

The Beryl Group – an Overview

概述綠柱石家族

Prof. Dr Henry A. Hänni, FGA 亨瑞 翰尼
GemExpert, Basel, Switzerland

Website: www.gemexpert.ch Email: info@gemexpert.ch



Henry A. Hänni
亨瑞 翰尼

綠柱石家族的六邊形結構是由鋁矽酸鹽組成。其晶格允許不同成分從原始態中進行各種替換，從而產生不同顏色的變體，並進一步形成相關的礦物質體。祖母綠、海藍寶石和摩根石是較著名的綠柱石寶石。同構類質同象替代機制已形成較鮮為人知的綠柱石成員。自1950年代以來，通過助熔劑、催化劑和水熱工藝製備了類似的合成物。

Abstract

The beryl group consists of beryllium aluminium silicates of hexagonal structure. The crystal lattice allows various replacements from the original formula, leading to differently coloured varieties and further to related minerals. Emerald, aquamarine and morganite are the better known gemstone beryls. Isomorphous replacement mechanisms have formed lesser known members. Synthetic counterparts have been made by flux catalyst and hydrothermal processes since the 1950s.

Introduction

The beryls $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ form a group of better known gemstones like emerald, aquamarine, golden beryl and morganite (Fig. 1). As the crystals are usually transparent, the material generally ends up as faceted gemstones. But cat's eyes and even rare star beryls are also reported (Schmetzer et al., 2004).

Fig. 2 shows some beryl crystals with the characteristic hexagonal form. Some crystals are etched due to dissolving after crystallisation. They crystallise – with the exception of emerald – in pegmatite, an igneous rock that forms in dykes that had penetrated older bedrocks. Pegmatites consist of residual melts of elements often left over after the crystallisation of granite. What is essential is that the pegmatites contain not only redundant light chemical elements, like silicon, aluminium and oxygen, but also elements with an odd ion size or charge (as e.g. lithium, boron or beryllium). As pegmatites crystallise slowly,



Fig. 1 A selection of cut stones in the colour varieties of the beryl family: red beryl, morganite, emerald, aquamarine, golden beryl, green beryl, trapiche emerald and aquamarine cat's eye. The large aquamarine weighs 13 cts.

Photo © H.A.Hänni

綠柱石家族中各種顏色的切磨樣本：紅色綠柱石、摩根石、祖母綠、海藍寶石、金黃綠柱石、綠色綠柱石、達碧茲祖母綠和海藍寶石貓眼石。上圖中大型海藍寶石重13克拉。



Fig. 2 Beryl crystals; longest piece 5 cm. From left to right: morganite, red beryl, light greenish beryl, emerald, aquamarine, goshenite, heliodor. The two samples on the right have been corroded by natural etching.

Photo © H.A.Hänni

綠柱石晶體；最長一塊高度為5厘米。從左至右：摩根石、紅色綠柱石、淺綠色綠柱石、祖母綠、海藍寶石、透明綠柱石、金黃綠柱石。右側的兩個樣本已被自然侵蝕。

large crystals are generally formed, such as beryl, topaz and spodumene. When pegmatites meet dark ultrabasic rocks that often contain chromium, they may react with them and the formation of emerald becomes possible. Red beryl has formed in a vapour phase in rhyolite, a volcanic rock, in Utah (USA) (Shigley et al., 2003).

In 1980 the author delivered his doctoral thesis on beryls from Swiss Alpine cleft occurrences (Hänni, 1980). Optical, structural and micro-chemical measurements were taken on a number of tiny crystals, usually in the mm to sub-mm order. Months after having finished his thesis the author started his professional life as a gemmologist at SSEF, The Swiss Gemmological Institute, and, with George Bosshart, looked at beautiful Colombian emeralds, but also Zambian and synthetic emeralds. It soon became clear that the so-called “constants” were not at all constant for a gemstone with the same nametag. Preliminary research on emerald chemical compositions (a comparison of natural with synthetic emerald, Hänni, 1982) was carried out and from this study it became obvious that various chemical replacement mechanisms influenced the physical data of emeralds.

