# X-ray diffraction study of emerald from Mingora and Charbagh deposits, Swat valley, Northwest Pakistan

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## Abstract

Samples of emerald collected from carbonate-talc rocks in Mingora and Charbagh mines in Swat valley were investigated by powder X-ray diffraction method. Qualitative phase analyses of the samples showed the presence of emerald as major phase with quartz, talc and magnesite as minor phases in Mingora, and emerald as major phase with traces of quartz and talc in Charbagh sample. Lattice parameters were determined by employing CuK $\alpha$  radiations using a computer program 'Powder'. The lattice parameters of the Mingora and Charbagh specimens (with CuK $\alpha$  wavelength = 0.15418 nm) are: a = 9.258 ± 0.009 (Å), c = 9.191 ± 0.017 (Å) and a = 9.259 ± 0.005 (Å), c = 9.214 ± 0.006 (Å) compared to NBS (National Bureau of Standards) beryl data a = 9.215 Å, c = 9.192Å. The deviations in the unit cell dimensions (especially the increase in a) of the samples are attributed to the presence of additional components (Cr, Fe, Na and Mg) detected by X-ray fluorescence method.

Keywords: Swat Valley; Mingora; Emerald; Powder diffraction; Lattice parameters.

# 1. Introduction

Nature has bestowed Pakistan with treasures of gemstones, such as emerald, ruby, sapphire, topaz, aquamarine, and tourmaline crystals. The deep green emerald of Swat valley and rare pink topaz of Katlang (Mardan district) are two of the most precious gemstones in the world market.

Although basically a silicate of beryllium and aluminium (Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>), beryl may contain a large number of trace elements, particularly alkali metals, depending on the type of host rocks. The green variety of beryl is called 'emerald' while its bluish type is called 'aquamarine. The Bravais lattice of beryl is hexagonal with space group, P6/mcc and 2 numbers of formula units per unit cell (Morosin, 1972). The structure of beryl was determined by Bragg and West (1926). They showed that the true axial ratio (c/a) is twice the ratio previously adopted by crystallographers. The Al or Y site is surrounded by six O atoms in octahedral coordination, whereas Be and Si both by four O atoms in tetrahedral coordination. The SiO<sub>4</sub> tetrahedra polymerize to form six-membered rings parallel to (001) plane and stacking of these rings results in large open channels parallel to z-axis in beryl structure. In these positions, they link oxygen atoms of Si<sub>6</sub>O<sub>18</sub> rings making the whole structure like a honeycomb, with open channels. The structure determined by Bragg and West (1926) was refined and confirmed by Belov and Mateeva (1950). Ginsburg (1955) suggested from X-ray and thermal data that the channels contain alkali metals and water molecules. Detailed work of Wood and Nassau (1968) using visible and infrared spectroscopy absorption led to the recognition of two types of water in beryl; Type I water oriented in the hollow channels with its dead axis perpendicular to the z-axis of beryl. Type II water molecule is rotated about 90° on the molecular dipole by the action of a nearby alkali ion and lies with its symmetry axis parallel to zaxis. The presence of appreciable alkali ions, particularly the large Cs<sup>+</sup> ion causes an increase in the cell parameters, with the 'c' dimension increasing more than the 'a' dimension (Sosedko, 1957). Radcliffe and Campbell (1966) suggested that where substitution of larger ion R+ occurs within the structure it gives an increase in 'c' dimension but when the substitution occurs in the channels, the unit cell expands in the 'a' dimension. For a series of 28 analysed Na-K beryls from Brazil, Filho et al.

(1973) obtained: a = 9.210 to 9.245 Å and c = 9.190 to 9.220 Å.

The aim of the present study on Swat emerald samples from Mingora and Charbagh deposits is two-fold: (i) to find the lattice parameters and (ii) to assess the effects of impurities on the lattice parameters. An X-ray powder diffractometer equipped with scintillation counter for qualitative analysis and X-ray fluorescence spectrometer for elemental analysis were employed. The lattice parameters were calculated by a computer program "Powder" (Taktai and Schaqnulis, 1972).

