

Composition of Logtung Beryl (aquamarine) by ICPES/MS: A Comparison with Beryl Worldwide

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INTRODUCTION

Beryl is a beryllium-aluminum-silicate mineral. When it grows unimpeded, it forms hexagonal prisms. In its simplest form, its chemical formula is $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$, and it is clear or white in colour. Addition of Cr, V, Mn, or Fe into the formula can result in some of the world's most sought after gemstones: green emerald (Cr, $\pm\text{V}$), pink morganite (Mn), yellow heliodor (Fe), and blue aquamarine (Fe). Yet, no simple addition of these key elements will do; the amount and valence of the element and site of its occupancy within the crystal lattice are key to colour. Beryl's molecular structure is dominated by hexagonal rings comprised of six Si-O tetrahedra (Figure 1). Linking the rings are tetrahedrally coordinated Be ($\pm\text{Fe}$, Mn, Mg) and octahedrally coordinated Al ($\pm\text{Fe}$, Cr, V). The rings are stacked parallel to the crystal prism (z axis) producing hollow channels. This "zeolite" structure, named after a family of minerals known as molecular sieves, permits occupancy of water and cations (particularly alkalis, Na, Li, K, Cs, Rb) within the crystal lattice, but outside of the crystal formula unit. Thus, up to 8% alkalis (Deer *et al.*, 1966) in igneous beryl, and an amazing 14% in hydrothermal beryl (Vianna *et al.*, 2002b) can be accommodated along with a charge balance not accounted for in the formula unit. Schaller *et al.* (1962) described beryl chemistry as an isomorphic series between the end members $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, $(\text{Na}, \text{Cs})\text{Be}_2\text{Al}(\text{Al}, \text{Li})\text{Si}_6\text{O}_{18}$, and $(\text{Na}, \text{K}, \text{Cs})\text{Be}_3\text{R}^{3+}\text{R}^{2+}\text{Si}_6\text{O}_{18}$ where $\text{R}^{3+} = \text{Al}, \text{Fe}, \text{Cr}$ and Sc , and $\text{R}^{2+} = \text{Be}, \text{Fe}, \text{Mn}$ and Mg . In consideration of the channel components, the formula may be generally presented as: $\text{R}^{2+}\text{Be}_2\text{R}^{3+}\text{Al}[\text{Si}_6\text{O}_{18}]\cdot(\text{H}_2\text{O})(\text{Na}, \square)$.

Refractive index of beryl increases with increasing content of alkalis in the channels as the channels would otherwise be empty space within the crystal structure. When iron occupies the channels it appears to be a quintessential agent in the colouration (*i.e.* the chromophore) of aquamarine gemstones (Price *et al.*, 1976; Vianna *et al.*, 2002a). A correlation between Fe content and colour of aquamarine has long been known, although some authors have attributed colouration to other agents such as Cs (Sosedko, 1957). Mössbauer spectroscopy in particular has helped to isolate the chromophore's position within the crystal lattice. Combining this technique with other spectroscopic methods it can be reasonably inferred that ferric iron with octahedral coordination produces a yellow colour, while

ferrous iron in the octahedral site has no effect on colour, and ferrous iron within channels produces a deep blue colour (Vianna *et al.*, 2002b). These same authors showed that in one small population of samples deep blue aquamarines have little Fe^{3+} and greener samples contain more Fe^{3+} or less Fe^{2+} in channels. The common process of heat-treating aquamarine to produce darker blue colour may work through charge transfer of Fe^{3+} to Fe^{2+} , thereby eliminating the greenish cast (Blak *et al.*, 1982).

In this paper we report on the chemical composition of blue beryl that is abundant at the Logtung tungsten-molybdenum deposit of northwestern BC (Figure 2). Mineralization is associated with a porphyritic quartz monzonite intrusion dated at ~ 58 Ma (U-Pb zircon; Mihalynuk and Heaman, 2002) although previous isotopic age determinations suggest an age of around 109 ± 2 Ma (K-Ar muscovite; Hunt and Roddick, 1987) to 118 ± 2 Ma (Rb-Sr; Stewart and Evensen, 1983). Observations reported on here are limited to a few person-days devoted mainly by Ministry of Energy and Mines personnel to mapping the area around the Logtung deposit as part of the National Mapping Program (Ancient Pacific Margin NATMAP, 1999-2000; Mihalynuk *et al.*, 2000). Geological work un-