The Basics of Beryl

The beryl group comprises silicate minerals of hexagonal structure. The crystal structure of beryl is determined by rings of 6 SiO_4 tetrahedra, stacked on top of each other to form a channel

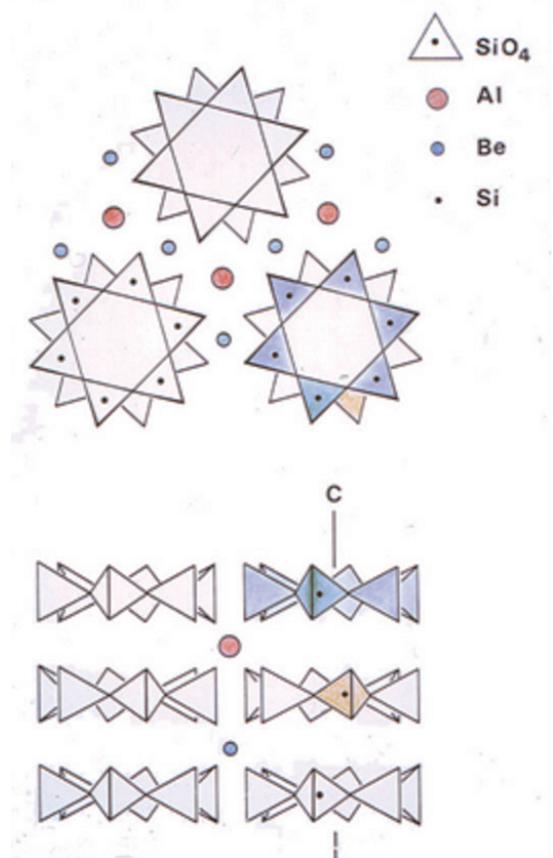


Fig. 3 A simplified model of the beryl structure. Oxygen not shown. Its position is at the corners of the SiO_4 tetrahedra. Si_6O_{18} rings stacked on top of each other form a channel where H_2O and alkali ions can be housed. Diagram modified after Strunz & Tennyson(1977).

綠柱石結構的簡化模型。氧元素並未顯示，它的位置在 SiO_4 四面體的角落。相互堆疊的 Si_6O_{18} 環形成一個通道，可以容納 H_2O 和鹼性離子。

in the centre. The channel direction is parallel to the crystallographic c-axis and optical axis (Fig. 2). Between the rings, and on intermediate horizontal layers, Be and Al ions link the rings. Al³⁺ ions are surrounded by 6 oxygens, forming an octahedron. The much smaller Be²⁺ ions are packed into 4 oxygens forming a tetrahedron.

Earlier papers have shown that the main formula of beryl can be modified by two major substitutions: the **tetrahedral substitution** of Be²⁺ by lithium (Li⁺ or Cs⁺) and the **octahedral substitution** of aluminium (Al³⁺) by other trivalent ions (Bakakin & Belov, 1962), see Fig. 4.

These direct substitutions are of the greatest importance for gem beryl when chromium (Cr³⁺) or vanadium (V³⁺) takes the Al lattice sites. By the introduction of bivalent ions like Fe²⁺ or Mg²⁺ on Al³⁺ positions a charge compensation is necessary in order to include the missing positive charge. This balance is usually realised by sodium (Na⁺) that is stored in the channel of the beryl structure. These coupled substitutions (e.g. Al³⁺ against Fe²⁺ plus Na⁺, or Al³⁺ against Mg²⁺ plus Na⁺) are very widespread and are the main reason for the variation of the physical data RI and SG.

Common substitution mechanisms in Beryl

Octahedral substitutions	Tetrahedral substitutions
direct substitution	coupled substitution
Al ³⁺ \longleftrightarrow Cr ³⁺	Be ²⁺ \longleftrightarrow Li ⁺ + Na ⁺
Al ³⁺ \longleftrightarrow V ³⁺	Be ²⁺ \longleftrightarrow Li ⁺ + Cs ⁺
Al ³⁺ \longleftrightarrow Fe ³⁺	
coupled substitution	
Al ³⁺ \longleftrightarrow Mg ²⁺ + Na ⁺	
Al ³⁺ \longleftrightarrow Fe ²⁺ + Na ⁺	

Fig. 4 Some of the more relevant substitutions in beryl. 綠柱石中一些比較相關的替代。

The fact that H₂O and CO₂ are also incorporated in channel positions further raises the physical data (Cerni & Hawthorne, 1967; Goldman et al., 1978). The beryl structure as described by Bragg & West, 1926, has seen a number of refinements (Gibbs et al., 1968; Artioli et al., 1993). Spectroscopic investigations have shown the relationship between chromophore trace elements and absorption spectrum, as well as traces and channel constituents in the infrared spectrum (Wood & Nassau, 1968).

