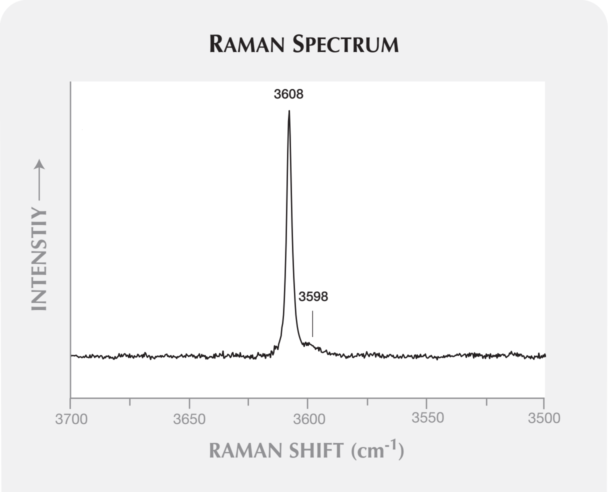

RAMAN SPECTRUM

Figure 7. Raman spectra of the aquamarine showed a band at 3608 cm^{-1} that is associated with type I H_2O. This indicates a very low alkali content.

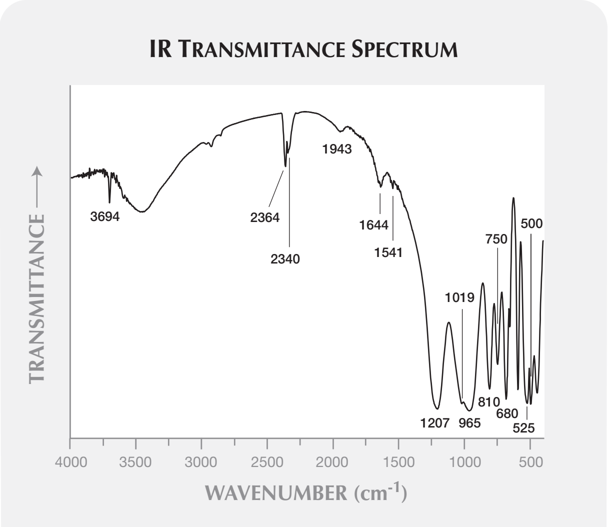

IR TRANSMITTANCE SPECTRUM

Figure 8. Infrared spectra of the Vietnamese aquamarine showed a band related to type I H_2O at 3694 cm^{-1} and a doublet at 2364 and 2340 cm^{-1} that is due to CO_2.

been assigned to internal Si-O vibrations (Gervais and Pirou, 1972; Adams and Gardner, 1974; Hofmeister et al., 1987; Aurisicchio et al., 1994). Bands appearing at ~750 and 680 cm^{-1} were ascribed to the Be-O cluster by Hofmeister et al. (1987). The two bands at 525 and 500 cm^{-1} correlate to Si-O-Al stretching (Plyusnina, 1964). The doublet at 2364 and 2340 cm^{-1} is due to carbon dioxide (Leung et al., 1983).

Features in the 1700–1500 cm^{-1} and 3800–3500 cm^{-1} ranges are generated by different types of H_2O (Wood and Nassau, 1967). In the latter range, the Thuong Xuan aquamarines showed only one band at 3694 cm^{-1}. This correlates to type I H_2O (Schmetzer and Kiefert, 1990), and is consistent with the Raman analyses and very low alkali contents of this aquamarine.

CONCLUSION

Since the early 2000s, a significant amount of gem-quality aquamarine has been recovered from the Thuong Xuan area by local people, and more production is expected in the future. Some of the aquamarine has been mounted into jewelry (figure 9) for distribution mainly into the Vietnamese market. This aquamarine contains low concentrations of alkali ions, and relatively high amounts of iron and cesium. The low alkalis were revealed by chemical analysis and by the sole presence of type I H_2O in Raman and IR spectra. In addition, the presence of CO_2 molecules in structural channels was indicated by Raman spectroscopy.

Figure 9. A limited amount of Vietnamese aquamarine has been faceted and mounted into jewelry, such as the 6.5 ct stone shown in this gold ring. Courtesy of Duong Anh Tuan, Doji Gold & Gems Group, Hanoi; photo by L. T.-T. Huong.

ABOUT THE AUTHORS
Dr. Huong (letth@vnu.edu.vn) is a lecturer in mineralogy, and Drs. Nhung and Khoi are associate professors, at the Faculty of Geology, Hanoi University of Science. Dr. Hofmeister is professor and the dean of the Faculty of Chemistry, Pharmacy and Geosciences, and head of the Centre for Gemstone Research, at Johannes Gutenberg University, Mainz, Germany. He is also head of the Institute of Gemstone Research in Idar-Oberstein, Germany. Dr. Häger is senior scientist at the Centre for Gemstone Research at Johannes Gutenberg University, lecturer in the Gemstone and Jewellery Design Department at the University for Applied Sciences in Idar-Oberstein, and managing director of the Institute of Gemstone Research. Ms. Atichat is director of the Gem and Jewelry Institute of Thailand. Dr. Pisutha-Arnond is associate professor in the Department of Geology, Chulalongkorn University, and advisor to the Gem and Jewelry Institute of Thailand (GIT), Bangkok.

ACKNOWLEDGMENTS
Analytical facilities were provided by the Institute of Geology at Johannes Gutenberg University, Mainz, Germany. The first author thanks the Vietnam National Foundation for Science and Technology Development (NAFOSTED) for financial support.