# 2. Emerald mineralization in Pakistan

A remarkable variety of gemstones like emerald, ruby, spinel, topaz, aquamarine, sapphire and quartz occurs in the northern parts of Pakistan. The four main districts known specially for emerald are the Swat Valley, the Malakand and Mohmand areas, the Bajaur Agency, and the Khaltaro area in the Gilgit district. The most important is emerald from the Swat Valley. The Swat Valley (latitude: 34° 44' 57.3756" N and longitude: 72° 21' 25.4268" E) is approximately 200 km NE of Peshawar (Fig. 1). The major deposits lie in an emerald-bearing belt that stretches from the town of Mingora northeast through Charbagh, Makhad, Malam, Gujar Killi and Bazarkot to Bar Kotkai. The largest mines are scattered around the NE edge of the town of Mingora. Gujar Killi is the second most important mining district in the Swat Valley. The emeralds in the Swat Valley are found mostly with fuchsite and Cr-rich green tourmaline in limonitized shear zones within talc-carbonate rocks traversed by minor quartz veins. The emerald occurs as disseminations and in clusters. In the Swat Valley emeralds also occur with quartz in veins and stock works within extremely fractured quartz-bearing magnesite rocks, again with fuchsite and Cr-rich tourmaline (Kazmi et al., 1986; Arif et al., 1996). At the Gandao deposit in the Mohmand area, 40 km NW of Peshawar, V-dominant beryl occurs in quartz veins in a dolomite host (Grundmann and Giuliani, 2002).

#### 3. Experimental methods and results

The samples of green emerald bearing rocks were collected from Mingora and Charbagh in Swat Valley famous for deposits of gem-quality. The crystals of emerald were crushed to 2-5 mm small pieces. Subsequently the pieces of green emerald were picked by a pair of tweezers from each sample, then pulverized with the help of an agate mortar and passed through 325 meshes (about 55  $\mu$ m) for



Fig. 1. Geological map of Swat area showing location of Mingora and Charbagh emerald deposits, Northwest Pakistan (modified after Kazmi et al., 1984).

getting uniform grain size. These sieved powders were pulverized again so that the grain size now was essentially less than 10µm. The ideal sample for X-ray diffraction is the one with homogeneous grain size of less than  $10 \,\mu m$ without any preferred orientation or strain. It is to be noted that in case of large grain size, a problem may arise simply due to statistics. Only the crystallites having reflecting planes parallel to the specimen surface can contribute to the diffracted intensity. When the number of such planes is too small to justify the supposed random distribution, an error about 5-10% in the intensity measurement occurs in normal circumstances. The pulverized samples were subsequently pressed gently in aluminium holders before mounting them on the diffractometer, for X-ray diffraction studies.

Qualitative phase analysis of single crystals was carried out using X-Ray Powder Diffractometer model Rigaku Geigerflex D/max-IIA at Centre for Solid State Physics, University of the Punjab, Lahore. Before collection of data, the diffractometer was calibrated by running standard pure materials of Cu, Si, Ag and SiO<sub>2</sub> in continuous and stepscan modes under the conditions given in Table 1. The powder X-ray diffractometer employed in the present study is equipped with a pulse height analyser, a rate meter, a recorder and a scintillation counter. The  $2\theta$  angles and intensity of each peak in the XRD patterns of Mingora and Charbagh were calculated. The relative integrated intensity, d-spacing's and miller planes of peaks in the patterns are given in the Tables 2 and 2'. First the d-values were found with the help of XRD tables (Fang and Bloos, 1966). The maximum intensity and full

width at half maximum of each peak were determined and then multiplied to find the interpreted intensity of each peak. Each pattern was qualitatively analyzed by the well-known Hanawalt method (Hanawalt et al., 1983).

Since every crystalline material gives its own characteristic X-ray diffraction pattern, the study of diffraction patterns of unknown phases offers a powerful mean of qualitative phase analysis. For the qualitative analysis, observed powdered diffraction patterns of each gemstone sample were compared with the data files of International Centre for Diffraction Data (ICDD) through a computer software program and identified properly. The XRD powder data (d-values and intensities) of the samples (Figs. 2 and 2') are almost totally similar to the XRD data of beryl in the NBS (National Bureau of Standards), JCPDS (Joint Committee on Powder Diffraction Standards) card no. 9-430. The Bravais lattice of the beryl (emerald variety) has been reported and indexed assuming them to be of hexagonal symmetry. The  $2\theta$ -values in the XRD powder data obtained for determination of lattice parameters of beryl were preliminary treated as suggested in Cullity (1978). The X-ray diffractometer employed in the present study does not give a monochromatic beam of X-rays. Hence the Xrays coming out of the Cu tube of the diffractometer are nickel filtered to eliminate Kβ radiation. The filtered radiation comprises almost of Cuka which is of much higher intensity (order of 100) than the suppressed K $\beta$ radiation. However, Ka peaks of large intensity do have  $K\beta$  peaks which appear on the lower angle side of the former peaks.

