

**Dissolved cobalt on
the Kerguelen
Plateau**

J. Bown et al.

This discussion paper is/has been under review for the journal Biogeosciences (BG).
Please refer to the corresponding final paper in BG if available.

Imprint of a dissolved cobalt basaltic source on the Kerguelen Plateau

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Received: 7 May 2012 – Accepted: 17 May 2012 – Published: 19 June 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Processes of cobalt (Co) entrainment from shelf sediments over the Kerguelen Plateau were studied during the KEOPS (Kerguelen Ocean Plateau compared Study) in order to explain the exceptionally high dissolved cobalt concentrations that have been measured in the surface waters above the Kerguelen Plateau, and in intermediate and deep waters above its eastern slope. Lateral advection and dissolution of Co contained in basalt sediments around Heard Island, a main source of lithogenic Co in the study area, were shown to imprint the process of surface enrichment over the plateau. Dissolved Co enrichment was strongest at the intercept of the eastern slope with intermediate and deep waters, probably due to more efficient mobilisation of the sediments in the slope current, in addition to advection of Co-enriched and low oxygenated ocean water-masses.

In surface waters, strong sedimentary Co inputs were estimated to be much higher than biological Co uptake in phytoplankton blooms, underlining the potential role of cobalt as lithogenic tracer. Based on a simple, steady state balance equation of the external input of dissolved iron over the plateau, the fertilization of iron inferred by using Co as a tracer of basalt sources is estimated to be $28 \times 10^2 \pm 21 \times 10^2 \text{ ton yr}^{-1}$ in surface waters of the Kerguelen Plateau. This estimate is consistent with preceding ones and the required iron supply matching the phytoplankton demand.

1 Introduction

Sediment inputs and transport from continental margins, islands, and shelf areas have been identified as important sources of dissolved cobalt to the open ocean (Noble et al., 2008; Bown et al., 2011). However, the processes of Co release from sediments and advection of Co-enriched intermediate and deep waters are poorly constrained. For instance, significant thermally-driven water-rock circulation through porous basalt, as inferred from excess ^{223}Ra measurements (Moore et al., 2008; van Beek et al., 2008),

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can contribute to the release of dissolved Co (DCo) from basaltic rock at intermediate depths, as exemplified in the Pacific waters surrounding the Hawaiian Islands (Noble et al., 2008). Furthermore, advection of Co-enriched intermediate and deep waters from continental shelf and slope can be favoured by the low oxygenation of waters (Noble et al., 2008; Bown et al., 2011) as well as by microbial reductive processes (Saito et al., 2004). These studies intrinsically suggest that DCo may imprint the sedimentary source in intermediate and deep ocean waters. However, the processes of Co entrainment from shelf sediments have not been extensively studied. These issues were addressed during the KEOPS (Kerguelen Ocean Plateau compared Study) cruise in order to better understand if cobalt could also be released from lithogenic material weathered from Heard Island and if cobalt entrainment could generate high DCo concentrations in the upper waters of the shallow plateau, at intermediate and deep depths on the eastern slope.

Previous studies have proposed different mechanisms for the natural Fe fertilization of surface waters over the Kerguelen Plateau (Blain et al., 2008a,b; Chever et al., 2010). However, only this last study proposes a comprehensive budget considering both particulate and dissolved Fe, suggesting that the predominant source of Fe above the Kerguelen Plateau may be lateral advection of waters that have been in contact with the shallow shoal around Heard Island (Chever et al., 2010). Indeed, this hypothesis was first raised by indirect geochemical tracers: rare earth elements (REE) concentrations and radium activities results strongly suggested that lateral advection of lithogenic materials weathered from Heard Island could be an important source of dissolved Fe for the water surrounding the plateau (van Beek et al., 2008; Zhang et al., 2008). Also, regeneration from sinking biogenic materials and input from bottom sediments have been proposed as major processes generating high dissolved Fe (DFe) concentration in the deeper waters below 150 m over the plateau (Blain et al., 2008b). Park et al. (2008b) suggested that diapycnal mixing enhanced by internal tides and convective winter mixing constitute the dominant mechanisms that make the deep Fe available for phytoplankton in surface waters in austral spring and summer. However,

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a short-term Fe budget by Sarthou et al. (2008) indicates that the vertical mixing process alone could not match the phytoplankton DFe demand and other mechanisms such as the dissolution of lithogenic Fe are required. The last part of the present study focuses on the latter mechanism, providing another estimate of the lithogenic Fe supply to the waters of the Kerguelen plateau, based on the distribution of Co.

2 Materials and methods

2.1 Study area

The KEOPS cruise was conducted around Kerguelen Islands from 19 January to 13 February 2005, aboard R/V *Marion Dufresne*. The primary objective of the KEOPS cruise was to demonstrate that the high-chlorophyll region located above the Kerguelen Plateau (Blain et al., 2007) is an area that is naturally fertilized in iron (Blain et al., 2008a).

