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U-Pb SIMS SHRIMP-II titanite ages and time-range of apatite-titanite mineralization within the Lovozero and Khibiny agpaitic massifs

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Despite the achievements of recent years, and the ability to analyze ultralow (10^{-9} g) quantities of substances with an accuracy better than 1%, the absolute dating of alkaline-ultramafic rocks, carbonatites and associated rare-metal mineralization remains arduous. It depends not only on the specific composition of the parental melts which are undersaturated in silica and thus often leads to a lack of the best geochronometer, zircon, but also low U content, a key element needed for geochronology. The interaction of fluids with crystallizing whole-rock forming and accessory minerals promotes intensive diffusion of parent/daughter elements of isotopic systems with complete or partial re-equilibration, and increased content of gas-fluid inclusions in these minerals. This leads to the fact that even at the micro level it is often not possible to obtain concordant U-Pb dates even for the highest temperature mineral zircon. Inaccurate measurements overestimate time-intervals attributed to the formation and evolution of alkaline ultrabasic massifs: from 25 to 150 Myr, which exceeds the formation time of other intrusions of different compositions (e.g. granite, gabbro, dikes), and the large igneous provinces (LIPs) as well.

A collection of titanites (sphenes) from different kinds of rocks from the layered alkaline complex and apatite-nepheline-(sphene) ore-deposits of the Kola Peninsula and the largest agpaitic nepheline syenite massifs - Khibiny and Lovozero were selected for study. Titanite ($CaTiSiO_5$) is especially well represented in alkaline rocks, where it often forms ore (Ti) mineralization. Titanites contain up to hundreds ppm of U and Th (Th/U ratio is usually >1), the system has a closure temperature for Pb diffusion at 700-750°C [Cherniak, 1993], and has been often successfully used as a mineral-geochronometer for U-Th-Pb dating by TIMS, SIMS and LA-ICP-MS methods.

The individual grains of titanites dated in this study were examined using electron microscopy and energy dispersive microanalysis. The grains from the Lovozero massif were homogeneous and characterized by a high sodium content (up to 4.5 wt.% Na_2O) whereas Khibiny massif titanites had <1.5 wt.% Na_2O. FeO content in all studied titanites does not exceed 3 wt. % and is characterized by the lack of mineral inclusions, with the exception of strontium apatite ones. However, normalized REE distribution clearly indicates the difference between magmatic titanites of alkaline silicate rocks and those from the fluid-metasomatic apatite-nepheline ores. It appears that there is a tetrahedral effect on the light REE which is determined by their elevated fractionation from the enriched ore fluid during crystallization.

U-Pb SIMS SHRIMP analysis of titanites from 12 samples (160 local analyses) showed that the isotopic system is stable in a fluid-saturated alkaline-ultramafic melt, and allows dating of Devonian polyphase massifs of the Kola Peninsula with a precision better than 1-1.5% (2σ). The estimated intrusion age of the agpaitic nepheline syenite Khibiny massif is 374.3 ± 9.2 Ma, and apatite-nepheline ore mineralization is determined to be 371.1 ± 9.4 Myr old, whereas intrusion of differentiated ijolite-urtites complex within the Lovozero massif occurred at 371 ± 11 Ma, and the superimposed mineralization formed 364.2 ± 4.2 Myr ago. Thus, the appearance of silicate rocks and ore-magmatic system formation for the largest agpaitic Khibiny and Lovozero complexes ocurred simultaneously, and took place over 10 million years.