Diffractometer conditions	Continuous-scan mode	Step-scan mode
X-Ray Tube voltage	35 kV	35 kV
Tube current	20 mA	20 mA
Radiation type	Cu Kα	Cu Ka
Start angle for Cu, Si and emerald	100°	5°
Stop angle for Cu, Si and emerald	5°	100°
Goniometer Scanning speed	1°/min	0.5 <sup>o</sup> /min
Preset time	1 sec	1 sec
Divergence slit/Anti scatter slit	1°	1°
Receiving slit	0.15 mm	0.15 mm
Radiation Detector	Scintillation counter	Scintillation counter

 Table 1. X-ray powder diffractometer conditions for calibration and collection of data on Mingora and Charbagh, Swat emeralds in continuous and step-scan modes

d-value Observed	d-value Standard	$I_{I_1}$ Observed	<sup>I</sup> / <sub>I1</sub> Standard	HKL
9.341+				
8.015	7.98	27	90	100
4.593+				
4.552	4.60	29	50	110,002
4.332*				
4.245	3.99	16	45	200, 102
3.986	3.254	68	95	112
3.361*				
3.259	3.015	22	35	210, 202
3.112+				
3.020	2.867	100	100	211
2.877	2.660	6	4	300
2.753^				
2.668	2.523	15	30	212
2.528	2.293	7	12	220, 302
2.460+				
2.295	2.208	5	4	104
2.187	2.152	6	16	311
2.158	1.9926	9	20	312, 204
2.102^				
1.993	1.7954	10	18	321, 313
1.840*				
1.799	1.7397	14	20	304
1.742	1.7110	6	14	411
1.716	1.5953	2	8	500, 314
1.601	1.5710	4	10	323
1.575	1.569	3	8	215
1.541	1.5138	7	16	413
1.517	1.4566	4	10	332
1.462	1.4324	5	14	510
1.437	1.3682	4	8	512
1.373	1.2657	2	14	415, 521
1.270	1.2170	6	2	610
1.210	1.1490	4	4	700
1.143	1.1173	4	7	442, 524
Plus weak				
reflections				
		1		

Table 2. X-ray diffraction data for dark green emerald from Mingora, Swat valley, Northwest Pakistan

\*Quartz + Talc ^ Magnesite

d-value Observed	d-value Standard	$I_{I_1}$ Observed	<sup>I</sup> / <sub>I1</sub> Standard	HKL
9.302+				
8.050	7.98	36	90	100
4.610	4.60	34	50	110,002
3.995	3.99	23	45	200, 102
3.349*				
3.264	3.254	90	95	112
3.112+				
3.026	3.015	29	35	210, 202
2.878	2.867	100	100	211
2.671	2.660	5	4	300
2.530	2.523	19	30	212
2.298	2.293	10	12	220, 302
2.218	2.213	6	8	310
2.158	2.152	7	16	311
1.998	1.9926	8	20	312, 204
1.913+				
1.799	1.7954	9	18	321, 313
1.745	1.7397	13	20	304
1.718	1.7110	8	14	411
1.630	1.6265	12	18	412, 224
1.601	1.5953	4	8	500, 314
1.575	1.5710	3	10	323
1.532	1.532	3	8	006
1.518	1.5138	10	16	413
1.454	1.4535	3	12	116
1.437	1.4324	7	14	510
1.379+				
1.371	1.3682	4	8	512
1.270	1.2774	2	12	520
1.211	1.2170	4	2	610
1.207	1.1630	5	7	442, 524
Diverse 1-				
Plus weak				
reflections				

Table 2. X-ray diffraction data for green emerald from Charbagh, Swat valley, Northwest Pakistan

+ Talc \* Quartz



Fig. 2. X-ray powder diffraction pattern of the sample from Mingora deposits, Swat valley, displaying beryl (emerald) as major phase with quartz, magnesite and talc as minor phases.



Fig. 2'. X-ray powder diffraction pattern of the sample from Charbagh deposits, Swat valley, displaying beryl (emerald) as major phase with quartz and talc as minor phases.