Water molecules in alkali-free emeralds have their dipole axis parallel to the channel (Type I water). The rotation of H₂O molecules with their axes perpendicular to the c-axis of the beryl molecules is a consequence of the presence of channel constituents such as Na⁺ or Li⁺ (Type II water). Flux grown synthetic emeralds are water free and contain no alkali metals. A rich display of beryl characteristics, origins and individual features has been given by Sinkankas (1981). A modern alternative to the FTIR identification of natural and synthetic emeralds is possible by Raman spectroscopy (Huong et al., 2010).

Chromophore trace element or solid solution admixture

Colour varieties are the same mineral but with different colours. Colourless beryl, goshenite, does not contain colour giving elements. Small amounts of transition elements (e.g. Fe, Cr, V, Mn) cause characteristic absorptions in the spectrum so that the transmitted residual light qualities produce the perceivable colour. In general, iron Fe²⁺ produces blue aquamarine, Fe³⁺ causes yellow golden beryl. A mixture of both creates greenish beryls. Cr³⁺ and V³⁺ lead to green beryls called emerald. Manganese is identified as the cause of colour both for red (Mn³⁺) beryl and the pink in morganite (Mn²⁺).

The colour of an emerald has always been attributed to traces of Cr and/or V. A typical Colombian emerald contains 3311 ppm Cr and 3416 ppm V, as analysed by Laser Ablation Inductively Coupled Mass Spectrometry. It might be interesting to note that in Colombian emeralds Cr and V are typically both present, and V is often the prevailing concentration.

These chromophore element contents correspond to concentrations of 0.48 wt% of Cr₂O₃ and 0.61 wt% V₂O₃. One could postulate new solid solution endmembers with the beryl structure, such as Be₃Cr₂Si₆O₁₈ or Be₃V₂Si₆O₁₈. The contents of 0.48 wt% Cr₂O₃ and 0.61 wt% V₂O₃ correspond to 1.7 Be₃Cr₂Si₆O₁₈ and 2.2 Be₃V₂Si₆O₁₈ molecules, the rest being 96 Be₃Al₂Si₆O₁₈ of 100. The Colombian emerald referenced above could therefore be plotted in a triangular graph, in the same way that mineralogists do for other minerals in solid solution situations like feldspar, garnet and so on. (Fig. 5).

Triangular plot for Al-Beryl, Cr-Beryl and V-Beryl

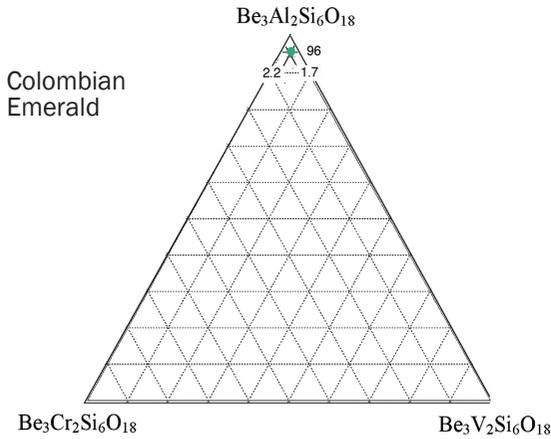


Fig. 5 Triangular plot of a typical emerald from Colombia containing 3311 ppm Cr, and 3416 ppm V. These concentrations are plotted in molecule units of the respective endmembers. *Diagram © H.A.Hänni.*
哥倫比亞祖母綠含3311 ppm鉻和3416 ppm 釩的典型三角替代關係圖。這些成分的濃度以相應末端成員的分子單位繪製。

More recent members of the beryl group

Thus far we have only looked at beryls in the strict sense of $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, with minor differences leading to differences in colour only. As shown in Fig. 6 the principle is to look at trace elements in substitution, which may lead to end members far removed from the common beryl. When the Al position is completely occupied by scandium for example, we have an entirely different mineral, bazzite. Or when beryllium Be^{2+} is significantly replaced by Li^{1+} with a charge compensation by Cs^{1+} the hexagonal symmetry may be affected. Thus, Pezzottaite is trigonal in its lattice structure.

