



Ferromanganese crusts as archives of deep water Cd isotope compositions

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[1] The geochemistry of Cd in seawater has attracted significant attention owing to the nutrient-like properties of this element. Recent culturing studies have demonstrated that Cd is a biologically important trace metal that plays a role in the sequestration of inorganic carbon. This conclusion is supported by recent isotope data for Cd dissolved in seawater and incorporated in cultured phytoplankton. These results show that plankton features isotopically light Cd while Cd-depleted surface waters typically exhibit complimentary heavy Cd isotope compositions. Seawater samples from below 900 m depth display a uniform and intermediate isotope composition of $\epsilon^{114/110}\text{Cd} = +3.3 \pm 0.5$. This study investigates whether ferromanganese (Fe-Mn) crusts are robust archives of deep water Cd isotope compositions. To this end, Cd isotope data were obtained for the recent growth surfaces of 15 Fe-Mn crusts from the Atlantic, Pacific, Indian, and Southern oceans and two USGS Fe-Mn reference nodules using double spike multiple collector inductively coupled plasma mass spectrometry. The Fe-Mn crusts yield a mean $\epsilon^{114/110}\text{Cd}$ of $+3.2 \pm 0.4$ (2 SE, $n = 14$). Data for all but one of the samples are identical, within the analytical uncertainty of $\pm 1.1\epsilon^{114/110}\text{Cd}$ (2 SD), to the mean deep water Cd isotope value. This indicates that Fe-Mn crusts record seawater Cd isotope compositions without significant isotope fractionation. A single sample from the Southern Ocean exhibits a light Cd isotope composition of $\epsilon^{114/110}\text{Cd} = 0.2 \pm 1.1$. The origin of this signature is unclear, but it may reflect variations in deep water Cd isotope compositions related to differences in surface water Cd utilization or long-term changes in seawater $\epsilon^{114/110}\text{Cd}$. The results suggest that time series analyses of Fe-Mn crusts may be utilized to study changes in marine Cd utilization.

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1. Introduction

[2] Cadmium is an interesting element in that its behavior in the oceans mimics that of phosphate, a major macronutrient [Boyle *et al.*, 1976]. Recent culturing experiments have shed light on this association, showing that Cd is a micronutrient with an important biological function in the process of inorganic carbon acquisition for oceanic primary producers [Price and Morel, 1990; Cullen *et al.*, 1999; Lane *et al.*, 2005; Xu *et al.*, 2008]. Isotopic measurements of dissolved Cd in seawater and sequestered in phytoplankton cultures have also shown that this utilization causes Cd isotope fractionation, with microorganisms in the photic zone preferentially utilizing the lighter isotopes [Lacan *et al.*, 2006; Ripperger and Rehkämper, 2007; Ripperger *et al.*, 2007]. These processes leave Cd-depleted surface waters with highly variable fractionated Cd isotope compositions of up to $\epsilon^{114/110}\text{Cd} \approx 38$. This stands in sharp contrast to seawater below 900 m depth, which displays a remarkably uniform isotopic composition of $\epsilon^{114/110}\text{Cd} = 3.3 \pm 0.5$ [Ripperger *et al.*, 2007]. The uniform Cd isotope composition of deep water is thought to relate to near-quantitative removal of Cd from surface waters, followed by a gradual remineralization of organic matter and release of Cd in the water column at depth.

[3] Despite the relatively large range of Cd isotope compositions encountered in Cd-depleted surface seawater (up to 1 ‰AMU⁻¹), most terrestrial rocks and minerals display limited Cd isotope variability (<0.1 ‰AMU⁻¹) [Wombacher *et al.*, 2003; Schmitt *et al.*, 2009a]. In order to resolve such small differences, a robust analytical technique that offers high precision and accuracy is paramount. To this end, a ¹¹¹Cd-¹¹³Cd double spike procedure for MC-ICPMS was set up, based on the recently developed methods of Ripperger and Rehkämper [2007]. The new technique was then applied to

measure Cd isotope compositions of hydrogenetic Fe-Mn crusts from all major ocean basins.