Table 3. X-ray diffraction data in Step- Scan mode with radiation CuKα for the dark green emerald from Mingora, Swat valley, Northwest Pakistan.

d-value Observed	d-value Standard	$I_{I_1}$ Observed	$I/_{I_1}$ Standard	HKL
8.018	7.98	27	90	100
4.593	4.60	29	50	002
3.987	3.99	16	45	102
3.259	3.254	68	95	112
3.020	3.015	22	35	202
2.877	2.867	100	100	211
2.668	2.660	6	4	300
2.528	2.523	15	30	212
2.295	2.293	7	12	302
2.187	2.208	5	4	104
2.158	2.152	6	16	311
1.993	1.9926	9	20	204
	I		0.050+0.000 (8)	0.101+0.017 (Å)
Bravais lattice type	Hexagonal	a =	=9.258±0.009 (A)	$c = 9.191 \pm 0.01 / (A)$

Table 3'. X-ray diffraction data in Step- Scan mode with radiation CuKα for green emerald from Charbagh, Swat valley, Northwest Pakistan.

d-value Observed	d-value Standard	$I_{I_1}$ Observed	<sup>I</sup> / <sub>I1</sub> Standard	HKL
8.059	7.98	36	90	100
4.611	4.60	34	50	002
3.995	3.99	23	45	102
3.266	3.254	90	95	112
3.026	3.015	29	35	202
2.878	2.867	100	100	211
2.671	2.660	5	4	300
2.530	2.523	19	30	212
2.298	2.293	10	12	302
2.218	2.213	6	8	310
2.158	2.152	7	16	311
1.998	1.9926	8	20	204
1.799	1.7954	9	18	313
1.745	1.7397	13	20	304
1.718	1.7110	8	14	411
1.630	1.6265	12	18	224
1.601	1.5953	4	8	314
1.575	1.5710	3	10	323
Bravais lattice type	Hexagonal	a=9.259±0.005	(Å) $c = 9.214 \pm 0$	0.006 (Å)
Wave length	1.5418 (Å)	Mode	Step-Sca	n

The Cuk $\alpha$  ( $\lambda = 1.5418$ Å) radiation also consists of two lines, Cuk $\alpha 1$  ( $\lambda = 1.5406$ Å) and Cuk $\alpha 2$  ( $\lambda = 1.5443$ Å) doublet. X-ray diffraction data (reflection plane spacing, relative intensity, miller indices and lattice parameters) in Step- Scan mode with radiation CuK $\alpha$  on Swat emeralds from Mingora and Charbagh mines are given in Tables 3 and 3', respectively. Lattice parameters were determined by employing CuK $\alpha$  radiations using a computer program. The lattice parameters of these specimen (with CuK $\alpha$  radiation) are a = 9.258 ± 0.009 (Å), c = 9.191 ± 0.017 (Å) and a = 9.259 ± 0.005 (Å), c = 9.214 ± 0.006 (Å) respectively compared to the Royal Stone (USA) beryl NBS data a = 9.215 Å, c = 9.192 Å.

The peaks in X-ray diffraction patterns are due to scattering from different subsets of particles in the material. If the particles are distributed in a truly random fashion, then the number of particles in each orientation should be identical or isotropic. In case of preferred orientation (texture of flat or needle like shape), the crystals making up the specimen are not randomly orientated in space. Preferred orientation of crystal grains causes large disagreements between calculated and observed intensities. The preferred orientation of a certain crystal plane (hkl) in a polycrystalline material can be described as:

$$TC (hkl) = \frac{I (hkl)/I_o (hkl)}{\left(\frac{1}{N}\right) \Sigma I(hkl)/I_o (hkl)}$$

Where TC (hkl) is the texture coefficient of the (hkl) plane, Io is the JCPDS standard intensity of the corresponding plane and N is the number of reflections observed in the X-ray diffraction pattern. The  $2\theta$ , d-values, the integrated intensities and the texture coefficients for different reflection planes in step-scan mode with nickel filtered radiation CuKa, of the samples are given in Table 4, 4'. The values of TC >1 for certain planes (211 and 300) in Mingora and (202, 211, 300, 112) planes in Charbagh samples, assume preferred orientation. Except for a few indications, the samples overall do not exhibit any preferred orientation. To find impurities in emerald samples, elemental analyses were performed using X-ray fluorescence spectrometer Model 3064 Higaku Corporation Japan, at Pakistan Institute of Nuclear Science & Technology, Nilore, Islamabad. The present investigations were carried out by operating the spectrometer X-ray tube at 50 KV voltage and 50 mA filament current. The XRF elemental analyses indicated the presence of Cr, Fe, Na and Mg in the emerald samples from Mingora and Charbagh.