Bazzite $\text{Be}_3\text{Sc}_2\text{Si}_6\text{O}_{18}$, originating from miarolitic occurrences (voids in granitic rocks), was discovered and described as long ago as 1916. Hydrothermal formations of bazzite were subsequently found in Alpine clefts and other hydrothermal deposits. Microprobe analyses

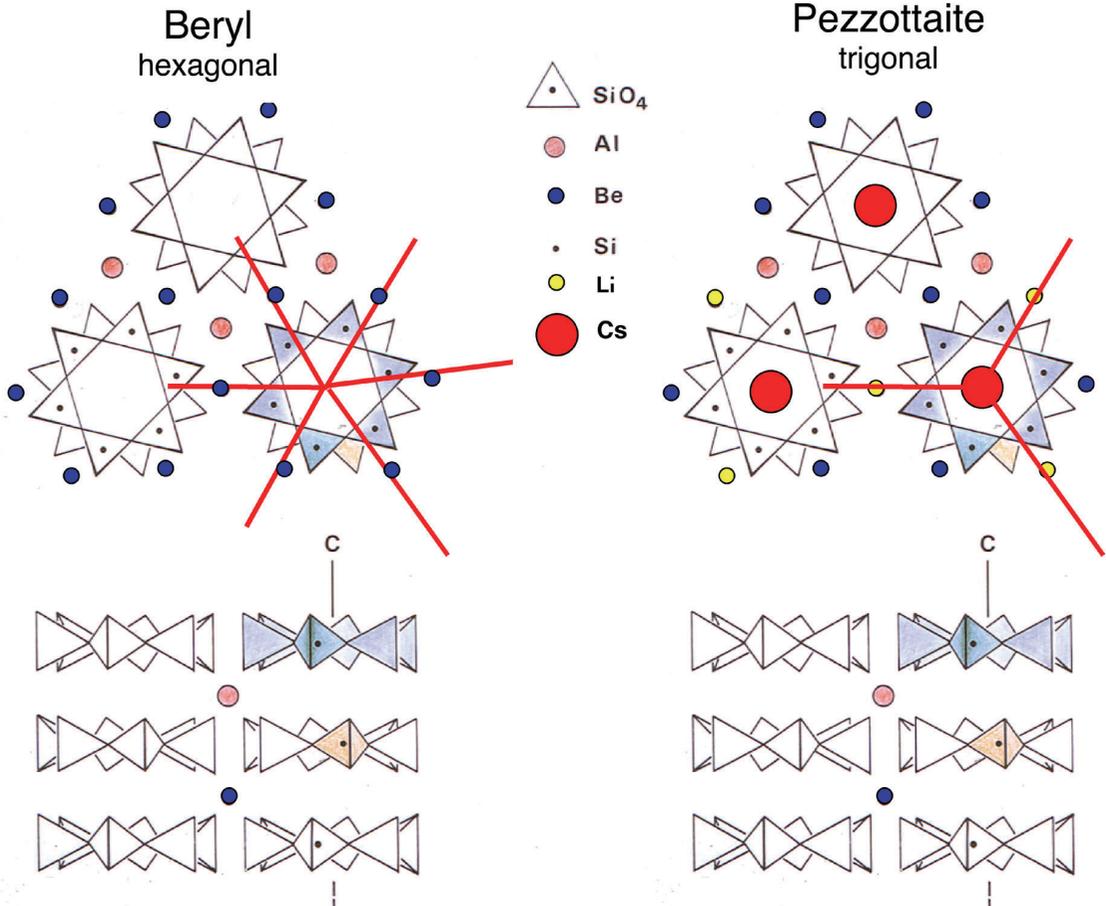


Fig. 6 Simplified model of the beryl structure in comparison with Pezzottaite.
與草莓紅綠柱石相比，綠柱石結構的簡化模型。