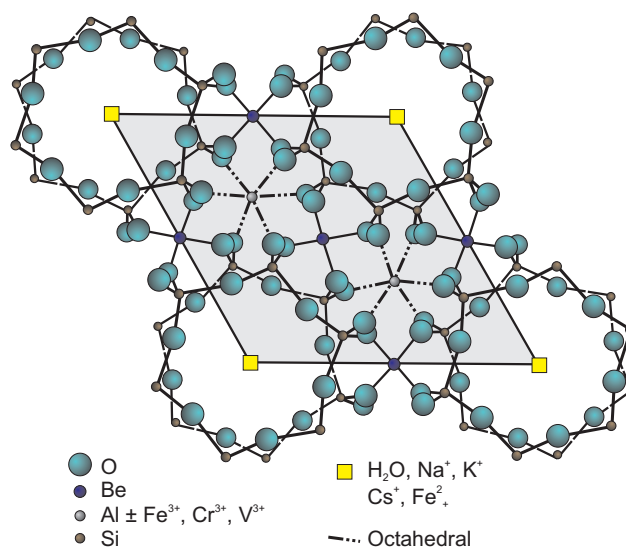


Figure 1. Atomic structure of Beryl, modified after (Deer *et al.*, 1966). Atom loci are projected onto basal 0001 plane and the lower Si-O ring is shown by dashed bonds. Grey trapezoid outlines the unit cell. Ring channels may be occupied by water alkalis and ferrous iron.

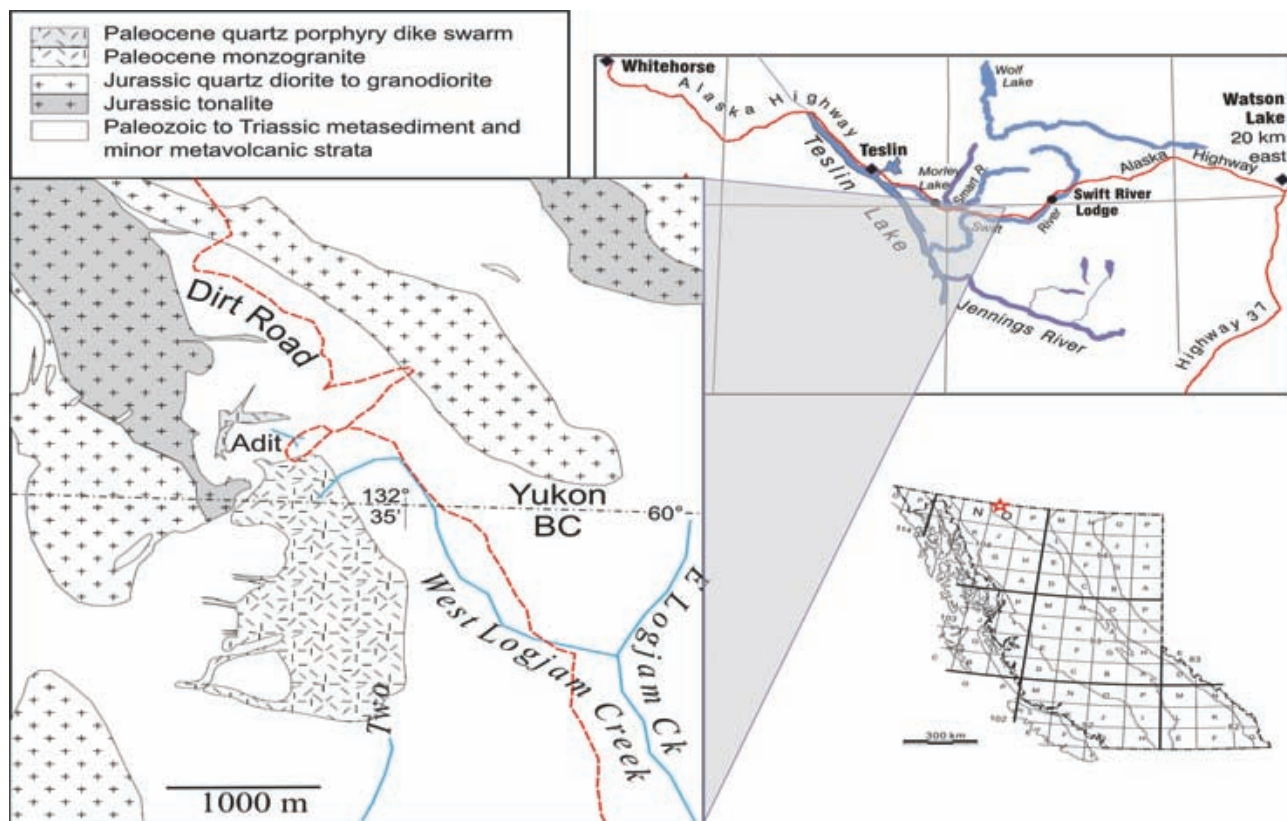


Figure 2. Location of the Logtung porphyry, adapted from (Mihalynuk and Heaman, 2002).

