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Sulfur isotopic evidence for sources of volatiles in Siberian Traps magmas

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ABSTRACT

The Siberian Traps flood basalts transferred a large mass of volatiles from the Earth's mantle and crust to the atmosphere. The eruption of the large igneous province temporally overlapped with the end-Permian mass extinction. Constraints on the sources of Siberian Traps volatiles are critical for determining the overall volatile budget, the role of crustal assimilation, the genesis of Noril'sk ore deposits, and the environmental effects of magmatism. We measure sulfur isotopic ratios ranging from −10.8‰ to +25.3‰ Vienna Cañon Diablo Troilite (V-CDT) in melt inclusions from Siberian Traps basaltic rocks. Our measurements, which offer a snapshot of sulfur cycling far from mid-ocean ridge and arc settings, suggest the $\delta^{34}S$ of the Siberian Traps mantle melt source was close to that of mid-ocean ridge basalts. In conjunction with previously published whole rock measurements from Noril'sk, our sulfur isotopic data indicate that crustal contamination was widespread and heterogeneous—though not universal—during the emplacement of the Siberian Traps. Incorporation of crustal materials likely increased the total volatile budget of the large igneous province, thereby contributing to Permian–Triassic environmental deterioration.

1. Introduction

Early research into the sulfur isotope ratios of Siberian Traps lavas, sills, and country rocks was driven by the need to understand the genesis of the massive Ni–Cu–Platinum Group Elements deposits in the Noril'sk region (Gorbachev and Grinenko, 1973; Grinenko, 1985). These deposits contain enough platinum to satisfy global demand for 10 years or more, and enough palladium for almost half a century (Hageluken, 2006). The mineralized intrusions are characterized by anomalously high $\delta^{34}S$ ratios, possibly as a result of contamination with crustal materials such as evaporite (Li et al., 2009a; Ripley et al., 2003).

In addition to the economic importance of the Siberian Traps, the apparent synchroneity of the eruption with the end-Permian mass extinction (Campbell et al., 1992; Reichow et al., 2009; Renne and Basu, 1991; Renne et al., 1995) provides significant scientific incentive to better understand the details and the effects of magmatism.

The end-Permian mass extinction was the largest loss of floral and faunal diversity in Earth's history (Erwin, 1994; Sepkoski et al., 1981). During the Permian–Triassic event, >90% of marine species and >70% of terrestrial species vanished; even insect diversity suffered (Erwin, 1994). Marine fossil size and diversity did not begin to recover until ∼5 Myr after the beginning of the extinction (Lehrmann et al., 2006; Payne et al., 2004), suggesting that environmental conditions could have been inhospitable for a prolonged period.

Ultra-high-precision single-grain zircon U–Pb dates from the Meishan section in China place the onset of the mass extinction at 251.941 ± 0.037 Ma, with a duration of 60 ± 48 Kyr (Burgess et al., 2014). U–Pb dates from zircon- and perovskite-bearing units in the Maymecha–Kotuy section, near the northeastern corner of the flood basalt province (Fig. 1), indicate that early lavas were erupted at 251.7 ± 0.4 Ma, and that the full duration of magmatism lasted less than 1 Myr (Kamo et al., 2003). Ar–Ar geochronology also suggests that the late stages of extrusive volcanism at Noril'sk occurred within error of the main pulse of the end-Permian mass extinction (Reichow et al., 2009). The high-MgO, olivine-phyric "maymechites"—which are defined as containing MgO > 18 wt%, TiO_2 > 1 wt%, total alkali content <2 wt%, and SiO_2 between 30 wt% and 52 wt% (Le Bas, 2000)—are thought to be among the

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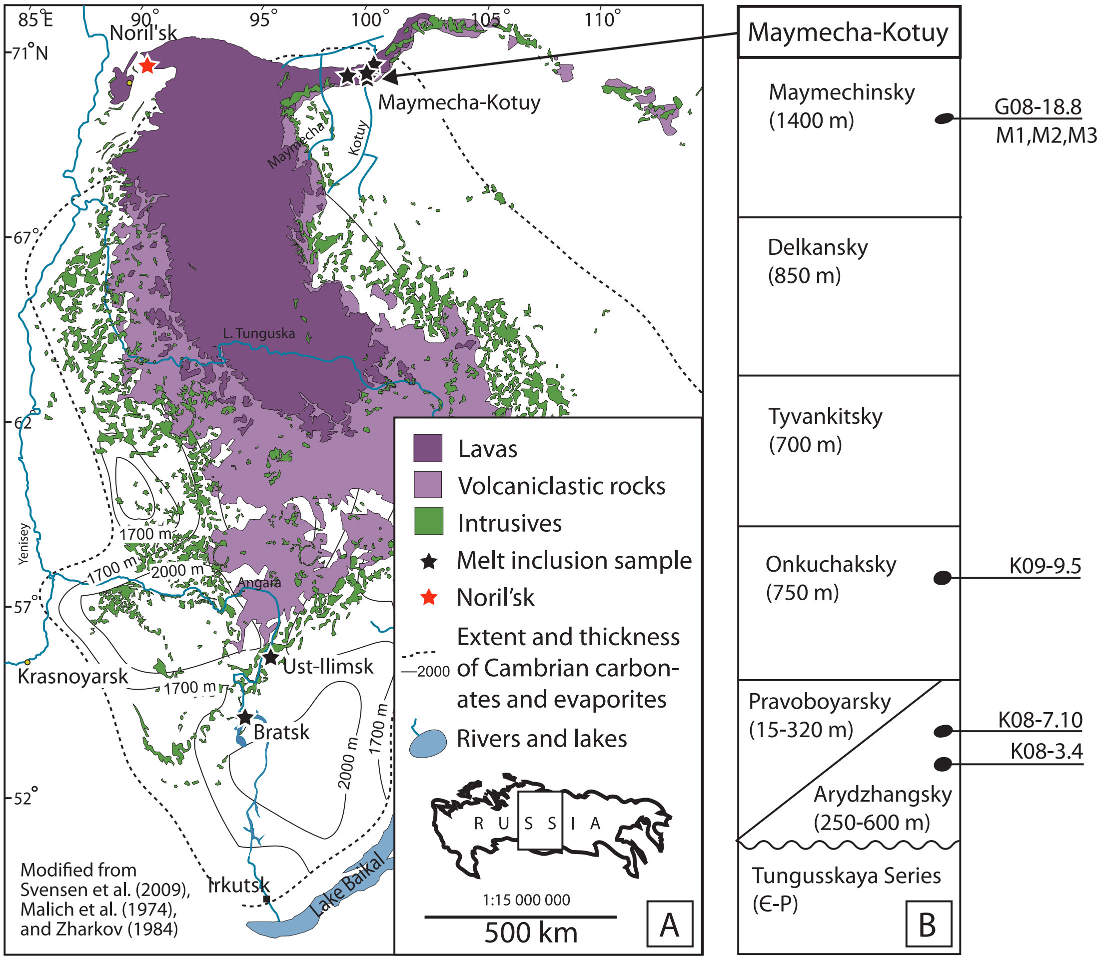