have shown the importance of scandium (Sc), iron (Fe) and magnesium (Mg). Some of the samples had large amounts of Sc and almost no Al, which corresponds to the mineral bazzite $\text{Be}_3\text{Sc}_2\text{Si}_6\text{O}_{18}$ (Artini, 1916). The blue colouration of the bazzites is due to Fe. Furthermore, some samples contained Sc, but not as much as would be needed for bazzite, raising the question as to whether there might be a mixed crystal series from beryl to bazzite. Scandium beryls and bazzites are found only as small crystals.

Further minerals with a beryl structure have been identified in the last 30 years. It is interesting to note that beryl research is predominantly done by Italian researchers, as seen by the names and authors of the following minerals.

Stoppaniite $\text{Be}_3\text{Fe}^{3+}_2(\text{Si}_6\text{O}_{18}) \cdot \text{H}_2\text{O}$ was found quite recently (Ferraris & Rossi, 1996; Della Ventura et al, 2000) and its real composition deviates slightly from the ideal formula by some replacements to $\text{Na}_{0.5}\text{Be}_3(\text{Fe}^{3+}, \text{Mg}, \text{Al})_2[\text{Si}_6\text{O}_{18}] \cdot \text{H}_2\text{O}$. Originating from volcanic pyroclastic rocks, these crystals are in the lower mm dimensions, as is also the case with bazzite.

It may be interesting to note that in 1978 this author (Hänni, 1980) produced synthetic Fe-Beryl in a hydrothermal experiment conducted while working on his doctoral thesis. As the result was not considered a novelty, it was not accorded individual publication. The data, of this new mineral like chemical composition, refractive indices and powder diffraction values were also published in the English abstract of

the thesis, but this material was not noted by the Italian researchers who later published work on Stoppaniite (Ferraris et al, 1998; Della Ventura et al., 2000).

Pezzottaite $\text{Cs}(\text{Be}_2\text{Li})\text{Al}_2(\text{Si}_6\text{O}_{18})$ was discovered in Madagascar in 2002 and first considered by some gemmologists to be a Cs-rich morganite, but was then identified as a new mineral (Laurs et al, 2003, Hawthorne et al. 2004). In this mineral Be the tetrahedral substitution of Be^{2+} by Li^+ goes far beyond what is encountered in morganites (Hänni & Krzemnicki, 2003). That 1/3 of the tetrahedral sites are occupied by Li^+ reduces the symmetry from hexagonal to trigonal (Liu et al., 2009). The charge is balanced by the introduction of Cs^+ in the channel position.

A Cs-beryl from Afghanistan with a Cs content of 9.7 wt% Cs_2O , (Pezzottaite has over 14.4 wt%), suggests that intermediate members between Pezzottaite and Morganite do exist (Hänni & Krzemnicki, 2003) (Fig. 7).

The colour of the pezzottaites found so far is pink, due to Mn traces. As the simplified Pezzottaite formula does not necessarily need Mn however, other chromophores are imaginable. Thus we are looking forward to finding blue pezzottaite with traces of Fe!

Johnkoivulaite. $(\text{Cs}[\text{Be}_2\text{B}]\text{Mg}_2\text{Si}_6\text{O}_{18})$ is the latest new member with a beryl structure. It is found in Myanmar and exhibits surprisingly strong pleochroism of violet blue and colourless. (Palke et al., 2019)



Fig. 7 Pezzottaite from Madagascar. The largest cut stone weighs 4 cts.

Photo © H.A. Hänni

來自馬達加斯加的草莓紅綠柱石。最大的一顆重4 cts。



Fig. 8 Hydrothermal synthetic emerald, red beryl and aquamarine. The emerald crystal is 6 cm long.

