

## **A Within-Sill Record of Chlorine Mobilization from Evaporites in Volcanic Basins**

Sara CALLEGARO<sup>1,2,✉</sup>, Hans Jørgen KJØLL<sup>3</sup>, Henrik H. SVENSEN<sup>3</sup>,  
Frances M. DEEGAN<sup>4</sup>, Manfredo CAPRIOLO<sup>5</sup>, Olivier GALLAND<sup>3</sup>,  
Michael R. ACKERSON<sup>6</sup>, and Thea H. HEIMDAL<sup>7</sup>

<sup>1</sup>Centre for Planetary Habitability, PHAB, University of Oslo, Oslo, Norway

<sup>2</sup>Department of Biology, Geology and Environmental Sciences, University of Bologna, Bologna, Italy

<sup>3</sup>Njord Center, Department of Geosciences, University of Oslo, Oslo, Norway

<sup>4</sup>Department of Earth Sciences, Natural Resources and Sustainable Development, Uppsala University, Uppsala, Sweden

<sup>5</sup>School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, United Kingdom

<sup>6</sup>Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, USA

<sup>7</sup>Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY, USA

✉ sara.callegaro@geo.uio.no

Exceptionally voluminous magmatic episodes in the deep geological past, known as Large Igneous Provinces (LIPs), emplaced millions of km<sup>3</sup> of magma in the crust and on Earth's surface in a geologically limited time (<1 Ma), and released vast quantities (Gigatons) of volcanic and thermogenic gases. The outgassing of volatiles was a significant environmental disruptor, leading in some case to global environmental change and biotic crises (Deegan et al. 2023). LIPs are in fact the only geologic source to rival anthropogenic emissions (Deegan et al. 2023, Capriolo et al. 2022) for volumes and rates of released climate-modifying gases. Reconstructing their degassing histories is thus important as analogue case-studies of present-day and future climate challenges. Studies of LIP volatiles discharge often focus on the two primary climate-modifying volatiles, carbon and sulphur. However, in LIPs whose plumbing systems intruded halogen-rich evaporites, the release of halogens might have been an important environmental

and biotic stressor (Svensen et al. 2023). The reactive halogen species generated during eruptions and upon interaction with halogen-rich sedimentary rocks in volcanic basins could cause acid rains and catalyse ozone layer depletion.

A paramount example is the Siberian Traps Large Igneous Province (STLIP), rapidly emplaced at the end of the Permian, synchronous with the most severe terrestrial ecological crisis in Earth's history (251.9 Ma), and the only known mass extinction among insects (Dal Corso et al. 2022, 2024). Palaeontological data suggest that halogens outgassing from the Siberian Traps could have facilitated mutations and DNA damage in life forms via enhanced UVB radiation (Liu et al. 2023). It is still debated whether the ultimate provenance of halogens was the STLIP mantle source or the evaporite series of the Tunguska basin (Broadley et al. 2018; Sibik et al. 2021). We studied 14 sills intercepted by 5 boreholes down to 4 km deep, obtained from locations straddling all across the Lower Tunguska basin (Fig. 1). Whole-rock data suggest that

