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Atmospheric outgassing and native-iron formation during carbonaceous sediment–basalt melt interactions

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ABSTRACT

Organic carbon-rich sediment assimilation by basaltic magmas leads to enhanced emission of greenhouse gases during continental flood basalt eruptions. A collateral effect of these interactions is the generation of low oxygen fugacities (fO_2) (below the iron-wüstite [IW] buffer curve) during magmatic crystallization, resulting in the precipitation of native-iron. The occurrence of native-iron bearing terrestrial basaltic rocks are rare, having been identified at three locations: Siberia, West Greenland, and Central Germany. We report the first combined study of Re–Os isotopes, highly siderophile element (HSE: Os, Ir, Ru, Pt, Pd, Re), and trace-element abundances for these three occurrences, in addition to host sediments at West Greenland. To quantify the amount of crustal assimilation experienced by the magmas, we present combined crystallization and assimilation models, together with fractional crystallization models, to assess how relative abundances of the HSE have been modified during crystallization. The radiogenic osmium isotopic compositions ($\gamma Os_{initial}$ +15 to +193) of mafic igneous samples are consistent with assimilation of old high Re/Os crustal contaminants with radiogenic $^{187}Os/^{188}Os$, whereas the HSE inter-element fractionations (Pd/Os 2 to >10,000) suggest that some Siberian samples underwent an early stage of sulfide removal.

Metalliferous samples from the Siberian intrusions of Khungtukun and Dzhaltul (associated with the Siberian flood basalts) yield internal ^{187}Re–^{187}Os ages of 266 ± 83 Ma and 249 ± 50 Ma, respectively, reflecting late-Permian emplacement ages. These results imply that crustal assimilation took place prior to crystallization of native-Fe. In contrast, metalliferous samples from Disko Island and Bühl (associated with the West Greenland flood basalts, and the Central European Volcanic Province, respectively) have trends in $^{187}Re/^{188}Os$–$^{187}Os/^{188}Os$ space corresponding to apparent ages older than their reported crystallization ages. These anomalous ages probably reflect concurrent assimilation of high Re/Os, radiogenic ^{187}Os crust during crystallization of native-Fe, consistent with the character of local West Greenland sediments. In all three locations, calculations of combined assimilation of crustal sediments and fractional crystallization indicate between 1–7% assimilation can account for the Os-isotope systematics. In the case of Siberian samples, incompatible trace-element abundances indicate that lower crustal assimilation may have also occurred, consistent with the suggestion that crustal assimilation took place prior to native-Fe precipitation. The extent of local crustal contamination at Siberia, West Greenland, and Bühl necessitates that significant quantities of CH_4, CO, CO_2, SO_2 and H_2O were released during assimilation of carbonaceous sediments. Consequently, carbonaceous sediment–basalt melt interactions have collateral effects on total gas output from flood basalt volcanism into the atmosphere. However, the amount of carbonaceous sediment contamination experienced by melts forming the Khungtukun and Dzhaltul intrusions alone, cannot explain the major C-isotope excursions at the Permo–Triassic mass-extinction event. Instead, further unsampled intrusions that also experienced significant carbonaceous sediment–melt interactions would be required. Enhanced greenhouse gas-emission during the Permo–Triassic mass extinction may have been facilitated by a combination of

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mantle melting and carbonaceous sediment–melt interactions, together with other proposed mechanisms, including wildfires, or by microbial metabolic exhalation.

1. Introduction

Assimilation of crust by basaltic magmas is a near-ubiquitous process during intra-plate volcanism (e.g., Carter et al., 1978; Cox, 1980; Carlson et al., 1981; Day, 2016), making the study of these processes critical for understanding the petrogenetic history of magmas. Occurrences of native-Fe in terrestrial basaltic rocks are rare, due to the generally more oxidizing magmatic conditions of Earth's crust. Magmatic oxygen fugacities (fO_2) in the crust are typically close to the quartz–fayalite–magnetite [QFM] buffer curve (e.g., Frost, 1991). In order to co-precipitate native-Fe and silicate minerals within terrestrial magmatic systems, fO_2 must be lowered at or below the iron-wüstite [IW] buffer curve ($\sim$5 log units below QFM). A primary mechanism to drive magmatic fO_2 conditions below the IW buffer curve is by assimilation of highly-reduced C-rich organic material, including carbonaceous shales or hydrocarbon-rich rocks (e.g., coal). Under these reducing conditions, Fe preferentially forms Fe–C metal alloys that have eutectic temperatures similar to typical basaltic magmas ($\sim$1200 °C; e.g., Chipman, 1973). Experiments have shown that assimilation of limited organic matter (<0.5 wt.%) can decrease the fO_2 conditions of a parental magma by several log units (Iacono-Marziano et al., 2012).