Photo © H.A. Hänni

水熱生長法的合成祖母綠、紅色綠柱石和海藍寶石。圖中合成祖母綠晶體長6cm。

Synthetic beryls

So far synthetic beryl crystals for commercial purposes have been created from both emerald and aquamarine. The first synthetic beryls were formed by the flux method in 1935. The main producers of commercial synthetic emeralds were Tom Chatham (1963) and Pierre Gilson (1964). A more effective technology was later applied, and emeralds were crystallised in autoclaves in a hydrothermal process by Linde (1965), Biron (1985) and then Russian (1989) and Chinese synthesisers (Fig. 8). Lechleitner, an Austrian experimentalist tried both the flux and the hydrothermal methods. He used faceted colourless beryls and coated them with synthetic emerald in a hydrothermal process. Red beryl with Ti as chromophore and aquamarines completed the supply, but today only a few companies produce synthetic beryls.

Discussion

In the last 30 years the beryl group has grown by at least two new members. The concept of solid solution seems to be a good perspective from which to discuss the relationships between members of the beryl group. Looking at hypothetical endmembers and plotting in triangles and tetrahedra will allow a presentation of beryl mineral relationships in addition to the concept of trace or minor elements indications. As in all high-end gemstones, origin determination is often required for certification and some laboratories specialise in this gemmological discipline. In the past

origin determination was mainly a matter of studying the inclusions in a stone (e.g. Gübelin & Koivula, 2004). However, identifications where the trace elements are considered are more reliable. Energy dispersive X-ray fluorescence is an analytical tool widely used in gemmological laboratories nowadays. It gives instant access to main-, accessory- and trace element levels. But only elements heavier than Sodium (Na) can be recognised by this method. The most up to date analytical method is mass spectrometry where not only the elements but also their isotopes are recorded. This gives precise fingerprint chemistry of gemstones and also allows age determination. With emeralds we are in the comfortable situation that the ages of emerald deposits do not overlap. Emeralds from Gravelotte (South Africa) are the oldest with an age of 2.6 billion years, those from Khaltaro (Pakistan) are the youngest formations being only 9 million years old (Giuliani et al, 2019). Age determination is thus another technique which can be used to attribute emerald gemstones to their geographic origin.

Acknowledgement

I should like to thank Dr Hao A.O. Wang, SSEF Swiss Gemmological Institute, Basel, Switzerland for the GEM TOF MS analysis of a representative emerald from Columbia. I am also grateful for constructive discussions with Dr Michael Krzemnicki (SEEF) and Prof. Dr Leander Franz, Earth Science Department, University of Basel.

About the Author

Henry A. Hänni (b. 1945) is renowned as the author of more than 200 papers. He has lectured to great acclaim around the world. Inspired by his early work as a technician at the Basel Mineralogical institute he furthered his studies in mineralogy, obtaining his doctorate in 1980. He joined SSEF, in 1976, becoming director of the Institute in 1990. A dedicated gem educationalist, he also took up a teaching position at the University of Basel in 1989 becoming a professor of gemmology there in 1996, specialising in gemstone identification with advanced instruments. Although he retired from these positions in 2010 his writing and lecturing continue.