der the NATMAP program was not specifically aimed at beryl, however, blue beryl was reported previously at the Logtung deposit (MINFILE number 104O 016) and we found it to be common, with crystals up to 1.5 cm in diameter and 3 cm long. Unfortunately, all large specimens observed were cloudy or heavily included. Clear crystals tended to be less than 3 mm in diameter.

If large, gem quality stones are to be found at Logtung, a more methodical and intense exploration program than our ancillary approach will be required. To help determine if such exploration is worthwhile, we analyzed a sample of Logtung beryl to compare its chemical affinity with known gem occurrences from around the globe. The chemistry and structure of beryl from some of these occurrences is very well characterized, providing a good benchmark for comparison.

Methods

About 2 grams of beryl were extracted from a single fist-sized sample, crushed with an agate mortar and pestle to a particle size of less than ~1 mm and then carefully sorted. Clear, inclusion-free grains were separated and powdered in the mortar and pestle, resulting in a final sample yield of 0.8 g. The powder was submitted to ACME Analytical Laboratories, Vancouver, for analysis by lithium metaborate (LiBO₂) fusion followed by Inductively Coupled Plasma Emission and Mass Spectrometry (ICPES/MS).

A sample aliquot of 0.2g was fused at 900°C with LiBO₂ which enables complete dissolution of the residue in HNO₃ for analysis by ICPES/MS. This technique provides an analytical sensitivity with a small sample size that is comparable to wet chemical or microprobe analyses of beryl published previously (Table 1). Benefits of ICPES/MS include ease of sample preparation, and the large number of major and trace elements can be determined simultaneously. Drawbacks include the inability to analyze Li₂O content because of the addition LiBO₂ and possible loss of Li during fusion, inability to distinguish Fe valance state, and lack of volatiles determination (e.g. H₂O). As discussed above, H₂O⁺ and H₂O⁻ are principally restricted to crystal channels and do not enter into the crystal structure. Fe³⁺/Fe²⁺ can be estimated from cationic site occupancy balance. However, lack of Li₂O is a serious drawback because the beryl crystal structure can incorporate a large proportion of Li. In the case of the Logtung beryl, Li may be an important constituent based upon the low oxide totals and the results of cationic ratio calculations (Tables 1 and 2).

Results

ICPES/MS analytical results are reported at the bottom of Table 1. ICPES/MS detection limits reported are comparable or better than those reported for the results by other methods listed in Table 1. Figure 3a shows that the most abundant oxides of Si and Al are low in the Logtung beryl

TABLE 1. COMPOSITION OF BERYL FROM OCCURRENCES WORLDWIDE.

