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Emeralds of the Ural mountains (Russia): Geology, fluid inclusions and Oxygen isotopes

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Introduction

Emerald deposits in the Urals are situated at 50 km north-east from Ekaterinburg. These deposits commonly known in Russia as "Emerald Mines" were firstly discovered in 1831. The Ural mountains deposits are considered worldwide as a classic object of pegmatite related "schist-type" deposits (Fersman, 1930). Nevertheless, their genesis is always in debate. The last detailed petrographical and mineralogical publication dates from 1960 (Vlasov and Kutukova). During the "soviet" times in Russia there were no interest on emerald as a gemstone and these deposits were exploited practically only for beryllium. The access to the region was closed for the majority of geologists and such important genetic questions as the sequence of mineral crystallization, age and fluid properties for emerald are still opened.

Geology

Emerald Mines belongs to the continental zone of the North Island-Arc Continental Sector of the Urals. In this sector, the magmatism is characterized by the emission of water-rich crustal granites dated between 260-280 Ma which intrude a metamorphic basement composed of Archaean and Lower Proterozoic rocks (Fershtater et al., 1997).

More than 20 emerald deposits are found along the eastern contact edge of the large Adui granitic massif with metamorphic terranes. The metamorphic host-rocks are composed of amphibolites, quartzites, gneisses and coaly-siliceous schists. They usually contain bodies of talc-chlorite schists derived from the serpentinization of ultramafic rocks. The metamrphic complex is strongly deformed and intruded by granitic pegmatites, diorites, quartz diorites and diorite porphyries.

Fluid percolation affect all the host rocks including talc schists, amphibolites and diorites. In the talc schists which usually contain high concentrations of Cr_2O_3 (0.22-0.52 %), this fluid percolation produced emerald bearing phlogopitic schist-like rock, forming large metasomatic veins. Emerald-bearing metasomatites are also developed at the contacts with dioritic dikes. Other common minerals of the metasomatic veins include fluorite, chrysoberyl (sometimes alexandrite) and phenakite. The central parts of the veins usually contain plagioclasite bodies composed of oligoclase and andesine.

Fluid inclusions

Fluid inclusions in emeralds of 4 different localities of the region of Emerald Mines were studied. 22 double polished plates were prepared and studied from 7 emerald samples.

Table 1. Brief sample description; quantities of fluid inclusions assemblages (FIA) and fluid inclusions (FI) measured.

No	Locality	Sample description	FIA	FI
P2	Cheremshanskoye	Emerald crystals with phlogopite and plagioclase	1	3
P3	Sretenskoye	Emerald crystals in phlogopite	3	12
P5	Mariinskoye	Emerald crystals in plagioclasite	1	4
P8	23 km	Emerald crystals in phlogopite	3	14
P9	Mariinskoye	Emerald crystals in plagioclasite	2	10
P10	---"---	Group of subparallel crystals of emerald in phlogopite	1	4
P11a	---"---	Zonal crystal of beryl-emerald from phlogopite: *Internal zone - emerald (a)*	2	7
P11b	---"---	*Middle zone - beryl (b)*	3	13
P 11c	---"---	*External zone - emerald (c)*	2	6

Principal types of fluid inclusions were determined on a basis of microscopic study: primary, pseudo-secondary and secondary fluid inclusions. All the crystals contain a lot of secondary fluid inclusions on healed fractures. Microscopic measurements were done only in the primary fluid inclusions assemblages with consistent phase filling and homogenization temperatures, without evidences of necking.

The phase filling of primary fluid inclusions in different samples is very consistent. They contain liquid phase (70-80 vol. %), vapor (CO_2, 15-30 vol. %), and also CO_2 liquid phase usually visible without freezing.

Frequently some inclusions of the same group contain also particles of solid phases. This particles are transparent and anisotropic under cross polars. Our observations show that they are not a daughter minerals precipitated from the fluid, but solid mineral relicts (usually, mica particles) trapped during the metasomatic crystal growth:

1. The cases when the solid particle is completely inside of the vacuole are very rare. Normally it situates on the border of inclusion (sometimes coming outside to the crystal), or in the extreme ends of the elongated inclusions.

2. Emerald crystals usually contain a lot of mineral inclusions of host rock minerals (phlogopite, actinolite and others). The points of trapping of these inclusions are also the most probable sites of fluid inclusions cavity.

3. The volume percentage of solid phase is very inconsistent, including the groups of fluid inclusions which are consistent in liquid / vapor relation and microthermometric measurements.

4. Small fluid inclusions normally does not contain solid phases.

5. Solid phase particles inside of the fluid inclusions do not dissolve during the heating up to the total homogenization and decripitation of inclusions.

So, once demonstrated that solid phases are trapped mineral inclusions, their presence were not taking into account during the further measurements and data interpretation.

The heating-freezing stage designed by T.J. Reynolds (Fluid Inclusion Co, USA) and synthetic calibration patrons (T-Calibration Standards by SIN-FLINC) were used for microthermometric studies.

