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A new emerald occurrence from Kruta Balka, Western Peri-Azovian region, Ukraine: Implications for understanding the crystal chemistry of emerald

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Abstract

We investigated emerald, the bright-green gem variety of beryl, from a new locality at Kruta Balka, Ukraine, and compare its chemical characteristics with those of emeralds from selected occurrences worldwide (Austria, Australia, Colombia, South Africa, Russia) to clarify the types and amounts of substitutions as well as the factors controlling such substitutions. For selected crystals, Be and Li were determined by secondary ion mass spectrometry, which showed that the generally assumed value of 3 Be atoms per formula unit (apfu) is valid; only some samples such as the emerald from Kruta Balka deviate from this value (2.944 Be apfu). An important substitution in emerald (expressed as an exchange vector with the additive component $Al_2Be_3Si_6O_{18}$) is $(Mg,Fe^{2+})NaAl_{-1}\square_{-1}$, leading to a hypothetical end-member $NaAl(Mg,Fe^{2+})[Be_3Si_6O_{18}]$ called femag-beryl with Na occupying a vacancy position ($\square$) in the structural channels of beryl. Based on both our results and data from the literature, emeralds worldwide can be characterized based on the amount of femag-substitution. Other minor substitutions in Li-bearing emerald include the exchange vectors $LiNa_2Al_{-1}\square_{-2}$ and $LiNaBe_{-1}\square_{-1}$, where the former is unique to the Kruta Balka emeralds. Rarely, some Li can also be situated at a channel site, based on stoichiometric considerations. Both Cr- and V-distribution can be very heterogeneous in individual crystals, as shown in the samples from Kruta Balka, Madagascar, and Zimbabwe. Nevertheless, taking average values available for emerald occurrences, the Cr/(Cr+V) ratio (Cr#) in combination with the Mg/(Mg+Fe) ratio (Mg#) and the amount of femag-substitution allows emerald occurrences to be characterized. The "ultramafic" schist-type emeralds with high Cr# and Mg# come from occurrences where the Fe-Mg-Cr-V component is controlled by the presence of ultramafic meta-igneous rocks. Emeralds with highly variable Mg# come from "sedimentary" localities, where the Fe-Mg-Cr-V component is controlled by metamorphosed sediments such as black shales and carbonates. A "transitional" group has both metasediments and ultramafic rocks as country rocks. Most "ultramafic" schist type occurrences are characterized by a high amount of femag-component, whereas those from the "sedimentary" and "transitional" groups have low femag contents. Growth conditions derived from the zoning pattern—combined replacement, sector, and oscillatory zoning—in the Kruta Balka emeralds indicate disequilibrium growth from a fluid along with late-stage Na-infiltration. Inclusions in Kruta Balka emeralds (zircon with up to 11 wt% Hf, tourmaline, albite, Sc-bearing apatite) point to a pegmatitic origin.

Keywords: Beryl, substitution mechanisms, ion microprobe analysis, electron microprobe analysis, optical spectroscopy, infrared spectroscopy, Kruta Balka, Ukraine; Lithium, Beryllium, and Boron: Quintessentially crustal