Sample No.	Ref.	Method**	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	V ₂ O ₃	FeO	BeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Rb ₂ O	Cs ₂ O	Li ₂ O	H ₂ O+	H ₂ O-	Total
1. Ingersoll	1		64.76	18.91					12.83	12.83				1.23	0.23			0.14	1.96	0.01	100.07
2. Aquamarine	1		64.99	17.17			0.97		12.89	12.89		0.31		1.08	0.29				1.62	0	100.08
3. Biotite schist	1		63.1	0.04	14.08				0.7	11.07	0.03	3.37	2.31	3.32	0.29				2.76	0	100.07
Be 609	2		66	0.03	19.34		2.04			10.75	0.02			0.04	0.03				0.59	0.38	99.22
Be 522	2		63.66	20.89			0.83		12.49	12.49	0.01	0.01		0.24	0.05				0.74	0.38	99.30
Be551	2		63.94	0.01	20.98		2.04		10.08	10.08	0.02			0.32	0.09				1.15	0.47	99.11
DHZ4	3		59.52	0.05	10.63	0.09	2.08		2.24	12.49	0.29	2.16	0.11	1.16	0.16		6.68	0.23	1.62		99.88
1	4	microprobe#	65.12	18.84	0.01			0.03	0.46	13.6		0.03		0.1				0.02	0.95		99.21
2	4	microprobe#	65.45	18.24					0.89	13.65		0.04		0.17				0.02	1.04		99.50
3	4	microprobe#	65.83	18.7	0.02			0.01	1.13	13.65		0.02		0.14				0.02	1.04		100.56
4	4	microprobe#	65.53	18.39	0.08			0.06	0.31	13.7		0.2		0.15				0.01	1.13		99.56
DHZ1	5*		65.14	0.06	18.2		0.65		0.28	12.82		0.5		0.4	0.05				1.98	0.23	100.31
DHZ2	6*		64.16	18.73			0.28		12.98	12.98				1.27	0.39		0.42	0.08	1.44	0.02	99.77
DHZ3	7		61.88	0.01	17.1		0.08		10.54	10.54		0.22	0.44	2.5			4.13	0.6	2.26	0.16	99.92
Rbba1	8	XRF/EDS/ICP	67.0	18.3			0.25		0.66	13.5	0.01	0.09	0.04	0.13			0.01	0.006	1.1	1.05	101.20
Rbba2	8	XRF/EDS/ICP	67.9	18.0			0.22		0.65	13.6	0.03	0.1	0.03	0.12			0.01	0.006	0.09	0.99	101.80
Rbip1	8	XRF/EDS/ICP	67.3	18.2					0.53	12.9	0.05	0.2	0.05	0.53			0.02	0.04	1.13	1.36	101.90
Rbip2	8	XRF/EDS/ICP	67.1	17.9					0.62	12.9	0.01	0.26	0.02	0.57			0.02	0.04	1.11	1.22	101.60
Rblf1	8	XRF/EDS/ICP	65.4	15.8			0.12		1.66	12.1	0.01	0.7	0.03	1.35	0.14		0.06	0.35	0.52	0.24	100.30
Rblf2	8	XRF/EDS/ICP	65.5	15.3			0.19		2.35	12.3	0.01	0.88	0.05	1.38	0.15		0.06	0.35	0.5	0.2	101.30
Rbsc1	8	XRF/EDS/ICP	66.5	17.7			0.05		0.76	12.4	0.02	0.1	0.09	0.36			0.01	0.04	1.12	1.25	99.70
Rbsc2	9	XRF/EDS/ICP	66.8	17.9			0.06		0.87	12.9	0.03	0.1	0.03	0.54			0.01	0.04	1.14	0.87	101.00
MM103-Be	9	ICPES/MS	64.36	0.02	16.83		1.52	0.008	10.838	10.838	0.02	0.2	0.01	0.49	0.1	0.014	0.209				94.62
ICPES/MS detection limit			0.01	0.01	0.01	0.001	0.01	0.0007	0.01	0.001	0.01	0.01	0.01	0.01	0.04	0.006	0.001				

References (Ref.): 1 = Jacob, J., 1938; 2 = Radcliffe and Campbell, 1966; 3 = Schaller, W.T., et al., 1962; 4 = Lind, T., et al., 1986; 5* = Hutton, C.O. and Seelye, F.T., 1945; 6 = Quesnel, P., 1937; 7 = Sosedko, T.A., 1957; 8 = Schaller, W.T. et al., 1962

* = in Deer, et al. (1966)

** = blank if not reported, incompletely reported, or if a wide variety of wet chemical and spectrographic methods employed on an element by element basis.

Mean SiO₂ and Al₂O₃ excluding Logtung analysis are: 65.12 and 17.7 Wt % respectively.

#-Li₂O, BeO and H₂O by standard wet chemical techniques; identical values for some oxides of samples 3 and 4 indicate not analyzed but averaged 1 and 4.

TABLE 2. NUMBER OF CATIONS IN BERYL ON THE BASIS OF 18 (O)