The measurements were realized using the following scheme:

1. Rapid freezing up to -100 -110°C ($CO_{2\ liq}$ freezing)

2. Slow heating with phase changes temperatures measurements:

- melting of $CO_{2\ solid}$ (about –57°C);
- ice melting (about –4°C);
- melting of clathrates (about 7°C);
- homogenization of $CO_{2\ liq} + CO_{2vapor} \rightarrow$ vapor (always to vapor, about 22°C);
- total homogenization of inclusion Liquid + Vapor $\rightarrow$ Liquid (between 250 and 300°C).

Decrepitations of the inclusion are frequent but normally occurred after the total homogenization.

A total of 73 inclusions were studied following this scheme. The results were treated with the PVTX 1.2. computer program for the calculation of salinity and CO_2 density values.

As a result of this study the following conclusions were formulated:

1. Emerald crystallization took place from the aqueous fluid with the density about of 0.82 g/cm^3 and 0.04-0.08 wt. % of CO_2 (density 0.13-0.31 g/cm^3). The CO_{2solid} melting temperaturs are very similar to those of pure CO_2.

2. The primary fluid has quite low salinity (about of 4 wt. % in NaCl equivalent).

3. Similarity of phase filling and of the microthermometric data for the primary fluid inclusions demonstrates that the formation of different deposits of the region of Emerald Mines of the Urals took place under the similar conditions. The variability of sizes, shapes, color and quality of emerald crystals is related with the local of host rocks and tectonic conditions.

Oxygen isotopes study

The oxygen isotopic composition of 14 emeralds originating from 5 different deposits and localities within the Urals emerald mining district were selected, trying to represent the most wide variations of size, color, quality, generations and mineral associations one can find for the Urals emeralds. The extraction of framework oxygen was realized using standard techniques with BrF_5 as the reagent (Clayton and Mayeda, 1963) and following the procedure described by Giuliani et al. (1998).

The oxygen isotopic composition reveals a range in $\delta^{18}O$ (SMOW) between 9.3 and 11.7‰ (mean $\delta^{18}O$ = 10.9 ± 0.6‰, n= 14 samples; Table 2). The $\delta^{18}O$ are comparable with the previous data obtained on 3 Uralian emeralds using the same analytic technique (10.6 ± 0.3 ‰; n= 3; Giuliani et al., 1998). Finally, the total medium value of $\delta^{18}O$ for the emeralds from the Urals is $\delta^{18}O$ = 10.8 ± 0.6‰, (n= 17). For comparison, one emerald from the greisen-granite type deposit of Delgebetey in Kazakhstan gave a $\delta^{18}O$ value of 11.3 ‰ which fit in the range defined for Ural deposits.

Table 2. Isotopic values of $\delta^{18}O$ (‰, SMOW) obtained for the Uralian emeralds

Sample number	Locality	$\delta^{18}O$	$\delta^{18}O$ medium for crystal	$\delta^{18}O$ medium for locality	$\delta^{18}O$ total medium value
p8	"23 km"	9.6	9.7	9.7 ± 0.1	10.81 ± 0.57
		9.8			
160	Ostrovnoye	9.4	9.35	9.35 ± 0.05	
		9.3			
p3	Sretenskoye	11.1	11.1	11.1	
99	Cheremshanskoye	11.0	11.0	10.96 ± 0.05	
101		10.9	10.9		
128		11.0	11.0		
p11 center	Mariinskoye	10.7	10.8	11.1 ± 0.27	
		10.9			
p11 border		10.9	10.9		
p9		11.7	11.7		
		11.7			
58		11.0	11.0		
81		11.1	11.1		
71		11.0	11.0		
107		11.4	11.4		
141		11.1	11.1		
Giuliani et al. (1998)					
OUR-3	Mariinskoye	10.6	10.6	10.6 ± 0.3	
OUR-4		10.2	10.2		
PRK-14/URA		11.0	11.0		

The $\delta^{18}O$ values are very homogeneous and plot in very sharp isotopic fields for each deposit. They are independent of the size, color zoning and location in the mineralized veins. As previously discussed by Giuliani et al. (1998), Ural mountains emeralds $\delta^{18}O$ values overlap those of Socoto in Brazil and Zambia which belongs to economic deposits.

The $\delta^{18}O$ data are similar to those found for beryl in pegmatites and other pegmatite-related emerald deposits. In Urals, as found for the majority of emerald-hosted hydrothermalised pegmatites in the world, the lattice oxygen composition is buffered by the host-rocks, here the pegmatite. The hydrogen isotopic composition of the channel water of emeralds of Mariinskoye deposit (δD= -40.8 ± 0.1‰, n=2) is close to that found for beryl from granitic prgmatites (δD= 42‰, Giuliani et al., 1997). These data combined with the oxygen composition of respective emeralds are compatible with magmatic and metamorphic fluids for the parent fluids of emerald.

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