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Highly siderophile element behaviour accompanying subduction of oceanic crust: Whole rock and mineral-scale insights from a high-pressure terrain

C.W. Dale [a,b,*], K.W. Burton [b,1], D.G. Pearson [a], A. Gannoun [b,1], O. Alard [b,2], T.W. Argles [b], I.J. Parkinson [b]

[a] *Department of Earth Sciences, Durham University, Science Laboratories, Durham DH1 3LE, UK*
[b] *Department of Earth Sciences, CEPSAR, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK*

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Abstract

Highly siderophile element concentrations (HSE: Re and platinum-group elements (PGE)) are presented for gabbros, gabbroic eclogites and basaltic eclogites from the high-pressure Zermatt–Saas ophiolite terrain, Switzerland. Rhenium and PGE (Os, Ir, Ru, Rh, Pt, Pd) abundances in gabbro- and eclogite-hosted sulphides, and Re–Os isotopes and elemental concentrations in silicate phases are also reported. This work, therefore, provides whole rock and mineral-scale insights into the PGE budget of gabbroic oceanic crust and the effects of subduction metamorphism on gabbroic and basaltic crust.

Chondrite-normalised PGE patterns for the gabbros are similar to published mid-ocean ridge basalts (MORB), but show less inter-element fractionation. Mean Pt and Pd contents of 360 and 530 pg/g, respectively, are broadly comparable to MORB, but gabbros have somewhat higher abundances of Os, Ir and Ru (mean: 64, 57 and 108 pg/g). Transformation to eclogite has not significantly changed the concentrations of the PGE, except Pd which is severely depleted in gabbroic eclogites relative to gabbros (~75% loss). In contrast, basaltic eclogites display significant depletion of Pt ($\geqslant$60%), Pd (>85%) and Re (50–60%) compared with published MORB, while Os, Ir and Ru abundances are broadly comparable. Thus, these data suggest that only Pt, Pd and Re, and not Os, Ir and Ru, may be significantly fluxed into the mantle wedge from mafic oceanic crust. Re–Os model ages for gabbroic and gabbroic eclogite minerals are close to age estimates for igneous crystallisation and high-pressure metamorphism, respectively, hence the HSE budgets can be related to both igneous and metamorphic behaviour. The gabbroic budget of Os, Ir, Ru and Pd (but not Pt) is dominated by sulphide, which typically hosts >90% of the Os, whereas silicates account for most of the Re (with up to 75% in plagioclase alone). Sulphides in gabbroic eclogites tend to host a smaller proportion of the total Os (10–90%) while silicates are important hosts, probably reflecting Os inheritance from precursor phases. Garnet contains very high Re concentrations and may account for >50% of Re in some samples. The depletion of Pd in gabbroic eclogites appears linked, at least in part, to the loss of Ni-rich sulphide.

Both basaltic and gabbroic oceanic crust have elevated Pt/Os ratios, but Pt/Re ratios are not sufficiently high to generate the coupled ^{186}Os–^{187}Os enrichments observed in some mantle melts, even without Pt loss from basaltic crust. However, the apparent mobility of Pt and Re in slab fluids provides an alternative mechanism for the generation of Pt- and Re-rich mantle material, recently proposed as a potential source of ^{187}Os–^{186}Os enrichment.

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[*] Corresponding author. Address: Department of Earth Sciences, Durham University, Science Laboratories, Durham DH1 3LE, UK. Fax: +44 0191 3342301.
E-mail address: christopher.dale@durham.ac.uk (C.W. Dale).

[1] Present address: Dept. of Earth Sciences, Oxford University, Oxford OX1 3PR, UK.

[2] Present address: Univ. Montpellier 2, CNRS, UMR 5243, CC 60, F-34095 Montpellier, France.

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1. INTRODUCTION

The platinum group elements (PGE: Os, Ir, Ru, Rh, Pt, and Pd) and Re are highly siderophile elements (HSE) that provide key information on the differentiation of the early Earth and the subsequent evolution of the silicate mantle. During core-mantle separation, the 'metal-loving' siderophile elements are strongly partitioned into the metallic core, leaving a highly depleted silicate mantle. However, actual mantle siderophile element abundances are much higher than might be expected for low pressure–temperature (*P–T*) metal-silicate equilibration (Borisov et al., 1994; Righter and Drake, 1997; Ertel et al., 1999; Holzheid et al., 2000), most likely due to high *P–T* silicate-metal equilibration or heterogeneous accretion (the so-called late veneer, Chou, 1978), where continued accretion of meteoritic material, after core formation, replenished the HSE.