References

- Artini, A. (1916): Due minerali di Baveno contenenti terre rare: Weibeite and Bazzite. *Atti Acca. Lincei Rend.*, 5, 24/1, 313-319
- Artioli, G., Rinaldi, R., Ståhl, K & Zanazzi, P.F. (1993): Structure refinements of beryl by single-crystal neutron and X-ray diffraction. *Am.Mineral.* 78, 762-768
- Bakakin, V., Belov, V. (1962): Crystal chemistry of beryl. *Geochemistry*, 5, 485-500
- Bragg, W.L. & West, J. (1926): The structure of beryl. *Proc. R. Soc. London, A*, 111, 691-714
- Cerni, P., Hawthorne, F.C. (1967): Refractive indices versus alkali contents in beryl: general limitations and applications to some pegmatite types. *Canad. Mineralogist*, 14, 491-497
- Della Ventura, G., Rossi, P., Parodi, G.C., Mottana, H., Raudsepp, M. & Prencipe, M. (2000): Stoppaniite, $(\text{Fe,Al,Mg})_4(\text{Be}_6\text{Si}_{12}\text{O}_{36} \cdot (\text{H}_2\text{O})_2 \text{Na}, \square)$ a new mineral of the beryl group from Latium (Italy). *Eur.J.Mineral*, 11, 121-127
- Ferraris, G., Prencipe, M. & Rossi, P. (1998): Stoppaniite, a new member of the beryl group: crystal structure and crystal chemical implications. *Eur.J.Mineral*, 10, 491-496
- Gibbs, G.V., Breck, D.W., Meagher, E.P. (1968): Structure refinement of synthetic hydrous and anhydrous beryl. *Lithos*, 1, 275-285
- Giuliani, G., Groat, L.A., Marshall, D., Fallick, A.E. & Branquet, Y. (2019): Emerald deposits: a review and enhanced classification. *Minerals*. Vol.9, No.2, 105-185 <https://doi.org/10.3390/min9020105>
- Goldman, D.S., Rossman, G.R., & Parkin, K.M. (1978): The channel constituents of beryl. *Phys. Chem. Minerals*, 3, 225-235
- Gübelin, E.J. & Koivula, J.I. (2004): *Photoatlas of Inclusions in Gemstones*. Opinio, ISBN 978-3-03999-041-2
- Hänni, H.A. (1980): *Mineralogische und mineralchemische Untersuchungen an Beryll aus alpinen Zerrklüften*. - Dissertation. Universität Basel. 107pp
- Hänni, H.A. (1982): A contribution to the separability of natural and synthetic emeralds. - *J.Gemmol.* XVIII, 138-144
- Hänni, H.A., Krzemnicki, M.S. (2003): Caesium-rich morganite from Afghanistan and Madagascar. *J. Gemm.*, Vol. 28, No. 7, 417-429
- Hawthorne, F.C., Cooper, M.A., Simmons, W.B., Falster, A.U., Laurs, B.M., Armbruster, T., Rossman, G.R., Peretti, A., Günter, D. & Grobóty, B. (2004): Pezzottaite $\text{Cs}(\text{Be}_2\text{Li})\text{Al}_2\text{Si}_6\text{O}_{18}$ A spectacular new beryl mineral from the Sakavalana pegmatite, Fianarantsoa Province, Madagascar. *Mineralogical Record*, Vol. 35, September-October
- Huong, T.T.L, Häger, T, & Hofmeister, W. (2010): Confocal micro-Raman spectroscopy: A powerful tool to identify natural and synthetic emeralds. *Gems & Gemology*, XLVI, Spring, 36-41
- Laurs, B., Simmons, W.B., Rossman, G.R., Quinn, McClure, S.F., Peretti, A., Armbruster, T., Hawthorne, F.C., Cooper, M.A., Falster, A.U., Günter, D., Cooper, M.A. & Grobóty, B. (2003): Pezzottaite from Ambatovita, Madagascar: A new gem mineral. *Gems&Gemology*, Winter, 284-301
- Liu Shang-i, Li Guo-Wu, Peng Ming-sheng (2009) *New Investigation of the crystal structure of Pezzottaite*. *Bulletin of Mineralogy, Petrology and Geochemistry*, 28 (suppl.):259 (in Chinese)
- Palke, A.C., Henling, L.M., Ma, C., Rossman, G.R., Sun, Z., Renfro, N., Thu, K., Myo, N., Wongrawang, P. and Weeramankhonlert, V. (2019) Johnkoivulaite, IMA 2019-046. *CNMNC Newsletter No. 51*; *European Journal of Mineralogy*, 31, <https://doi.org/10.1127/ejm/2019/0031-2894>
- Schmetzer, H., Kiefert, L., & Hänni, H.A. (2004) Asterism in beryl, aquamarine and emerald – an update. *JoG,GB*, 29, 2, 65-71
- Shigley, J.E., Thompson T.J., and Keith, J.D. (2003) Red Beryl from Utah: A review and update. *Gems & Gemology*, Winter, 302-313
- Sinkankas, J. (1981): *Emerald and Other Beryls*. Chilton Book Company. Radnor, Pennsylvania. ISBN 0-8010-7114-4. 665pp
- Strunz, H. & Tennyson, C. (1977) *Mineralogische Tabellen*, 6. Auflage, Leipzig, Akademische Verlagsgesellschaft
- Wood, D.L. & Nassau, K. (1968): The characterization of beryl and emerald by visible and infrared absorption spectroscopy. *Amer. Mineralogist*, 53, 777-800