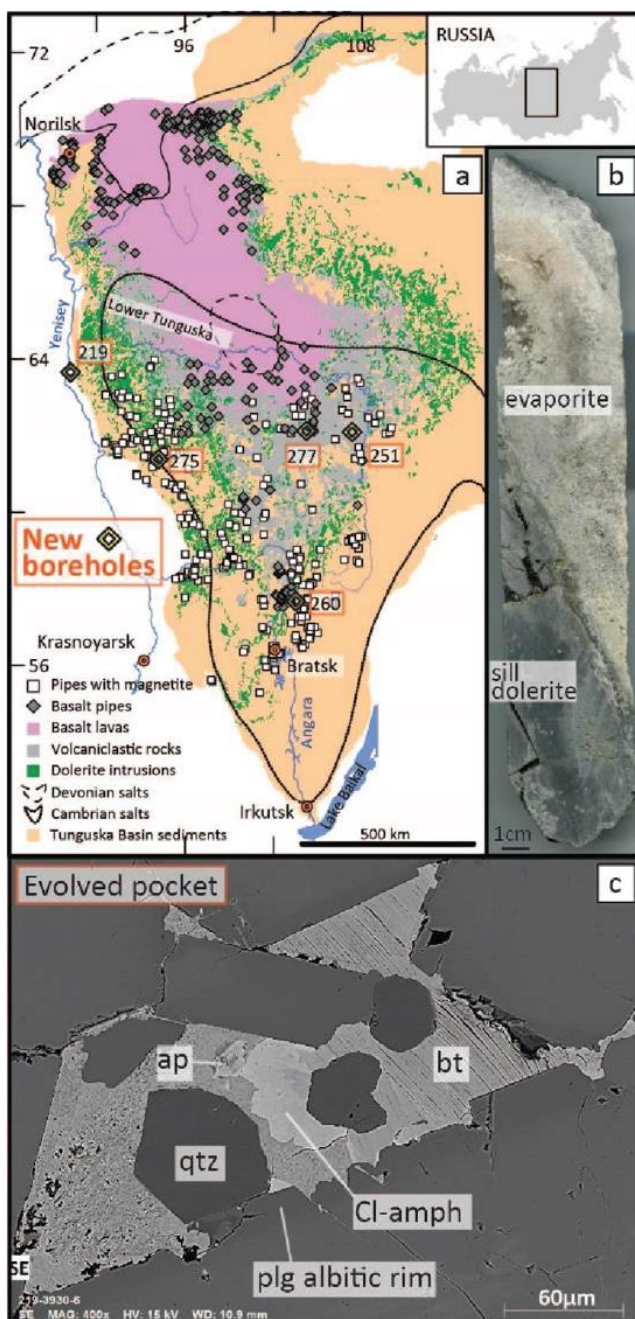


Fig. 1: a) Outline of the Siberian Traps (modified after Svensen et al. 2009) and locations of the available boreholes; b) Core intercepting a sill in direct contact with a halite- and anhydrite-rich evaporitic host-rock; c) SEM image of diktytaxitic pocket containing quartz, apatite, Cl-rich biotite, and Cl-amphibole.



Fig. 2. Sill of the High Arctic Large Igneous Province intruding Permian evaporites of the Gipshuken Formation, in James I Land of Spitzbergen, Svalbard Islands. The sill in this outcrop is 10+ m thick. The black circle indicates the location of the samples with high-Cl biotite. Photo: Hans Jørgen Kjøll, summer 2021.

significant interaction occurred between sills and evaporitic host-rocks (Sibik et al. 2021; Callegaro et al. 2021). The sills are geochemically correlated to the main tholeiitic phase of the Siberian Traps, and with the Noril'sk intrusion, dated coeval to the extinction event (Dal Corso et al. 2024; Callegaro et al. 2021). In addition, we found evidence for late-stage enrichment in chlorine within the sills at the mineral scale. The doleritic sills that developed a relative coarse-grained texture show late-stage evolved pockets. These are pore-filling mineral that form at the late-magmatic to hydrothermal stage among the main framework of doleritic minerals (plagioclase, clinopyroxene, olivine, and oxides, in order of abundance), and comprise a granitic assemblage of quartz, biotite, K-feldspar, apatite, amphibole, and Zr-bearing minerals (Fig. 1). Biotite shows a tendency to incorporate growing amounts of chlorine towards the rims, up to 4.5 wt.%. Mineral boundaries are sometimes filled with pyrosmalite, a Mn- and Cl-rich phyllosilicate. These mineral compositions likely reflect the late-stage circulation of a Cl-rich brine and/or vapor phase in the system, produced by thermal interaction between the sills and the evaporitic host-rocks. Temperatures of crystallization of ca. 600 °C as suggested by Ti-in-quartz geothermometry agree with this interpretation. The presence of hydrothermal vent complexes over the basin suggests abrupt discharge of Cl-rich vapours following pressure buildup at the sills margins (Polozov et al. 2016). The fact that we find high-Cl biotite in sills from all the studied boreholes indicates that Cl mobilization was relevant at the basin scale, and not only a local peculiarity. Overall, these observations support a shallow crustal origin, i.e. from the sedimentary basin, for the halogens released by the STLIP, but further data are needed to confirm the hypothesis (e.g. Cl or S isotope composition). The presence of Zr-rich minerals in the

late-stage pockets will potentially allow to obtain an absolute age for the extensive Cl mobilization and release.

Interestingly, similar evidence is found in sills of the Central Atlantic Magmatic Province (ca. 201 Ma) intruded in the Amazonas basin (Heimdal et al. 2019), and in sills of the High Arctic Large Igneous Province in Svalbard (James I Land) intruded in Permian evaporites (Fig. 2). We propose that the Cl concentrations of late-formed minerals serves as a powerful within-sill proxy to detect halogen mobilization from evaporites in volcanic basins.

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