## 4. Discussion

Emerald occurs as nuggets and disseminated grains in the talc-altered ultramafic rocks at a number of localities in Swat Valley. Crystals of emerald, with or without chromium muscovite and tourmaline also occur within the quartz veins that cut through the highly fissile altered ultramafic rocks. Detailed studies by Arif et al., (1996) suggest that Cr-bearing silicates (like chromium muscovite, tourmaline and emerald) are contemporaneous and formed as a result of a single episode of hydrothermal activity related to the injection of quartz veins. The hydrothermal fluids supplied Be (emerald), B (tourmaline) and K (muscovite). The Cr, Mg and Fe (also Ni in case of muscovite) were derived from the host rocks (Arif et al., 2011). The XRD patterns (Figs. 2, 2') of Mingora sample show about 30 peaks of emerald and 4, 3, 1 of talc, quartz and magnesite respectively whereas Charbagh sample show about 25 peaks of emerald and 4, 1 of talc and quartz respectively. The presence of only a few peaks of talc and quartz with weak relative intensities is due to host talc-carbonate rocks traversed by minor quartz veins. From such analyses, emerald is a major constituent with minor amounts of quartz, talc and magnesite. Lattice parameters are determined considering only major phase reflections of emerald neglecting weak reflections of miner phases such as talc, quartz and magnesite.

HKL	2θ (degree) Observed	2θ (degree) Calculated	d-value Standard Å	d-value Observed Å	d-Value Calculated Å	Texture Coefficients
100	10.977	11.033	7.98	8.015	8.005	0.47
110	19.246	19.186	4.60	4.592	4.608	0.92
200	22.226	22.192	3.99	3.987	3.987	0.57
210	29.498	29.501	3.254	3.259	3.281	0.99
211	31.043	31.061	3.015	3.020	3.014	1.14
300	33.526	33.524	2.867	2.877	2.866	2.37
212	35.449	35.451	2.660	2.668	2.660	0.79
220	39.148	38.961	2.523	2.528	2.522	0.92
104	41.220	41.036	2.293	2.295	2.303	0.78
311	41.801	41.779	2.152	2.158	2.152	0.59
312	45.460	45.430	1.993	1.992	1.991	0.87
321	50.682	50.734	1.831	1.799	1.795	0.85
304	52.374	52.436	1.795	1.742	1.740	0.67
411	53.278	53.284	1.717	1.716	1.711	0.89

Table 4. X-ray diffraction data for the dark green emerald from Mingora, Swat valley, Northwest Pakistan with nickel filtered radiation CuKα in Step-Scan mode.

HKL	2θ (degree) Observed	2θ (degree) Calculated	d-value Observed Å	d-value Standard Å	d-Value Calculated Å	Texture Coefficients
100	11.024	11.059	8.059	7.98	8.059	0.63
002	19.312	19.216	4.611	4.60	4.611	0.81
102	22.278	22.339	3.995	3.99	3.994	1.32
112	29.548	29.542	3.266	3.254	3.266	1.51
202	31.048	31.152	3.026	3.015	3.025	1.32
211	33.560	33.608	2.878	2.867	2.879	1.59
300	35.475	35.589	2.671	2.660	2.673	1.98
212	39.206	39.001	2.530	2.523	2.532	1.00
302	41.220	41.036	2.298	2.293	2.312	0.78
310	41.821	41.896	2.218	2.213	2.201	0.59
311	45.460	45.430	2.158	2.152	1.997	0.69
204	50.682	50.734	1.998	1.992	1.991	0.71
313	52.479	52.710	1.799	1.7954	1.740	0.67
304	53.309	53.432	1.745	1.7397	1.711	0.89

Table 4'. X-ray diffraction data for green emerald from Charbagh, Swat valley, Pakistan with nickel filtered radiation CuKα in Step-Scan mode