Fig. 1. A: Map showing present day extent of Siberian Traps lavas and volcaniclastics in the Tunguska basin based on Svensen et al. (2009) and Malich et al. (1974). Thickness and extent of Cambrian evaporites, including limestone, halite, dolomite and anhydrite, are based on Zharkov (1984). Maymecha-Kotuy, Bratsk, and Ust-Ilimsk are the three areas from which we obtained melt inclusion samples (starred on the map). Noril'sk is also marked. Reichow et al. (2009) have argued that the distribution of intrusions and basaltic subcrop supports a much larger original extent of the Siberian Traps, reaching into the adjacent West Siberian Basin (not shown here). B: Volcanic stratigraphy in the Maymecha-Kotuy region, adapted from Fedorenko and Czamanske (1997), Kamo et al. (2003), and Black et al. (2012). Not to scale.

final extrusive products of Siberian volcanism (Fedorenko and Czamanske, 1997).

The climatic potency of the eruption depends on the mass and composition of gases released to the atmosphere. Two related models link gas release from the Siberian Traps to environmental change. In the first model, volatiles were primarily mantle derived (Campbell et al., 1992), possibly from volatile-rich recycled material (Sobolev et al., 2011). The second model hypothesizes that assimilation and metamorphism of particularly thick and volatile-rich country rocks produced carbon and halogen compounds, supplementing gases sourced from the mantle and contributing to the deterioration of environmental conditions (Beerling et al., 2007; Ganino and Arndt, 2009; Svensen et al., 2009). Total estimates for sulfur release from degassing Siberian Traps magmas range from ~6300–7800 Gt S based on melt inclusions (Black et al., 2012). CO_2 degassing may have ranged from 64,000 Gt CO_2 (Beerling et al., 2007) to 170,000 Gt CO_2 (Sobolev et al., 2011). Atmospheric modeling suggests that sulfur release from Siberian volcanism could have produced intense acid rain, while metamorphic gases and halogens could have driven ozone depletion (Black et al., 2014).

In order to further evaluate the contributions of crustal contamination to the total magmatic volatile budget—and by implication the contribution of crustal contamination to the environmental consequences of the eruption—we measured $\delta^{34}S$ in melt inclusions from the Siberian Traps. The $\delta^{34}S$ is defined as:

$$\delta^{34}S = 1000 \times \frac{(^{34}S/^{32}S)_{unknown} - (^{34}S/^{32}S)_{standard}}{(^{34}S/^{32}S)_{standard}}$$

where the isotopic composition of the unknown is referenced to that of Vienna Cañon Diablo Troilite (V-CDT). Because magmatic isotope ratios can be compared with isotope ratios in country rocks to ascertain the extent of crustal contamination, $\delta^{34}S$ provides a useful tracer for interaction between magmas and crustal rocks. Sulfur isotope ratios are relatively well-known for seawater sulfur (+10 to +35‰ V-CDT in the Phanerozoic ocean; Claypool et al., 1980) and mid-ocean ridge sulfur (0 ± 2‰ V-CDT; Sakai et al., 1984), though Labidi et al. (2013) have recently suggested that depleted mantle sulfur is closer to -1.28 ± 0.33‰ V-CDT. Other crustal materials are variable, with reduced sulfur materials tending to have lower $\delta^{34}S$ (Thode, 1991). Sub-arc mantle sulfur is slightly higher (+4.7 ± 1.4‰ V-CDT in Indonesia), and may depend on the composition of subducting sediments (de Hoog et al., 2001) and fractionation of sulfur during slab dehydration (Alt et al., 2012). Along with data from Hawaii (Sakai et al., 1982) and Iceland (Torssander, 1989) and in concert with previously published whole rock analyses from the Siberian Traps (Grinenko, 1985; Ripley et al., 2003), our results provide one of the few available datasets constraining the $\delta^{34}S$ isotopic composition of melts potentially sourced from a mantle plume. Our measurements thus offer an opportunity to parse the history and composition of sulfur routed through the deep mantle.