To date, native-Fe occurrences have been reported at three locations worldwide: the Permo–Triassic Siberian traps (Khungtukun and Dzhaltul intrusions, Yakutia, Russia); Paleocene West Greenland lavas (Disko Island), and Miocene volcanics from Central Germany (Bühl). All three localities form part of larger volcanic provinces, including the voluminous Siberian large igneous province (LIP), the North Atlantic LIP, and the Central European Volcanic Province (CEPV) (Fig. 1) respectively. These volcanic provinces are situated within continental crustal terranes with thick sedimentary packages, potentially giving rise to complex crust/magma interactions. Constraining the effects of crustal contamination is necessary in studies investigating mantle sources and processes, due to extensive geochemical modification that can occur to parental magmas during contamination. Here we use rhenium–osmium isotopes and highly siderophile element (HSE: Os, Ir, Ru, Pt, Pd, Re) abundances, coupled with trace element abundances, to assess the role that fractional crystallization and crustal contamination play in modifying the siderophile element and isotope systematics using combined assimilation and fractional crystallization modeling. This form of investigation not only enables quantification of how native-Fe crystallization can act to modify the ^{187}Re–^{187}Os and HSE abundance systematics of magmas traversing through the continental crust, but also allows estimates of crustal assimilation that took place in these settings. Using these crustal assimilation estimates, it is possible to calculate the amount of carbonaceous sediment assimilation that took place during native-Fe formation and to assess the collateral effects of C-rich sediment–basaltic melt interactions, such as the liberation of volatile species, including H_2O, CO, CO_2, CH_4, or SO_2.

2. Samples and analytical methods

2.1. Samples

Samples used in this study represent all textural occurrences of magmatic native-Fe recognized to date on Earth. Oldest occurrences are from the tholeiitic Khungtukun and Dzhaltul intrusions, part of the Permo–Triassic Siberian LIP (250 ± 2 Ma; Kamo et al., 2003). These mafic intrusions are in an area known for economic deposits of Cu–Ni–PGE rich sulfides (e.g., Noril'sk, Yakutia; Fig. 1a). Both Khungtukun and Dzhaltul are directly underlain by Carboniferous–Permian coal-bearing terrigenous deposits (Ryabov et al., 2014). All samples have a typical basaltic/doleritic silicate mineral assemblage consisting of olivine, clinopyroxene, and plagioclase. Khungtukun samples have variable metal content ranging from high (YHM; >50 vol.% metal), intermediate (YIM; 25–50 vol.% metal), to relatively low (YLM; <25 vol.% metal). Dzhaltul samples, OZ-82, OZ-101, OZ-244, and OZ-601 represent Fe-rich nodules, whereas sample OZ-01-3 is a native-Fe bearing dolerite dike that cuts the Dzhaltul intrusion, containing $\sim$25 to 30 modal% native-Fe. The remaining silicates consists of $\sim$5 to 10 modal% olivine, $\sim$15 to 20 modal% plagioclase, and $\sim$40 to 50 modal% pyroxene. No chromite grains have been observed within these samples. Sulfides (mostly troilite) are not common (<0.1 modal%), occurring as sparsely disseminated fine-grained ($\lesssim$30 μm) phases. Within the dike (OZ-01-3), graphite is also preserved.

West Greenland native-Fe tholeiitic basalt occurrences (61 ± 1 Ma, Storey et al., 1998) are associated with the North Atlantic LIP (Fig. 1b). Sample AS-80-2B is from the main sequence of extrusive units at Disko (Qeqertarssuaq) Island, whereas, sample HC-80 represents a sub-volcanic intrusive complex (the Hammers Dal Complex). On average, the silicate mineralogy consists of $\sim$10 to 15 modal% olivine, $\sim$20 to 25 modal% plagioclase, and $\sim$50 to 60 modal% pyroxene within the extrusive and sub-volcanic units sampled; no chromite grains have been observed within these samples. Large native-Fe rich (>50 vol.%) boulders, which probably weathered out of pockets in the sides of dikes where they accumulated, are present along the Disko Island coastline (Clark and Pedersen, 1976). Sample WGLB was obtained from such a boulder and contains >90 vol.% metal; the remaining mineralogy of this sample consists of clinopyroxene and plagioclase. Rare small sulfides ($\lesssim$100 μm) are present enclosed within native-Fe grains in all West Greenland samples investigated here, typically at similar modal abundances as the Siberian samples (<0.1 modal%), and samples can also contain several weight percent carbon. Basaltic units at West Greenland are underlain by Cretaceous–Paleogene carbonaceous deltaic sediment and Archean–Proterozoic basement (Clark and Pedersen, 1976). Studied sediment samples from Disko Island include a C-rich shale (AS-80-4), a C-rich sandstone (AS-80-9), and a C-poor sandstone (AS80-2sst). Xenoliths of C-rich plagioclase-spinel (HC80-103) and graphite (DIGX) were also analyzed.

The Bühl basalt is an alkali–basalt dike within the upper Rhine Graben region of SW Germany (Fig. 1c). Silicate mineralogy consists predominantly of clinopyroxene and plagioclase, with lesser (<10 modal%) olivine, with no chromite grains being identified. Native-Fe is present as disseminated globules 20 to 80 μm in size ($\sim$30 modal%). In some cases, the globules are surrounded by sulfides (<1 modal%). No absolute age has been determined for Bühl, however, based on age estimates from other volcanic fields within southwestern and central Germany (Eifel, Rhön, Urach) volcanism in this region occurred between 11 and 26 Ma (Lippolt, 1982). Together, these volcanic fields form part of the Central European Volcanic province (CEVP; Wimmernauer, 1974). At present, there is little consensus as to whether the CEVP was the result of an upwelling plume, as suggested for Siberia and West-Greenland (Basu et al., 1995; Saunders et al., 1997). Due to the destruction of the