[4] Hydrogenetic Fe-Mn crusts precipitate directly from seawater [Hein *et al.*, 1997] and as such they have been used as paleoceanographic recorders of changes in seawater chemistry over time. The slow growth rates of Fe-Mn crusts (<10 mm Myr⁻¹ [Hein *et al.*, 1997; Henderson and Burton, 1999]) render them ideal archives of long-term variations in marine isotope compositions [e.g., Burton *et al.*, 1997; Christensen *et al.*, 1997; Zhu *et al.*, 2000]. Furthermore, the chemical and mineralogical composition of Fe-Mn crusts is not influenced by the substrate rock [Hein and Morgan, 1999]. This differs from Fe-Mn nodules, which are typically of hydrogenetic-diagenetic origin [Hein *et al.*, 2000], implying that hydrogenetic Fe-Mn crusts are more likely to record seawater Cd isotope compositions than Fe-Mn nodules.

[5] The new Cd isotope analyses of this study test the potential of hydrogenetic Fe-Mn crusts to monitor seawater Cd isotope variations through the Cenozoic. Such an archive will be useful to further investigate the marine biogeochemical cycling of Cd and the application of Cd isotopes as a proxy for nutrient utilization.

2. Samples

[6] A suite of 15 hydrogenetic Fe-Mn crusts with a global distribution was carefully chosen for analysis (Figure 1). The most recent growth surfaces were deduced through way-up indicators, such as a rock substrate or primary texture, and a surface section (0–0.5 mm) from each Fe-Mn crust was sampled. To facilitate interlaboratory comparison, we also analyzed two USGS reference materials, the powdered Fe-Mn nodules Nod-A-1 and Nod-P-1 [Flanagan and Gottfried, 1980].

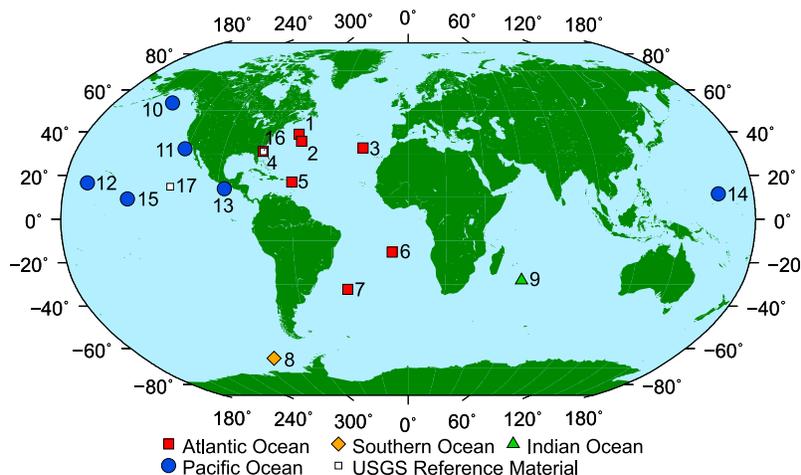


Figure 1. Sample locations of the Fe-Mn crusts and USGS reference nodules analyzed in this study. Numbers refer to the sample names given in Table 2.

[7] The Fe-Mn crust samples of this study were chosen because they cover all major ocean basins (Figure 1) and all were previously characterized for one or more radiogenic and stable isotope systems, including Pb [Reynolds *et al.*, 1999; Rehkämper *et al.*, 2002], Nd [O’Nions *et al.*, 1998; Burton *et al.*, 1999; Reynolds *et al.*, 1999], Hf [David *et al.*, 2001], Fe [Zhu *et al.*, 2000; Lévassieur *et al.*, 2004], and Ti [Rehkämper *et al.*, 2002].

