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Platinum-group element abundances and Re–Os isotopic systematics of the upper continental crust through time: Evidence from glacial diamictites

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Abstract

The fine-grained matrix of glacial diamictites, deposited periodically by continental ice sheets over much of Earth history, provides insights into the average composition and chemical evolution of the upper continental crust (UCC) (Gaschnig et al., 2016, and references therein). The concentrations of platinum-group elements (PGEs, including Os, Ir, Ru, Pt and Pd) and the geochemically related Re, as well as ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios, are reported here for globally-distributed glacial diamictites that were deposited during the Mesoarchean, Paleoproterozoic, Neoproterozoic and Paleozoic eras. The medians and averages of PGE concentrations of these diamictite composites decrease from the Mesoarchean to the Neoproterozoic, mimicking decreases in the concentrations of first-row transition elements (Sc, V, Cr, Co and Ni). By contrast, Re concentrations are highly variable with no discernable trend, owing to its high solubility. Assuming these diamictites are representative of average UCC through time, the new data are fully consistent with the previous inference that the Archean UCC contained a greater proportion of mafic–ultramafic rocks relative to younger UCC. Linear regressions of PGEs versus Cr and Ni concentrations in all the diamictite composites from the four time periods are used to estimate the following concentrations of the PGEs in the present-day UCC: 0.059 ± 0.016 ng/g Os, 0.036 ± 0.008 ng/g Ir, 0.079 ± 0.026 ng/g Ru, 0.80 ± 0.22 ng/g Pt and 0.80 ± 0.26 ng/g Pd (2σ of 10,000 bootstrapping regression results). These PGE estimates are slightly higher than the estimates obtained from loess samples. We suggest this probably results from loess preferentially sampling younger UCC rocks that have lower PGE concentrations, or PGEs being fractionated during loess formation. A Re concentration of 0.25 ± 0.12 ng/g (2σ) is obtained from a regression of Re versus Mo. From this, time-integrated ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios for the UCC are calculated, assuming an average UCC residence duration of ~2.0 Ga, yielding ratios of 20 ± 12 and 0.80 ± 0.38 (2σ), respectively.

Keywords: Platinum-group elements; Re–Os isotopes; Glacial diamictite; Secular variation; Upper continental crust

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1. INTRODUCTION

Quantification of the average composition of the continental crust with associated uncertainties, and recognition of secular compositional changes are critical for understanding the origin, differentiation and evolution of the continents. Among the three commonly-defined layers of the continental crust (upper, middle and lower), the upper continental crust (UCC) is the most accessible region and its chemical composition has been the focus of numerous studies (Rudnick and Gao, 2003, and references therein; Kamber et al., 2005; Hu and Gao, 2008; Gaschnig et al., 2016). The average abundances of the major elements and some trace elements (most of the transition elements, Rb, Sr, Y, Zr, Nb, Ba, rare earth elements, Hf, Ta, Pb, Th and U) in the UCC are generally well known, with most estimates falling within a 20% deviation of the averages of all estimates. Other element abundances are less well constrained, especially the halogens, S, Ge, As, Se, In, Sn, Au, Re and platinum-group elements (PGEs, including Os, Ir, Ru, Rh, Pt and Pd), where estimates of average UCC can vary by factors of two or more. This study seeks to provide new constraints on the average abundances of the PGEs and the geochemically related Re, as well as Re–Os isotopic systematics in the UCC through time.

Owing to their highly siderophile and chalcophile nature, the PGEs tend to partition strongly into metallic and sulfide phases, and as a consequence, ~98% of the Earth's PGEs are estimated to be in the core (McDonough and Sun, 1995; McDonough, 2003). Accordingly, PGE concentrations in the silicate Earth are typically low (low ng/g to pg/g range). In addition, PGEs are often concentrated in minute accessory phases, which may be heterogeneously distributed within sample powder aliquots (giving rise to the so-called "nugget effect", Ravizza and Pyle, 1997) so that multiple analyses of the same sample powders may yield concentrations that vary beyond the precision of a single measurement. Both of these factors present challenges to estimating PGE abundances in the UCC.