2.2 Sampling and methods

Seawater samples for the determination of DCo concentrations were collected at stations shown in Fig. 1. Stations A01, A03 and C01 are located over the shallow plateau, stations A07, A08, and C11 above and at the end of the eastern slope, and station A11 in oceanic waters (e.g., not influenced by the plateau; Fig. 1). Samples were collected using acid-cleaned 12-L Go-Flo bottles mounted on a Kevlar line, in an over-pressurized class 100 clean air container, after on-line filtration through Sartoban cartridges (0.2 μm with 0.4 μm prefilter, Sartorius) at a high-purity nitrogen pressure of 0.5 bar. Filtered samples were acidified to pH \sim 2.0 with Ultrapur hydrochloric acid (HCl, Merck), and stored in double bags at room temperature until measurements 5 yr after the cruise.

DCo concentrations were measured in acidified and UV-digested samples by Flow-Injection Analysis (FIA) and chemiluminescence detection, following the method of

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Bown et al. (2011) adapted from Shelley et al. (2010). The method includes UV oxidation of the acidified sample (30 ml) for 3 h in clean silica tubes using a 600 W high-pressure mercury-vapor lamp and an equilibration time of 48 h before analysis (Noble et al., 2008; Bown et al., 2011). The mean reagent blank (based on all blank determinations) in MilliQ water was 6.70 ± 1.20 pM ($n = 12$). The mean detection limit of the method, estimated as three times the standard deviation of the average reagent blank, was 3.60 pM ($n = 12$).

Samples for particulate cobalt concentrations (PCo) were collected at stations A03, A11 and C11 (only) using the same Go-Flo samplers on separate deployments, which were over-pressurised with high-purity nitrogen at ~ 0.5 bar. Suspended particulate material was collected on acid-washed 47 mm 0.2 μ m polycarbonate membranes (Nuclepore) housed in Teflon PTFE in-line filter holder. Typically 2–10 l of seawater was passed across the filter, depending on the suspended particulate load. Gentle suction was applied to the base of the filter holder to remove residual seawater, filter membranes were dried under a class 100 laminar flow hood and then stored in acid-washed petri dishes until analysis in the shore-based laboratory. Particulate Co concentrations were measured using magnetic sector inductively coupled plasma–mass spectrometer (ICP–MS) following strong acid digestion (using a mixture of nitric and hydrochloric acids), following methods published in Bowie et al. (2010) and Cullen and Sherrell (1999).

3 Results and discussion

3.1 Origin and process of dissolved cobalt enrichment in surface waters and above the eastern slope of the Kerguelen Plateau

The vertical distribution of DCo over the shallow plateau shows different behaviours depending on stations location (Fig. 2): a vertically homogeneous distribution at A01, except for a slight increase just above the bottom; a complete homogenization from

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the surface to the bottom at C01 which is the shallowest station located near Heard Island; and anomalous concentration maxima ($\sim 175\text{--}300\text{ pM}$) confined in the surface layer at A03, A07 and A08 below which the concentration is either homogenous until a slight increase at the bottom (A03), or increases with depth and reaches highest DCo levels (200–400 pM) at the intercept of the eastern slope with intermediate and deep waters (A07 and A08, Fig. 2). At the end of the eastern slope (C11 station), high DCo values (150 pM) were also found in the surface layer (200 pM, Fig. 2), and at depths between 500 and 600 m (200 pM, Fig. 2) corresponding to the minimum oxygen core of the Upper Circumpolar Deep Water (Park et al., 2008b, 2009). All the DCo levels over the plateau and its slope were much higher than the concentrations measured at A11 (open-ocean station reference, Fig. 2) which ranged from 20 to 75 pM, and higher than cobalt maximum that have been previously reported (DCo ranging from 50 to 80 pM) and attributed to lithogenic sources (Noble et al., 2008; Bown et al., 2011).

Consequently, high positive horizontal gradients (increasing in the upstream direction) in DCo were observed in the surface layer ($< 150\text{ m}$) between C01 and A03, A07 and A08 and above the eastern slope in intermediate and deep waters between C11 and A08 (0.62, 0.37, 0.21 and 0.59 pmol m^{-4} respectively). Because plateau waters flow anticyclonically around the shallow slope ($< 500\text{ m}$) widely developed around Heard Island (Park et al., 2008b), this indicates that DCo source(s) may exist between C01 and A03, A07, A08, generating high DCo concentration in the surface waters. In the same manner, DCo inputs are occurring in intermediate and deep waters that flows along the eastern slope between C11 and A07, A08 stations.