3. Analytical Methods

[8] Sample preparation was carried out at the Imperial College MAGIC (Mass Spectrometry and Isotope Geochemistry at Imperial College London) Laboratories using Class 10 laminar flow workstations for all sensitive work. The acids were purified prior to use by subboiling distillation in quartz glass stills and the water was obtained from an 18.2 M Ω grade Milli-Q Academic purification system.

3.1. Sample Preparation

[9] Approximately 20–50 mg of sample material was weighed, to obtain ~50 ng of Cd for analysis, and transferred into small (7 mL) Teflon vials. Subsequently, the powdered material was leached in 6 M HCl for 10 minutes at ~50°C and centrifuged to dispose of any detrital material. The samples were then taken to complete dryness before adding a few drops of concentrated HNO₃ and evaporating to convert the samples into NO₃⁻ form. Based on published geochemical data from Hein *et al.* [2000], the Cd content of the various Fe-Mn crust samples was

estimated to be approximately 3.5 ppm Cd. An appropriate amount of Cd double spike solution (dissolved in 2 M HNO₃) was then added to obtain a molar spike to sample-derived Cd concentration ratio (*S/N*) of 1. Subsequently, the samples were converted back into Cl⁻ form through repeated addition and evaporation of 6 M HCl.

[10] The two-stage column chemistry procedure for the separation of Cd from the geological matrix was adapted from Wombacher *et al.* [2003]. The samples were loaded in 3 M HCl onto precleaned Teflon columns that were filled with 200 μ L of AG 1-X8 (200–400 dry mesh size) anion exchange resin. Following anion exchange, the samples were evaporated and converted back into Cl⁻ form before loading in 8 M HCl onto 200 μ L of precleaned Eichrom TRU (200–400 dry mesh size) extraction chromatographic resin. The complete elution sequence is shown in Table 1. The two-stage procedure was calibrated to minimize both loss and isotopic fractionation of Cd, although the latter is not a significant concern when a double spike is applied. Following the ion exchange chemistry, each sample was taken up in an appropriate volume of 2% HNO₃ ready for mass spectrometry.

3.2. Mass Spectrometry

[11] Recent studies have shown that the use of a double spike methodology is beneficial for determining mass-dependent stable isotope effects in geological samples with low Cd concentrations [Ripperger and Rehkämper, 2007; Schmitt *et al.*, 2009b]. To this end, we have set up and applied a ¹¹¹Cd-¹¹³Cd double spike procedure.

Table 1. Cd Separation Chemistry Used in This Study^a

Eluent	Quantity (μL)	Purpose
<i>First Stage Column Chemistry: 200 μL Biorad AG 1-X8 Anion Exchange Resin (Dry Mesh: 200–400)</i>		
2 M HNO_3	1000	resin cleaning
18.2 M Ω H_2O	100	rinse
6 M HCl	2000	resin cleaning
0.5 M HCl	1000	resin conditioning
3 M HCl sample solution	1000	elute matrix
0.5 M HCl	3000	elute matrix
1 M HCl	1000	elute matrix
2 M HCl	1000	elute matrix
6 M HCl	1000	elute matrix (Ag)
0.5 M HNO_3 + 0.1 M HBr mixture	1000	elute matrix (Zn)
2 M HNO_3	<1500	elute Cd
<i>Second Stage Column Chemistry: 200 μL Eichrom TRU Resin (Dry Mesh: 200–400)</i>		
6 M HCl	9000	resin cleaning
8 M HCl sample solution	200	elute Cd
8 M HCl	200	elute Cd
6 M HCl	<2000	elute Cd

^aColumns were made from shrink-fit Teflon and have a resin bed volume of approximately 200 μL .