Sample	Location	Colour	Si	Al	Ti	Fe ³⁺	Cr	Be	Mg	Li	Fe ²⁺	Mn	Na	Ca	K	Cs	Rb	Cations	Th	Oh	R+
1Ingersoll	S. Dakota	clear	5.974	2.054				2.843					0.22	0.027				11.118	2.817	2.054	0.247
2Aqua	Switzerland	blue	6.027	1.875		0.068		2.872	0.043				0.194	0.034				11.113	2.899	1.986	0.228
3Bt schist	Austria	green	6.001	1.577	0.003			2.529	0.478		0.056		0.612	0.235				11.528	2.586	2.055	0.647
Be 609	Saskatchewan	green	6.11	2.108	0.002	0.142		2.391			0.002		0.007	0.004				10.766	2.501	2.25	0.011
Be 522	Saskatchewan	yellow	5.862	2.265		0.057		2.763	0.001				0.001	0.043	0.006			10.998	2.625	2.323	0.049
Be551	Colorado	aqua	5.998	2.318	0.001	0.144		2.271					0.002	0.058	0.011			10.803	2.269	2.462	0.069
DH24	Arizona	bluish	6.003	1.263	0.004	0.158	0.007	3.026	0.325		0.189	0.025	0.227	0.012	0.021	0.287		11.547	3.029	1.942	0.535
1 Nigeria		med. blue	5.957	2.03			0.001	2.989	0.004		0.035		0.018					11.034	2.981	2.035	0.018
2 Nigeria		light blue	5.983	1.964				2.997	0.005		0.068		0.03					11.047	3.048	1.969	0.03
3 Nigeria		light green	5.965	1.995			0.001	2.971	0.003		0.086		0.025					11.046	3.022	1.999	0.025
4 Nigeria		med. green	5.977	1.975			0.006	3.002	0.027		0.024		0.027					11.038	3.003	2.008	0.027
DH21	New Zealand	pale green	5.998	1.974	0.004	0.045		2.836	0.069		0.022		0.071	0.006				11.025	2.856	2.088	0.077
DH22	Sweden	clear	5.937	2.041		0.019		2.886					0.228	0.046	0.017			11.174	2.823	2.06	0.291
DH23		pink	6.003	1.954	0.001	0.006		2.456	0.032	0.39			0.47	0.046	0.171			11.529	2.849	1.992	0.641
Rbba1	Brazil	green-blue	6.032	1.94		0.017		2.92	0.012		0.05	0.001	0.023	0.004			0.001	11	3.002	1.969	0.024
Rbba2	Brazil	green-blue	6.068	1.894		0.015		2.92	0.013		0.049	0.002	0.021	0.003			0.001	10.986	3.037	1.922	0.022
Rbip1	Brazil	light blue	6.083	1.937				2.801	0.027		0.04	0.004	0.093	0.005		0.002	0.001	10.993	2.924	1.964	0.096
Rbip2	Brazil	light blue	6.089	1.913				2.812	0.035		0.047	0.001	0.1	0.002		0.002	0.001	11.002	2.948	1.948	0.103
Rb1f1	Brazil	dark blue	6.071	1.727		0.008		2.698	0.097	0.373	0.129	0.001	0.243	0.003	0.017	0.014	0.004	11.385	3.271	1.832	0.278
Rb1f2	Brazil	dark blue	6.119	1.683		0.013		2.76	0.123		0.184	0.001	0.25	0.005	0.018	0.014	0.004	11.174	3.063	1.819	0.286
Rbsc1	Brazil	light blue	6.126	1.92		0.003		2.744	0.014		0.059	0.002	0.064	0.009		0.002	0.001	10.944	2.929	1.937	0.067
MM103-Be	Logtung, BC	light blue	6.19	1.906	0.001	0.11		2.502	0.029			0.002	0.091	0.001	0.012	0.009	0.001	10.854	2.692	2.045	0.113

Notes: "Th" is total cations estimated in the tetrahedral site calculated as: Be + (Si-6) + Mg + Mn + FeO. "Oh" is total number of cations in the octahedral site calculated as: Al2O3 + Cr2O3 + Fe2O3 + V2O3. "R+" is estimated total cations in channels calculated as: Na + K + excess FeO.