In order to investigate the origin and processes yielding the DCo enrichments in the surface waters of the plateau, especially between C01 and A03 on the one hand and C11 and A07–A08 on the other hand, we constructed comparative biogeochemical cobalt budgets based on two vertical layers separated by the depth 150 m (Fig. 3), following the general water circulation on the plateau described by (Park et al., 2008b). For the deeper waters (150-bottom) cobalt budgets have also been constructed

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following the upstream-downstream circulation scheme along the eastern slope, that is between stations C11 and A07–A08 (Fig. 4).

3.1.1 Dissolved Co enrichment in surface waters of the plateau

Evidences of a lithogenic source in the vicinity of Heard Island

5 Other trace elements, such as dissolved REE, radium isotopes and total dissolvable Fe, exhibit their highest concentrations at C01, indicative of a nearby lithogenic source (Blain et al., 2008b; van Beek et al., 2008; Zhang et al., 2008; Chever et al., 2010). Furthermore, the dissolved neodymium (Nd) isotopic composition at C01 and A03 was significantly less negative ($-8 \leq \varepsilon_{Nd} \leq -4$) than in open ocean waters ($-10 \leq \varepsilon_{Nd} \leq -8$),
10 reflecting lithogenic input into surface waters of these two plateau stations (Jeandel et al., 2011). All these authors hypothesized that release of tracers from the lithogenic fraction of the sediment deposited on the shelf is the main source for these tracers. There are potentially two lithogenic sources of cobalt into the surface waters of the plateau: one is aeolian deposition of terrestrial dust and the other is entrainment from shelf sediments. The atmospheric deposition flux (dry and wet) of total (dissolved and particulate) Co (TCo) inferred from direct analyses of the aerosols on the Kerguelen Islands ranges from 0.24 ± 0.03 to $0.40 \pm 0.05 \text{ nmol m}^{-2} \text{ d}^{-1}$ (Heimbürger and Losno, LISA, France, personal communication; see Fig. 3). This TCo deposition flux is slightly
15 lower than the soluble Co deposition flux observed in the Atlantic sector of the Southern Ocean ($0.42\text{--}0.66 \text{ nmol m}^{-2} \text{ d}^{-1}$) (Bown et al., 2011). Considering a 4 month atmospheric deposition period (which corresponds to the residence time of the waters) and assuming 18% dissolution of the atmospheric supply in surface waters (derived from cumulated solubility of cobalt contained in coal ash dust after 4 months, (Thuróczy et al., 2010), such inputs would increase DCo concentrations by 0.036 to 0.058 pM in
20 the 0–150 m surface layer, hence representing < 0.1% of the observed DCo increase described above. In other words, aeolian inputs of cobalt are negligible on the Kerguelen Plateau, and they cannot generate surface DCo maxima observed at A03, A07 and A08. Therefore, the latter DCo maxima most likely originate from the entrainment of

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shelf sediments, consistent with the surface circulation scheme and with the conclusions proposed for other tracers (van Beek et al., 2008; Zhang et al., 2008; Chever et al., 2010) (Fig. 1).

Dissolution of PCo as the main source of DCo in surface waters over the plateau

The fairly constant DCo concentrations in the 0–150 m surface layer at the shallowest station near Heard Island, C01 (~60 pM), which are significantly higher (Student *T*-test, $p < 0.001$) than at the open ocean reference station A11 (28.2 ± 5.80 pM, see Table 1) suggests that inputs of Co from sediments can impact the whole water (Fig. 2). At A03 and even more pronounced at A01, the slight increase of DCo observed at the bottom could result from diffusion from bottom sediments (Figs. 2 and 3). However, this added Co does not likely reach the surface because of the near zero vertical gradient of DCo below the surface layer. At A07 and A08 the vertical diffusion flux across the pycnocline remains negligible preventing any impact to the surface of the high levels of DCo detected at intermediate and deep depths (Fig. 3). Therefore the local inputs from the bottom are likely not the source of DCo into the surface waters over the plateau. Hence the lateral advection from C01 is the most likely process explaining the DCo enrichment at A03, A07 and A08.

Suspended PCo concentration that would be released from mechanical weathering of the basalt has been estimated by using the particulate Nd concentration measured at C01 (see legend in Fig. 3), because no direct measurement of PCo was available at this station. This calculation leads to an estimation of PCo concentration of 580 ± 360 pmol l⁻¹ at 20 m depth at C01, indicating that PCo could be extremely high around Heard Island and that weathering of basalts is a major source of PCo at the study site. Assuming that the calculated Co abundance is also applicable to lithogenic material south of Heard Island and considering the general circulation over the plateau (Park et al., 2008b), basaltic sediments could be an important source of Co for plateau waters circulating downstream from the island, as they are for REE (Zhang et al., 2008) and Fe (Blain et al., 2008b; Chever et al., 2010). The dissolved Nd isotopic composition of the waters at C01 ($-6 \leq \epsilon_{Nd} \leq -4$) (Jeandel et al., 2011) further supports the

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enrichment of plateau waters from basaltic sediments ($\epsilon_{\text{Nd}} \sim -2$) (Weis et al., 2002; Doucet et al., 2005). This is consistent with the REE and radium isotope distributions showing that lateral advection of inputs from the shelf in surface waters from C01 to A03 is possible and consistent to physical observations (Park et al., 2008a,b), combined with measured ^{228}Ra activities (van Beek et al., 2008). At C11 (depth < 100 m), relatively high ^{228}Ra activities (van Beek et al., 2008) and a less negative neodymium isotopic composition than the oceanic signature (Jeandel et al., 2011) were also recorded, both indicative of lithogenic inputs there.