Beryl usually contains some alkalis and in certain varieties, the total alkali contents may rise from 5 to 8 wt% (Folinsbee, 1941). Folinsbee further pointed out that whereas some Na may substitute for Be, the larger ions K and Cs cannot replace Be in the bervl structure. Alkali and alkaline earth metal ions would occupy the centres of the planes of Al and Be ions. In view of wide hexagonal channels, it is probable that large alkali ions are present in channels. Schaller et al. (1962) and Bakakin et al. (1969) have agreed that the octahedral positions occupied by Al in the beryl structure may be substituted by Cr, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mg and Li. The variation in the colour of beryl generally reflects variation in composition (Hammarstrom, 1989). The green colour of beryl is associated with Cr, pink colour with Mn while pale yellow and inky blue due to Fe. Hammerstrom (1989) also reported about 0.02-0.08 wt% Cr<sup>3+</sup>, 0.36-0.38 wt% Na<sup>+1</sup>, 0.02-0.04 wt%  $Fe^{2+}$  and 0.36-0.37 wt%  $Mg^{2+}$  in emeralds from different localities in Swat valley. Generally, in synthetic crystals, the hue of green colour of emerald deepens with the addition of Cr<sup>3+</sup>. The molar volume of the synthesized crystals was found to increase with the incorporation of Cr<sub>2</sub>O<sub>3</sub> dopant (Lee, et al., 2013). The substitution of  $Cr^{3+}$  for  $Al^{3+}$  in the octahedral sites of beryl results in the expansion of a-axis, while c-axis remains nearly unchanged. The lattice parameters of the natural specimen of Mingora and Charbagh emeralds (with CuKa radiation) as determined

in the present study are:  $a = 9.258 \pm 0.009$  (Å), c = 9.191 ± 0.017 (Å) and  $a = 9.259 \pm 0.005$  (Å), c = 9.214 ± 0.006 (Å) respectively compared to the Royal Stone (USA) beryl NBS data reported in 1960: a = 9.215 Å, c = 9.192 Å with an error of 0.003%. The present cell dimensions data on Swat emerald are similar but not identical to the NBS data. The presence of Fe, Cr, Na and Mg in the studied samples probably accounted for the observed changes in the lattice parameters of the Mingora and Charbagh samples through structural substitutions. The corresponding cationic proportions in the standard NBS beryl are 0.1-1.0 mole % Fe, Na and Zn; 0.001-0.01 mole % Mg, Mn, Sr and Ti.

According to Sosedko (1957), the presence of appreciable amount of alkali metals (i.e.  $Na_2O$ ,  $Li_2O$  and  $Cs_2O$ ), particularly the large Cs+ ion causes an increase in the cell parameters, with the 'c' dimension increasing more than the 'a' dimension. Radcliffe and Campbell (1966) suggested when the substitution of somewhat larger R+ ion (alkali and alkaline earth metal ion Na and K etc.) occurs within the structure itself, the 'c' dimension increases. When the substituting ions are located in the channels, once a possible threshold value of about 2.5 mol % R<sub>2</sub>O has been exceeded, the cell expands in the 'a' dimension. The results of studies performed by Bowersox and Anwar (1989) on Gujar Killi emerald show that the main substitutions concern divalent and Li ions for Al in octahedral and Be in tetrahedral sites. In general, the Gujar Killi emerald has high Mg, Fe, Cr, V and Al values as compared to average composition of natural emeralds of Swat District. The Cr which colours the beryl to make it emerald, does not substitute any element in the beryl structure, rather it is present as an impurity in the crystal matrix. Both substitutions need the entry of alkali at the position  $2a(0, 0, \frac{1}{4})$  in the channels between the rings, whereas the position 2b(0, 0, 0) at the center of each ring occupied by water molecules. Three beryl series are distinguished on the basis of c/a ratio (Bowersox and Anwar (1989)): (i) 'octahedral' beryl with c/a = 0.991-0.996; (ii) 'tetrahedral' beryl with c/a = 0.999-1.003; and (iii) 'normal' beryl with c/a = 0.997-0.998. A compositional gap exists between 'octahedral' and 'tetrahedral' beryls with the chemical constraints of bulk-rock chemistry, fluid phase composition and the physical chemical conditions during mineral growth. The c/a ratios of Mingora and Charbagh emerald samples (0.993 and 0.995, respectively) fall in the range of 'octahedral' beryl. Filho et al. (1973) analysed Na-K beryl varieties with low alkali contents from Brazil and obtained cell dimensions range; 'a'=9.210-9.245 Å and 'c'=9.190-9.220 Å. From statistical analysis of their data, they showed that an increase of Fe and (Fe + Mn + Mg) increase 'a' but no influence on 'c'. The presence of Fe, Cr, Na and Mg in the studied samples by XRF accounts for changes in lattice parameters. This relation infers positive correlation with Li and negative correlation with Be. The positive correlation between Fe and increase in 'a' with no effect on 'c' in addition to c/a ratio, predict the 'octahedral' beryl type of Swat valley deposit.

# Authors' contribution

Manzoor Ahmed Badar performed experiment and write up. Safdar Hussain was involved in write up and prepared tables. Shanawer Niaz performed data processing, plots and figures. Saif ur Rehman did geology of the samples.

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