[12] The mass spectrometric measurements of samples were carried out at the University of Oxford on a Nu Plasma HR MC-ICPMS in low-resolution mode. A desolvation nebulizer system (Nu Instruments DSN-100) was used with uptake rates of $\sim 100 \mu\text{L min}^{-1}$. Each sample was bracketed by a spiked solution standard (the Alfa Zürich Cd Standard [Ripperger and Rehkämper, 2007]) in order to correct for instrumental drift and to assess the external reproducibility of the data generated in the measurement session. The data acquisition sequence comprised 30 integrations (10 s per integration), in which the ion currents of ^{111}Cd , ^{112}Cd , ^{113}Cd , ^{114}Cd , ^{115}In , and ^{117}Sn were monitored simultaneously. Measurements of the various Cd isotope reference standards (Table 2) were performed at the MAGIC Laboratories, also using a Nu Plasma HR MC-ICPMS, with nearly identical measurement parameters.

3.3. Data Reduction

[13] The ^{117}Sn signal was used to correct for isobaric Sn interferences on ^{112}Cd and ^{114}Cd . The ion current on mass 115 (^{115}In and ^{115}Sn) was monitored and, once corrected for ^{115}Sn , utilized to check for the isobaric interference of ^{113}In on ^{113}Cd . Processing of the data with or without an In correction was found to yield identical results, within uncertainty. The data presented in Table 2

are uncorrected, as this was found to yield slightly more precise results. The double spike data reduction was carried out off-line, by solving the relevant equations in $^{112}\text{Cd}/^{111}\text{Cd}$ - $^{113}\text{Cd}/^{111}\text{Cd}$ - $^{114}\text{Cd}/^{111}\text{Cd}$ isotope ratio space using a spreadsheet-based adaptation of the iterative methods described by Siebert *et al.* [2001]. For instrumental mass bias correction, the generalized power law (GPL [Maréchal *et al.*, 1999]) was used:

$$R = r \times f^{(m_i^2 - m_j^2)} \quad (1)$$

In this notation, R is the true ratio, corrected for instrumental mass bias; r is the measured (uncorrected) ratio; f is the fractionation factor; m_i is the mass of isotope i ; and n is the exponent that determines the mass dependence of the instrumental mass bias [Maréchal *et al.*, 1999], optimized for our study at -0.15 . The data were subsequently converted and presented using the ϵ notation of Wombacher and Rehkämper [2004] relative to the Alfa Cd Zürich standard:

$$\epsilon^{114/110}\text{Cd} = \left(\frac{^{114/110}\text{Cd}_{\text{spl}}}{^{114/110}\text{Cd}_{\text{std}}} - 1 \right) \times 10,000 \quad (2)$$

[14] Table 2 documents the isotopic offset between Alfa Cd Zürich, which was also used by Ripperger and Rehkämper [2007] and Ripperger *et al.* [2007] as the reference standard and two other $\epsilon^{114/110}\text{Cd} \equiv 0$ reference materials, namely JMC Cd Münster [Wombacher *et al.*, 2003, 2008] and JMC Cd Mainz [Schmitt *et al.*, 2009a, 2009b].

3.4. Uncertainty Reporting

[15] The uncertainties quoted in Table 2 denote two standard errors (2 SE) and represent the within-run precision of each individual Cd isotope measurement. These errors should only be taken as an indication of data quality, however, because they often underestimate the true uncertainty. A more realistic measure for the reproducibility of the sample data is given by the external uncertainty, reported as two standard deviations (2 SD). The external uncertainty is based on multiple measurements of the bracketing Cd standard solution during a measurement session. This has been shown by Ripperger and Rehkämper [2007] to provide a valid estimate for sample reproducibility, even for seawater samples with Cd/Matrix ratios approaching 10^{-11} . (The Fe-Mn crusts analyzed in this study have more favorable Cd/Matrix ratios of $\approx 10^{-6}$.) The overall Cd concentration and S/N ratio of the bracketing standard was varied to match the S/N ratio of each sample. While optimal spiking is achieved for the