The advection alone of DCo from C01 towards the other stations of the plateau does not account for the surface enrichment observed at A03, A07 and A08. Indeed the significant positive DCo gradient of 0.62 pmol m^{-4} between C01 and A03 needs to be explained. The budget proposed in Fig. 3 allows estimating a concomitant loss of PCo of $995 \pm 905 \text{ nmol m}^{-2} \text{ d}^{-1}$ between these 2 stations ($[\text{PCo}]_{\text{mean}} = 0.85 \pm 0.23 \text{ pM}$ at A03, standard error, $n = 4$). Two potential processes could remove PCo from the surface waters: the dissolution of PCo (thus production of DCo) and its removal by physico-chemical processes (e.g., particles aggregation, precipitation and sinking). The important positive advective term calculated for DCo ($581 \pm 142 \text{ nmol m}^{-2} \text{ d}^{-1}$, Fig. 3) between C01 and A03 is supporting the dissolution hypothesis. Furthermore, the dissolution of PCo advected from C01 would increase the initial DCo inventory by $104 \pm 65 \text{ pM}$ in surface waters of A03, considering a dissolution of PCo of $\sim 18\%$ derived from the cumulated solubility of cobalt contained in coal ash dust after 4 months (e.g., residence time of the waters flowing on the plateau) (Thuróczy et al., 2010). This estimate accounts for about half of the DCo inputs detected in surface waters of A03 ($175\text{--}300 \text{ pM}$; Fig. 2), further supporting that dissolution of PCo is a main source of DCo in surface waters of the plateau.

Between C11 and A07 lateral DCo advection was the dominant source flux in the upper layer, contrasting with the DCo sink observed between C11 and A08 (Fig. 4). Biological uptake, export and atmospheric input terms were calculated to be about equal at A07 and A08 due to the proximity of these stations and their comparable

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biological activity (Fig. 4). Nevertheless A07 was shallower and located at the top of the slope (Fig. 3); hence the advection of DCo-enriched surface waters of the plateau reaching this station is also conceivable in addition to advection from C11. Thus the enrichment of the upper waters between C11 and A07 may arise from the transport of lithogenic DCo and potential mixing with the upper waters of the plateau that have been shown to be enriched in DCo.

To date only dissolution kinetics of Co and extrapolated cumulated solubility over months from coal ash dust in seawater are available for our estimations (Thuróczy et al., 2010). A dissolution experiment of basalt in acidic MilliQ water (pH = 6) suggested that the dissolution rate of Co from the basalt ($0.062 \times 10^{-16} \text{ mol m}^{-2} \text{ s}^{-1}$) is significantly lower than the Fe release rate ($0.11 \times 10^{-16} \text{ mol m}^{-2} \text{ s}^{-1}$) (Hausrath et al., 2009). This would indicate that basalt dissolution rates are element-specific and that Co dissolution could be slower than Fe dissolution, which partially explains why DCo concentrations do not display their highest values close to C01, suspected to be the most impacted station by the lithogenic inputs for Fe, REE and Ra (Blain et al., 2008b; van Beek et al., 2008; Zhang et al., 2008; Chever et al., 2010). In addition, the organic complexation of DCo may enhance both the basaltic dissolution (Hausrath et al., 2009) and the stabilization of Co in the dissolved phase as previously observed in waters of the Southern Ocean (Bown et al., 2012). Finally, regeneration of DCo has been previously suggested to be an important internal Co source that could represent ~ 70 % of the biological uptake south of the Polar Front (Bown et al., 2011). Hence, such regeneration processes, associated with the rather low export flux estimated at A03, A07 and A08 would increase the residence time of DCo in surface waters of the shallow plateau.