Rhenium is a trace element that is geochemically similar to the PGEs in that it is strongly siderophile and can also be chalcophile. ^{187}Re decays to ^{187}Os (half-life $= 4.16 \times 10^{10}$ y), providing a radiogenic isotopic system that is useful for dating melt depletion events in the mantle (e.g., Carlson and Irving, 1994), molybdenites (e.g., Stein et al., 1997) and black shales (e.g., Ravizza and Turekian, 1989). In addition, during mantle melting, Re typically behaves as a moderately incompatible trace element, whereas Os is strongly compatible. Therefore, average crust has a much higher Re/Os ratio than the mantle (Shirey and Walker, 1998). Over time the high parent/daughter ratio results in the development of highly radiogenic ^{187}Os/^{188}Os in crustal rocks that can be used as a tracer for crust-mantle interaction (e.g., Saal et al., 1998). Characterizing the average Re/Os and ^{187}Os/^{188}Os ratios of the UCC, is, therefore, critical for mass-balance calculations involving this geochemically important reservoir.

Only a few attempts have previously been made to estimate the PGE and Re abundances, and ^{187}Os/^{188}Os ratio of the UCC (Table 1, Fig. 1). Some of these efforts have estimated the UCC PGE abundances by taking the average concentrations in different rock types and weighting them in proportion to the relative surface area over which they are exposed (Shaw et al., 1976; Gao et al., 1998). Another approach is to use data for fine-grained sediments and sedimentary rocks (e.g., loess and shale) to infer the PGE and Re abundances in the UCC exposed to weathering and erosion (Esser and Turekian, 1993; Wedepohl, 1995; Peucker-Ehrenbrink and Jahn, 2001; Park et al., 2012). In addition, Schmidt et al. (1997a) used impact melts to estimate the PGE and Re abundances in the upper crust of the Baltic Shield. As shown in Table 1 and Fig. 1, the abundance estimates for Os, Ir and Re fall within a relatively narrow range of ~30%, 50% and ~30% deviation from their average values, respectively. However, Ru, Pt, and Pd estimates obtained from fine-grained sediments and sedimentary rocks (Wedepohl, 1995; Peucker-Ehrenbrink and Jahn, 2001; Park et al., 2012), are generally lower, in some cases by more than one order of magnitude, compared to averages determined from large area surface sampling (Gao et al., 1998) and impact melt samples (Schmidt et al., 1997a). In addition, most of the previous estimates are not accompanied by uncertainties, except for the relatively large uncertainties reported by Schmidt et al. (1997a, b).

In this study, we use precise analytical techniques to determine PGE and Re concentrations, as well as ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios for globally-distributed glacial diamictites deposited during the Mesoarchean, Paleoproterozoic, Neoproterozoic and Paleozoic eras. The major and trace element concentrations of these individual samples and composite samples (see Section 2) have been reported by Gaschnig et al. (2014, 2016). Our objectives are to: (1) investigate how PGE and Re abundances, as well as Re–Os isotopic systematics changed in the UCC over time, (2) provide new estimates of PGE and Re abundances, as well as ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios in the present-day UCC, and (3) assess the uncertainty of the new estimates.

2. SAMPLES

About 150 individual diamictite samples were collected globally from four geological eras: the Mesoarchean (~2.9 Ga), Paleoproterozoic (~2.2–2.5 Ga), Neoproterozoic (~0.58–0.75 Ga) and Paleozoic (0.30 and 0.33 Ga) (Tables A1 and A2). Samples are composed of a fine-grained matrix containing a wide range of clasts with different shapes and sizes. The individual diamictite samples come from 24 stratigraphic units or time periods and, thus, 24 diamictite composites were made, with each composite representing one stratigraphic unit or time period (Tables A1 and A2). Geological background information about the stratigraphic units and the GPS co-ordinates of the individual samples are reported in Gaschnig et al. (2014).

3. ANALYTICAL TECHNIQUES

Individual diamictites were first broken into smaller fragments using a rock hammer with the sample placed between thick plastic sheets. The fragments were then