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Did the Siberian Traps eruptions emit enough halogens to have an impact on ozone geochemistry?

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The Siberian Traps Large Igneous Province is thought to have formed over 1 Ma at the end of the Permian, synchronous with the largest mass extinction in Earth's history. There remains much controversy as to the exact mechanism of the mass extinction, but all hypotheses revolve around the emission of volatiles in various forms. The research to date has tended to focus on sulfur and carbon rather than halogen degassing, despite this being probably critical in terms of environmental impact as they might have been played a crucial role in ozone layer depletion and therefore promote mass extinction.

Current study aims to look at the behaviour of chlorine, bromine, iodine and fluorine to evaluate the halogen budget contribution from heterogeneous mantle source and from evaporates, which dominate in the south (Cambrian evaporites) and north (Devonian evaporites) of Siberian platform. For this study we use basaltic sills and lava flows emplaced in the area with no volatile-rich sediments south-east from Norilsk (Dyupkin lake and Lower Tunguska river regions) and a sill intruded into evaporates in Nepa location in the south of the platform, originally aimed at prospecting for potassium salts. Borehole samples of basalts intruded into evaporites might have been penetrated by salts and anhydrite. In order to eliminate this effect and ensure that we analyse halogen contents in pure basalts prior to any further analysis the samples were specifically treated so that penetrated material was removed as leachates. Whole rock fine powders of basalts were analysed for halogens, major and trace elements. The solutions obtained by basalt pyrohydrolysis extraction, leachates of basaltic powders and dissolved evaporites were analysed by ion chromatography for chlorine and fluorine and by ICP-MS for bromine and iodine.

Basalts intruded into evaporites demonstrate predicted pronounced chlorine, bromine and iodine enrichments associated with salt assimilation. The results show that bromine and iodine are decoupled from chlorine and fluorine, presumably due to their more extensive degassing. Moreover, bromine and iodine are probably degassing more profoundly not only from the basalts but from the salts as well. These two arguments imply that bromine and iodine budget of Siberian Traps are of high importance and need to be quantified, which has not been done previously. Observed positive correlation between F/Cl and K/Cl ratios suggests the preferential preservation of fluorine relative to chlorine. Being a subduction fingerprint it supports the hypothesis of unique pyroxenite-rich primary melt of Siberian Traps Large Igneous Province.