3.1.2 Dissolved Co enrichment above the eastern slope of the plateau

In deeper waters, lateral advection of DCo between C11 and A08 along the eastern slope was the highest source calculated in the present study ($2046 \pm 470 \text{ nmol m}^{-2} \text{ d}^{-1}$, Fig. 4). Mean current velocity along the slope ($\sim 0.08 \text{ ms}^{-1}$) was twice as high as on

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the plateau ($\sim 0.04 \text{ ms}^{-1}$) (Bown et al., 2011; Park et al., 2008b, 2009), which in turn may intensify the resuspension of lithogenic particles from deposited sediments and explain the amount of DCo advected from C11 to A08. The DCo entrainment by the slope current may also be promoted in the low oxygenated UCDW that flows along the eastern slope. Indeed DCo can be produced by reduction of manganese oxides contained into the sediments and released at the sediment-water interface by diffusion of DCo from the pore waters (Heggie and Lewis, 1984; Johnson et al., 1988), in addition to the dissolution of resuspended lithogenic particles in the waters above the sediment. According to budgets at station A08, the intensity of the vertical diffusion between 600 and 1000 m depth ($4.41\text{--}31.1 \text{ nmol m}^{-2} \text{ d}^{-1}$, Fig. 4) combined with lateral advection of DCo from C11 might significantly increase DCo concentrations to the 800 m depth (Fig. 2). At A07, the vertical diffusion of DCo from bottom sediments was less intense than at A08 ($2.0\text{--}14.0 \text{ nmol m}^{-2} \text{ d}^{-1}$ between 550 and 200 m depth, Fig. 4). Consequently the enrichment was more important at the intercept of the eastern slope in intermediate and deep waters. The elevated DCo levels recorded in the UCDW at C11 could also be due to enrichment in DCo and its stabilization as this water mass flowed within the Antarctic Circumpolar Current and across the Fawn Trough, similarly to previous observations in UCDW at other locations (Bown et al., 2011; Park et al., 2008b, 2009).

3.2 Sedimentary inputs of dissolved Fe as inferred from Co entrainment fluxes

Dissolved Fe concentrations (DFe) in the surface layer over the plateau in late summer indicate that removal terms such as biological uptake by phytoplankton and/or abiotic scavenging are high enough to mask the sedimentary inputs of DFe in surface waters (Blain et al., 2008b; Chever et al., 2010). Contrastingly, lateral advection of DCo in surface waters at A03 was much higher than either the biological uptake of DCo or the downward particulate export fluxes (Fig. 3), which makes possible the use of DCo as a lithogenic source tracer. This means that the basaltic Co

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source could be used to estimate the lithogenic dissolved Fe input on the plateau. In this goal we propose to use the same approach as Zhang et al. (2008). Assuming steady state and mass conservation, the external input of DCo, F_{DCo} , can be written as: $F_{\text{DCo}} = F_w \times ([\text{DCo}]_{\text{plateau}} - [\text{DCo}]_{\text{ocean}})$, where F_w stands for a mean water flux through the surface layer (0–150 m) over the plateau, $[\text{DCo}]_{\text{plateau}}$ is the mean DCo concentration in the surface layer averaged over the whole plateau shallower than 1000 m, and $[\text{DCo}]_{\text{ocean}}$ is the surface layer DCo concentration at A11, our open ocean reference station (Table 1). F_w is estimated as $2.0 \pm 0.5 \text{ Sv}$ ($1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$) based on the top-to-bottom water transport associated with the anticyclonic circulation over the Northern Kerguelen Plateau of 4 Sv (Park et al., 2009), and considering the surface intensification of geostrophic currents suggesting a roughly equal partition of water flux above and below 150 m (Park et al., 2008a). The error bar of F_w corresponds to the 25 % errors in estimation of mean currents (Park et al., 2008a). Finally, the external DFe input flux, F_{DFe} , was estimated as F_{DCo} multiplied by the ratio of relative abundances of Fe to Co in basalts, their solubility ratio, and considering that DFe accounts for 5 % of the total Fe (dissolved + particulate) above the plateau (Chever et al., 2010): $F_{\text{DFe}} = F_{\text{DCo}} \times (\text{Fe}/\text{Co})_{\text{basalt}} \times (\text{Fe}/\text{Co})_{\text{solubility}} \times 5 \%$. All parameter values used in this equation are listed in Table 1. The resulting external inputs of DFe to the surface waters of the plateau are $(28 \pm 21) \times 10^2 \text{ tonDFeyr}^{-1}$ (Table 1). The error bar was calculated by propagating the uncertainties of all variables indicated in Table 1. The DFe external input estimated here is close to that estimated independently from Nd ($(60 \pm 42) \times 10^2 \text{ tonDFeyr}^{-1}$) based on the initial model of Zhang et al. (2008), recalculated for the 0–150 m depth layer and considering that DFe accounts for 5 % of the total Fe above the plateau (Chever et al., 2010).