REFERENCES

Adamo I., Pavese A., Prosperi L., Diella V., Ajo D., Gatta G.D., Smith C.P. (2008) Aquamarine, Maxixe-type beryl, and hydrothermal synthetic blue beryl: Analysis and identification. *G&G*, Vol. 44, No. 3, pp. 214–227.

Adams D.M., Gardner I.R. (1974) Single-crystal vibrational spectra of beryl and dioptase. *Journal of the Chemical Society, Dalton Transactions*, Vol. 1974, No. 14, pp. 1502–1505.

Aines R.D., Rossman G.R. (1984) The high temperature behavior of water and carbon dioxide in cordierite and beryl. *American Mineralogist*, Vol. 60, pp. 319–327.

Atichat W., Khoi N.N., Pisutha-Arnond V., Wathanakul P., Sriprasert B., Sutthirat C., Leelawattanasuk T., Tay T.S., Saejoo S., Naruedeesombat N., Rochd C., Makakum C., Pttharapanich W. (2010) Properties of aquamarine from central Vietnam. *5th International Workshop on Provenance and Properties of Gems and Geo-Materials*, October 17–24, Hanoi, pp. 135–139.

Aurisicchio C., Grubessi O., Zecchini P. (1994) Infrared spectroscopy and crystal chemistry of the beryl group. *Canadian Mineralogist*, Vol. 32, pp. 55–68.

Bach L.D., Quan T.D. (1995) *Geology and Mineral Resources of Vietnam*. Thanh Hoa sheet (E-48-IV), scale 1:200,000, Vietnam Department of Geology and Minerals, Hanoi.

Bank F., Bank H., Villa E. (2001) Santa Maria aquamarine. *Journal of Gemmology*, Vol. 27, No. 5, pp. 257–258.

Charoy B., De Donato P., Barres O., Pinto-Coelho C. (1996) Channel occupancy in an alkali-poor beryl from Serra Branca (Goias, Brazil): Spectroscopic characterization. *American Mineralogist*, Vol. 81, pp. 395–403.

Gervais F., Piriou B. (1972) Étude des spectres de réflexion infrarouge du beryl dans les région 280-1400 cm^{-1}. *Comptes Rendus de l'Académie des Sciences Paris*, Vol. 274, pp. 252–255.

Hofmeister A.M., Hoering T.C., Virgo D. (1987) Vibrational spectroscopy of beryllium aluminosilicates: Heat capacity calculation from band assignments. *Physics and Chemistry of Minerals*, Vol. 14, pp. 205–224.

Huong L.T.-T. (2008) Microscopic, Chemical and Spectroscopic Investigations on Emeralds of Various Origins. PhD dissertation, Johannes-Gutenberg University, Mainz.

Huong L.T.-T., Khoi N.N., Nhung N.T., Häger T., Hofmeister W. (2008) A study on aquamarine from Thuong Xuan deposit, Thanh Hoa Province, Vietnam. *Proceedings of the 2nd International Gem and Jewelry Conference*, March 9–12, 2009, Bangkok.

Huong L.T.-T., Häger T., Hofmeister W. (2010) Confocal micro-Raman spectroscopy: A powerful tool to identify natural and synthetic emeralds. *G&G*, Vol. 46, No. 1, pp. 36–41.

Kim C., Bell M.I., McKeown D.A. (1995) Vibrational analysis of beryl ($Be_3Al_2Si_6O_{18}$) and its constituent ring (Si_6O_{18}). *Physica B: Condensed Matter*, Vol. 205, No. 2, pp. 193–208.

Laurs B.M. (2010) Gem News International: Aquamarine and heliodor from Indochina. *G&G*, Vol. 46, No. 4, pp. 311–312.

Leung C.S., Merigoux H., Poirot J.P., Zecchini P. (1983) Sur l'identification des pierres fines et de synthèse par spectroscopie infrarouge. *Revue de Gemmologie a.f.g.*, Vol. 75, pp. 14–15.

Pham Van L., Giuliani G., Garnier V., Ohnenstetter D. (2004) Gemstones in Vietnam—A review. *Australian Gemmologist*, Vol. 22, No. 4, pp. 162–168.

Plyusnina I.I. (1964) Infrared absorption spectra of beryls. *Geokhimiya*, Vol. 1, pp. 31–41 [in Russian].

Schmetzer K., Kiefert L. (1990) Water in beryl—A contribution to the separability of natural and synthetic emeralds by infrared spectroscopy. *Journal of Gemmology*, Vol. 22, No. 4, pp. 215–223.

Shigley J.E., Laurs B.M., Janse A.J.A., Elen S., Dirlam D.M. (2010) Gem localities of the 2000s. *G&G*, Vol. 46, No. 3, pp. 188–216.

Viana R.R., Jordt-Evangelista E.H., Magela da Costa E.G., Stern W.B. (2002) Characterization of beryl (aquamarine variety) from pegmatites of Minas Gerais, Brazil. *Physics and Chemistry of Minerals*, Vol. 29, No. 10, pp. 668–679.

Webster R. (2002) *Gems: Their Sources, Descriptions and Identification*, 5th ed. Rev. by P.G. Read, Butterworth-Heinemann, Oxford, UK.

Wood D.L., Nassau K. (1967) Infrared spectra of foreign molecules in beryl. *Journal of Chemical Physics*, Vol. 47, No. 7, pp. 2220–2228.