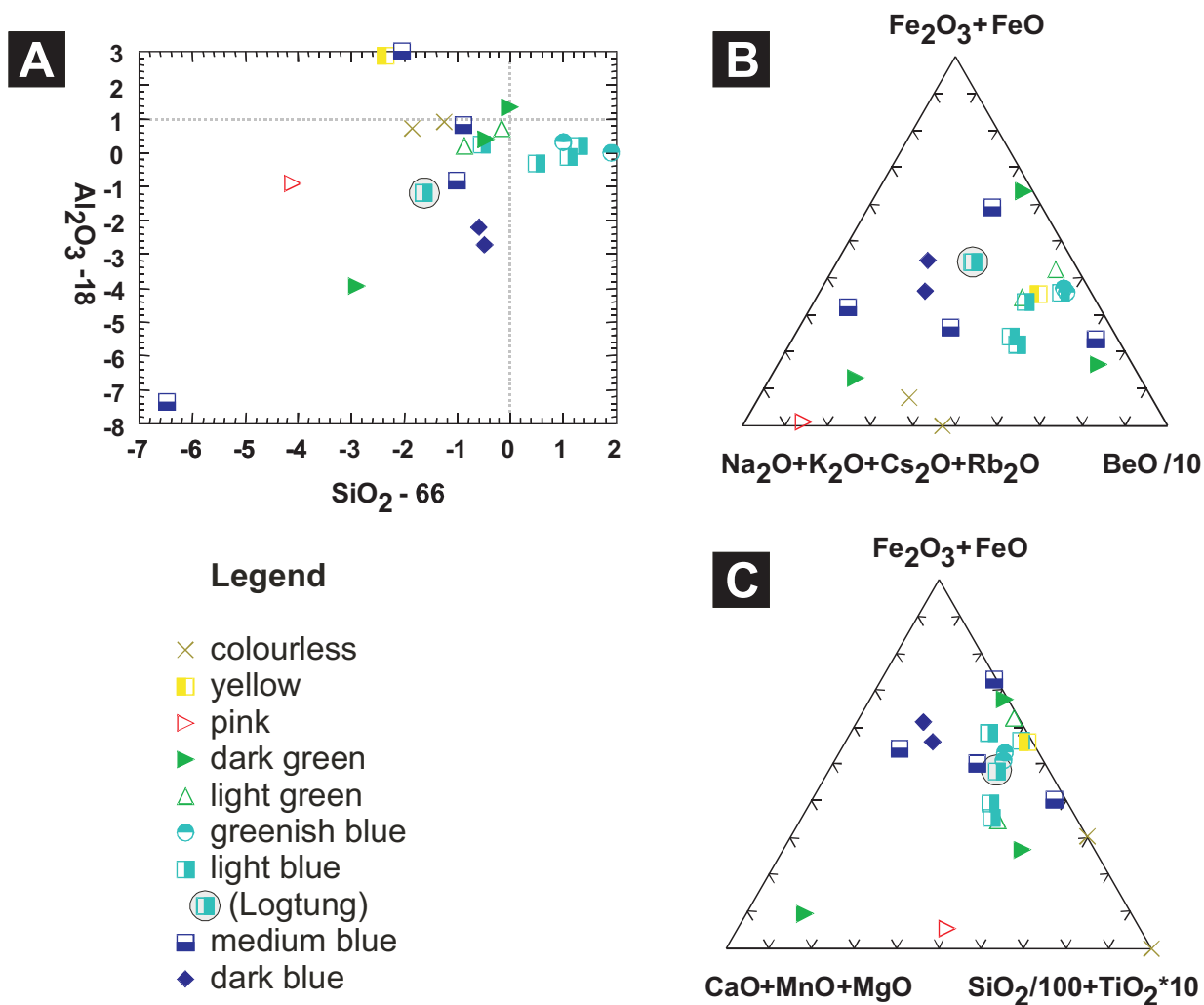


Figure 3. A. variance of SiO_2 and Al_2O_3 content of beryl about a visually estimated mode from analyses in Table 1 of 66 wt. % SiO_2 and 18 wt. % Al_2O_3 . Logtung analysis is highlighted by a shaded circle.

when compared to the visually estimated mean of 65 wt. % SiO_2 and 18 wt. % Al_2O_3 from the data set, possibly contributing to the low total and the 0.3 atomic formula unit deficit in the tetrahedral site (Th, Table 2).

Iron on the other hand, compares favourably with Fe contents in blue (and green) gem beryl worldwide (Figure 3b, c). Only beryl which lack blue or green colouration have lower Fe contents as listed in Table 1 and shown on Figures 3b and 3c.

Conclusions

Inductively Coupled Plasma Emission and Mass Spectrometry (ICPES/MS) permits analysis of small samples (0.2g) with low detection limits. As a result, the method is ideally suited to elemental determination of coarse, single crystals. Drawbacks of the method are acute for minerals that contain significant Li_2O because fusion of the sample for ICPES/MS analysis requires addition of LiBO_2 . Where OH- is a key components of the crystal chemistry, it must be also be determined by a separate method. Nevertheless,

ICPES/MS provides a quick and cost effective method for determining the elemental abundance of key chromophores. In the case of the Logtung beryl, Fe content compares with gem aquamarine (and emerald) elsewhere in the world. On the basis of Fe content, the Logtung beryl can be classified as aquamarine, although the presence of gem-quality aquamarine at this locality has yet to be established.

Acknowledgments

Dave Lefebure collected the sample of aquamarine and generously allowed us to destroy one of the large crystals for analysis. Sample collection was made possible by joint Federal and Provincial funding of the Ancient Pacific Margin NATMAP program.

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