It is interesting to check whether our estimate is also consistent with the advective DFe supply required to sustain the phytoplankton bloom during KEOPS. Based on the results of Sarthou et al. (2008), Blain et al. (2008b) reported that the net Fe demand of the phytoplankton community over the plateau is $208 \text{ nmolm}^{-2} \text{ d}^{-1}$, for which $31 \text{ nmolm}^{-2} \text{ d}^{-1}$ is provided by the vertical diffusive supply. The remainder

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177 nmol m⁻² d⁻¹, should then be provided by both winter stock and lateral advection. Given the seasonal DFe flux ratio of about 3.36 between winter stock utilisation and vertical diffusive supply according to Table 2 of Blain et al. (2008b), the winter stock should provide as much as 104 (= 31 × 3.36) nmol m⁻² d⁻¹ of DFe, leaving 73 nmol m⁻² d⁻¹ for lateral advection. Assuming a bloom surface area over the Northern Kerguelen Plateau of the order of 9 × 10¹⁰ m² (or 300 km × 300 km), the annual Fe supply by lateral advection amounts to 1.3 × 10² ton yr⁻¹. This value is in the order of magnitude, yet somewhat lower than the external DFe input estimated from DCo ((28 ± 21) × 10² ton DFeyr⁻¹), indicating that the external DFe input is more than sufficient for phytoplankton demand. Here the advective DFe flux estimated from the short-term Fe budget can be underestimated by the portion of the DFe winter stock which includes advected (and regenerated) DFe. Furthermore the flux estimated from DCo can be overestimated as it considered a constant (Fe/Co)_{solubility} ratio in acidic MilliQ water, while recent work on other trace metals dissolution from basalt in seawater showed more complex dissolution kinetics (C. Jeandel, personal communication). Despite these uncertainties, estimated rates of advective supply and phytoplankton demand in excess of that supplied by other processes varied within the same order of magnitude supporting the use of DCo as a new tracer of the natural iron fertilization over the Kerguelen Plateau.

4 Conclusions

Basalt weathering in the vicinity of the Heard Island has been identified as the main source of particulate cobalt that could be partially dissolved during lateral advection to generate the very high DCo concentrations observed in surface waters of the Kerguelen Plateau. Intermediate and deep waters that flow along the eastern slope even exhibited even higher DCo concentrations which can be due to lateral advection of DCo with additional enrichments due to enhanced DCo diffusion at the bottom water sediment interface and enhanced advection and dissolution of PCo.

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The lateral advection term for DCo in the surface waters of the plateau is much higher than the main sink term linked to biological uptake, indicating that DCo could be used as a lithogenic source tracer in the study area. We have obtained encouraging results in estimating the DFe external input from DCo, yielding values larger or comparable to the advective supply of DFe that is needed for phytoplankton to bloom over the Kerguelen Plateau (Sarhou et al., 2008). We believe that future observations of missing data (e.g., PCo near Heard Island) and better knowledge on the regional circulation and trace element exchanges between particulate and dissolved phase, especially dissolution kinetics of cobalt from lithogenic material, would further narrow the uncertainties of these estimates.

Acknowledgements. We are grateful to the Project Coordinator Stéphane Blain, to Bernard Quéguiner, the Chief Scientist, and to the captain and crew of R/V *Marion Dufresne II* for their support on board. We also would like to thank T. Wagener for his help during sampling operations. This work was supported by the Institut National des Sciences de l'Univers (INSU), the French Polar Institute (Institut Polaire Paul Emile Victor, IPEV) and the Antarctic Climate and Ecosystems Cooperative Research Centre. The Region Bretagne was supporting the PhD fellowship of J. B.



The publication of this article is financed by CNRS-INSU.

BGD

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Table 1. Terms to calculate the external inputs of dissolved Co and Fe to the surface waters of the Kerguelen Plateau.

Pools

Mean DCo concentration at A11 (pM) within 0–150 m depth ($[\text{DCo}]_{\text{ocean}}$) 28.2 ± 5.80 (standard error, $n = 3$)

Mean DCo concentration over the plateau (pM) within 0–150 m depth ($[\text{DCo}]_{\text{plateau}}$) 104 ± 16.2 (standard error, $n = 25$)

Water mass depth (m) 150

Water mass width (m) 350×10^3

Current velocity (cm s^{-1})^a 4 ± 1

(Fe/Co)_{basalt} ratio^b 652 ± 98.4

(Fe/Co)_{solubility} ratio^c ~ 0.30

Fluxes

Water flux (F_w , $\text{m}^3 \text{s}^{-1}$) $(2.0 \pm 0.50) \times 10^6$

DCo external input (F_{DCo} , ton DCo yr^{-1})^d 287 ± 175

DFe external input (F_{DFe} , ton DFe yr^{-1})^e $(28 \pm 21) \times 10^2$

^a From Park et al. (2008b).

^b Obtained for Keremis Dredged Basalts (samples# 4–6), from Weis et al. (2002).

^c A (Fe/Co)_{solubility} ratio of ~ 0.30 was used based on solubility rates for Fe and Co from Saharan aerosols in acidified MilliQ water (pH = 5.5) (Shelley et al., 2012).

^d $F_{\text{DCo}} = F_w \cdot ([\text{DCo}]_{\text{plateau}} - [\text{DCo}]_{\text{ocean}})$.

^e $F_{\text{DFe}} = F_{\text{DCoinput}} \cdot (\text{Fe/Co})_{\text{solubility}} \cdot (\text{Fe/Co})_{\text{basalt}} \cdot 5\%$ (see text for explanation).