The HSE are also chalcophile ('sulphur-loving') and hence strongly partitioned into sulphide minerals in the silicate mantle itself. Sulphide is generally thought to be a residual phase during moderate mantle melting (e.g. <20%, during the generation of mid-ocean ridge basalts (MORB)), and those melts are also commonly sulphur saturated prior to or during eruption, resulting in sulphide crystallisation during magmatic differentiation (e.g. Lorand et al., 1999; Luguet et al., 2003; Bezos et al., 2005). Thus, the HSE are preferentially retained in residual sulphide in the mantle during melting, and further removed from such melts during the crystallisation and segregation of magmatic sulphide. Available data indicate that during magmatic crystallisation sulphide/melt partition coefficients are of a similar order of magnitude for all of the PGE (e.g. Peach et al., 1990; Fleet et al., 1996). In contrast, experimental and natural observations of mantle sulphides suggests that they melt incongruently releasing a Cu–Ni rich sulphide melt, and leaving a refractory Fe-Ni monosulphide solid solution that concentrates Os, Ir and Ru, relative to Pt, Pd and Re (e.g. Alard et al., 2000; Bockrath et al., 2004; Peregoedova et al., 2004). Thus, the HSE variations in MORB are consistent with the widely accepted order of decreasing compatibility, from highly compatible for Os and Ir, through Ru, Pt, and Pd, to moderately incompatible for Re (e.g. Barnes et al., 1985).

Amongst the HSE, Re and Os are linked through β-decay of ^{187}Re to ^{187}Os. Due to the marked difference in compatibility during mantle melting, both oceanic and continental crust possess very high Re/Os ratios relative to the silicate mantle, and over time evolve to radiogenic Os isotope compositions. Consequently, the Re–Os isotope system potentially serves as an exceptional tracer of recycled crustal material in the convective mantle. However, recent studies have shown that during high-pressure (eclogite-facies) metamorphism accompanying subduction, Re and Os exhibit differential mobility between different rock types in the oceanic crust. Basalts show evidence for significant Re mobility and loss (50–60%, Becker, 2000; Dale et al., 2007) whereas gabbros preserve Re–Os isotope signatures consistent with little mobility of either element subsequent to igneous crystallisation (Dale et al., 2007). Such differential behaviour most likely relates to the degree of hydration of the original rock type and its deformation history, but variable behaviour of the mineral assemblage, particularly sulphides (the principal host for many HSE), may also play a role. However, the distribution and behaviour of other platinum-group elements (PGE) in the oceanic crust (both gabbro and basalt) remain poorly constrained (cf. Lorand and Juteau, 2000), as does their behaviour during high-pressure metamorphism accompanying subduction, and it is not clear to what extent HSE abundances in the silicate mantle may be affected by the recycling of oceanic crust, and in particular the extent to which Pt and Re mobility could potentially generate coupled ^{186}Os–^{187}Os enrichments observed in some mantle melts.

This study presents HSE abundances and Re–Os isotope data for basalts and gabbros from the Zermatt–Saas ophiolite, metamorphosed to eclogite-facies conditions during the Alpine orogeny. This includes whole rock and mineral data (silicate, oxide and sulphide) for gabbroic eclogites and their un-metamorphosed igneous precursors, and whole rock data for basaltic eclogites. As no precursor basalt has been preserved, basaltic eclogite data have been compared to MORB. These results provide the first insight into the distribution of HSE in gabbroic and basaltic crust (and amongst gabbroic minerals) and their behaviour during high pressure metamorphism, with the potential consequences for their redistribution in the subduction zone environment and recycling into the mantle.

2. GEOLOGICAL SETTING, SAMPLE PETROGRAPHY AND *P–T* ESTIMATES

Samples were collected from the Zermatt–Saas ophiolite (ZSO), Switzerland, which originally formed part of the Mesozoic Tethyan oceanic crust (~164 Ma, Rubatto et al., 1998). The ZSO underwent Eocene high- to ultra-high- pressure (UHP) metamorphism during south-easterly directed subduction and the subsequent continental collision that formed the Alpine mountain belt. Sampling of the variably metamorphosed Allalin Gabbro body and nearby metabasaltic eclogite units (Täschalp-Pfulwe) was aimed at retrieving lithologies representative of the mafic lower and upper oceanic crust, much of which was recrystallised under metamorphic conditions comparable to those present in subduction zones. Details of sampling area and localities can be found in Dale et al. (2007).

2.1. Petrology and silicate mineralogy

Samples of gabbroic origin preserve a range of *apparent* metamorphic conditions, although field (and even hand-specimen) evidence indicates that all parts of the Allalin unit experienced similar eclogite-facies *P–T* conditions. In some cases, the magmatic mineralogy of the gabbros, principally forsterite-rich olivine, augite and labradoritic plagioclase (compositions in Table EA-1, electronic annex), is preserved entirely. This metastable preservation probably results from the local absence of fluid infiltration, anhydrous mineralogy and a relatively low peak temperature (~600 °C, see below). In contrast, other samples from the same body have recrystallised entirely during metamorphism and comprise an eclogite-facies mineralogy (including garnet, omphacite, zoisite, paragonite, talc and glaucophane, Table EA-1). Although a complex spectrum exists, most gabbros and gabbroic eclogites chosen for this study represent the two end-members. However, several samples from the Allalin Gabbro display a transition from gabbro to metagabbro/eclogite on the scale of an individual hand specimen (referred to as transitional gabbros). These samples probably experienced some fluid infiltration and recrystallisation