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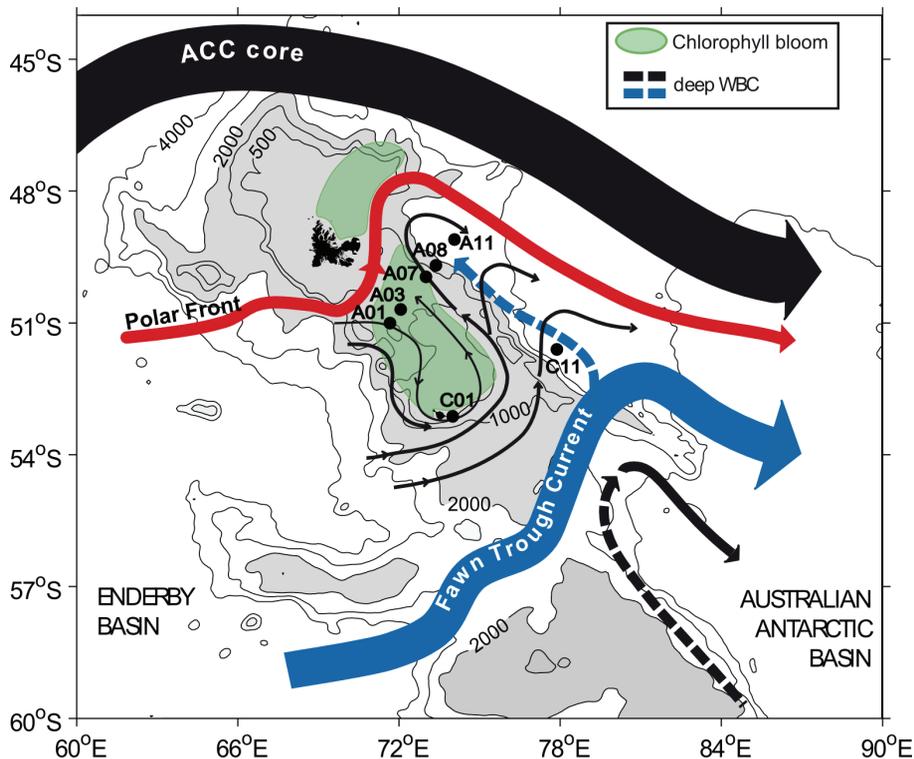


Fig. 1. Sampling locations for dissolved cobalt during the KEOPS cruise (black circles) with bloom location (green area), the bathymetry of the Kerguelen Archipelago and the general circulation (arrows). ACC: Antarctic Circumpolar Current; WBC: Western Boundary Current (Park et al., 2008b).

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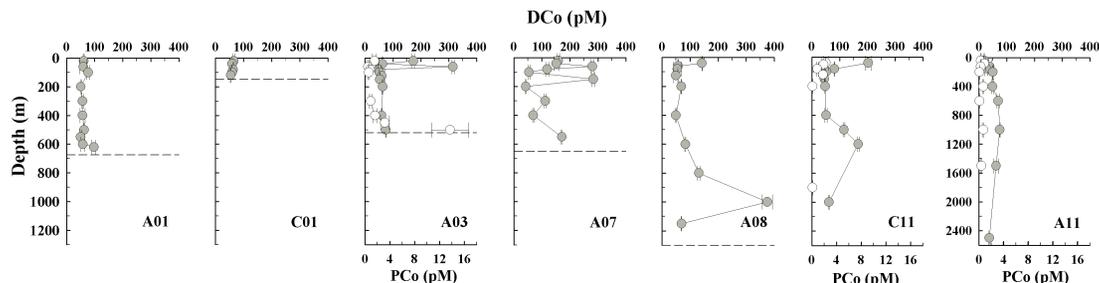


Fig. 2. Distribution of dissolved (DCo, pM, grey circles) and particulate (PCo, pM, white circles) cobalt during the KEOPS survey. The DCo error bars represent the standard deviation of triplicate analysis. The PCo error bars were calculated according to error percentages (A03: $\pm 21.8\%$; A11: $\pm 19.6\%$; C11: $\pm 16.5\%$), which are based on duplicate analysis of individual digestions of the same sample. The dashed lines correspond to the bottom depth.

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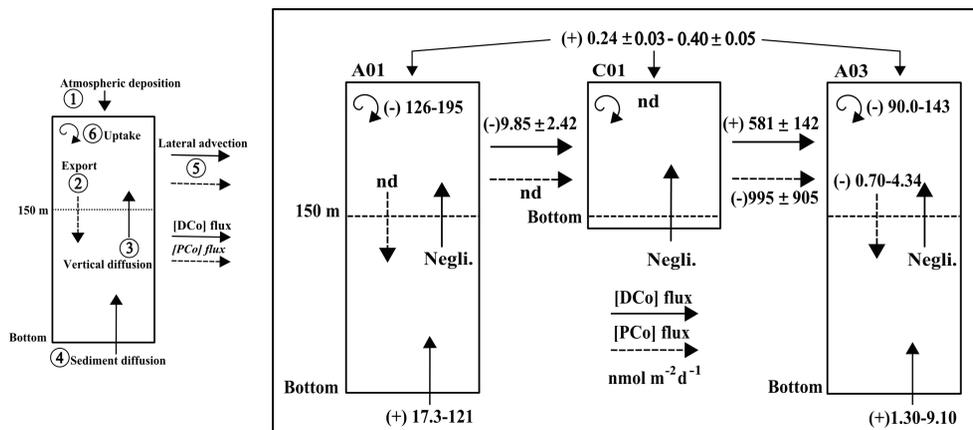


Fig. 3. Budget of dissolved cobalt (DCo) and particulate cobalt (PCo) over the shallow Kerguelen Plateau. All estimated fluxes are in $\text{nmol Co m}^{-2} \text{d}^{-1}$, and based on an assumption of steady state. (1) Total atmospheric Co deposition flux on Kerguelen Island (Heimburger and Losno, personal communication). The downward PCo export flux (2) was estimated using PCo measured in sediment trap at A03. The vertical diffusion flux across the pycnocline (3) was negligible at A01 and A03 since there was no gradient of [DCo] within pycnocline. The sediment diffusion flux (4) was determined using the [DCo] gradient in the 20 m above the bottom and K_z ranging from 1.0×10^{-4} to $7.0 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ as determined in bottom waters of the Santa Monica Basin (Johnson et al., 1988). This flux could not be determined at C01 since no [DCo] gradient was observed above the sediment. The lateral advective flux in the top 150 m (5) was estimated using the gradients of [DCo] and [PCo] between A01 and C01, and between C01 and A03 (only considering DCo inputs at A03) and using a mean current velocity of $4.0 \pm 0.5 \text{ cm s}^{-1}$ (Park et al., 2008b). As sediments at C01 are mainly composed of coarse-grained basalts (Viollier et al., 2005), [PCo] at C01 was estimated from the average Co abundance in dredged basalts north of Heard Island of $69.2 \pm 8.60 \text{ ppm}$ (standard error, $n = 8$) (Weis et al., 2002), and by using the particulate Nd concentration measured at C01 ($141.3 \pm 4.6 \text{ pM}$ at 20 m depth; Jeandel et al., 2011) and a mean lithogenic Co/Nd ratio of 4.01 ± 2.40 (standard error, $n = 8$), representative of the basalts in the vicinity of Heard Island (Weis et al., 2002). The error bar was calculated by propagating the uncertainties of all variables. The uptake by diatoms (6) was estimated from recorded fucoxanthin concentrations (J. Ras and H. Claustre, personal communication) and the corresponding cobalt uptake rate reported by Saito et al., (2010).

Note: "nd" means not determined; "negli." means negligible term.

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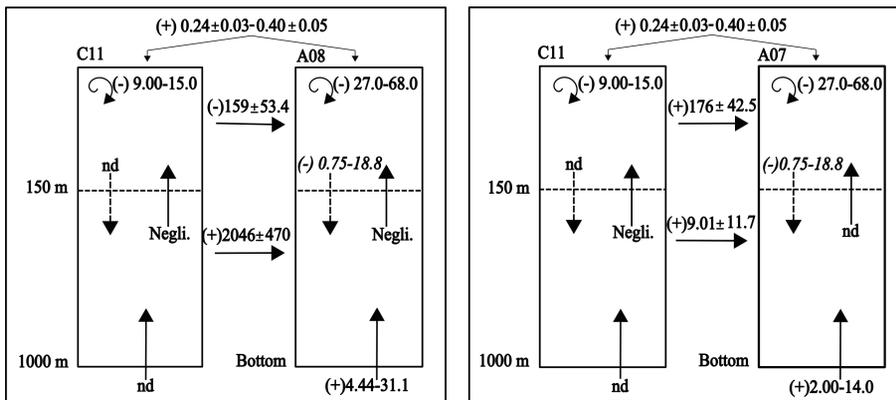


Fig. 4. Budget of DCo and PCo on the eastern slope of the Kerguelen Plateau. All fluxes are in $(\text{nmolCo m}^{-2} \text{d}^{-1})$ and estimated for an assumed steady state. All estimates are derived as described in Fig. 3, except the lateral advective fluxes of DCo and PCo (5) which were estimated from cobalt concentrations gradients between C11 and A07 and between C11 and A08 in the 0–150 m depth upper water layer and in the deep water layer between 400 and 1000 m depth, with a mean current velocity of 0.08 m s^{-1} (Park et al., 2008a).

Note: "nd" means not determined; "negli." means negligible term.

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