Table 2. Summary of Cd Isotope and Concentration Data Obtained in This Study

Cruise/Supplier	Sample	Sample Number	Section (mm)	Location	$\epsilon^{114/110}\text{Cd} \pm 2 \text{ SE}^a$	N^b	Cd Concentration (ppm)	Latitude (decimal deg)	Longitude (decimal deg)	Depth (m)
Hudson St. 54	BM1969.05	1	0–0.5	N. Atlantic	3.1 ± 0.5	1	1.83	+39.00	-060.95	1850
Alv 539	2-1A	2	0–0.5	N. Atlantic	4.0 ± 0.6	1	1.73	+35.61	-058.79	2665
Discovery 144	D 10979	3	0–0.5	N. Atlantic	2.4 ± 0.7	1	5.69	+32.60	-024.42	4867–5347
ArcI TR079	BM1963.897	4	0–0.5	N. Atlantic	2.6 ± 0.7	1	5.24	+30.97	-078.50	850
ArcI TR079	D-14	5	0–0.5	N. Atlantic	3.4 ± 0.6	1	3.65	+16.92	-061.17	2000
SO-84	DS43	6	0–0.5	S. Atlantic	3.2 ± 0.6	1	2.35	-15.15	-008.35	1966–1990
Endeavor EN063	32D	7	0–0.5	S. Atlantic	1.8 ± 0.9	1	0.96	-32.19	-032.72	3310
TBD 463	DR 153	8	0–0.5	Southern Ocean	0.2 ± 0.5	1	3.27	-64.96	-091.27	3150–3300
Antipode	I09D-C	9	0–0.5	Indian Ocean	2.6 ± 0.4	1	2.23	+32.60	-024.42	5178–5698
S6-79-NP	D4-13A	10	0–0.5	Pacific Ocean	3.1 ± 0.7	1	5.30	+53.54	-144.37	2100
F7-87-SC	D9-16	11	0–0.5	Pacific Ocean	2.5 ± 1.0	1	9.57	+32.26	-121.27	2235–2300
F7-86-HW	CD29-2	12	0–0.5	Pacific Ocean	4.0 ± 0.7	1	3.45	+16.71	-168.24	1970–2390
GMAT	14D	13	0–0.5	Pacific Ocean	3.5 ± 0.7	1	1.70	+13.98	-096.13	4119
F10-89-CP	D11-1	14	0–0.5	Pacific Ocean	3.7 ± 0.6	1	3.49	+11.65	+161.68	1690–1870
VA13/2	237KD	15	0–0.5	Pacific Ocean	4.6 ± 0.6	1	2.65	+09.30	-146.05	4830
USGS	Nod-A-1	16	bulk sample	Atlantic Ocean	2.5 ± 0.6	2	6.81	+31.03	-078.37	788
USGS	Nod-P-1	17	bulk sample	Pacific Ocean	2.2 ± 0.6	3	20.9	+14.83	-124.47	4300
Alfa Aesar	Alfa Cd Zürich ^c	-	reference std.	-	$\equiv 0$	-	-	-	-	-
Johnson Matthey	JMC Cd Münster ^d	-	reference std.	-	-0.5 ± 0.4^e	5	-	-	-	-
Johnson Matthey	JMC Cd Mainz ^f	-	reference std.	-	$2.6 \pm 0.4^{e,g}$	7	-	-	-	-

^aA full discussion of the uncertainty reporting is provided in section 3.4.

^bNumber of replicates run (both through separation chemistry and mass spectrometric analysis). For samples with $N > 1$, the $\epsilon^{114/110}\text{Cd}$ values and associated errors presented are simple arithmetic means.

^cIsotopic reference standard from Ripperger and Rehkämper [2007], Ripperger *et al.* [2007], and this study.

^dIsotopic reference standard from Wombacher and Rehkämper [2004].

^eReported as 2 SD external.

^fIsotopic reference standard from Schmitt *et al.* [2009a, 2009b].

^gReported relative to JMC Cd Münster (offset between Alfa Cd Zürich and JMC Cd Mainz inferred to be 2.1).

^{111}Cd - ^{113}Cd double spike when $S/N = 1$, minimal error magnification is expected between $S/N = 0.5$ and 2 according to *Rudge et al.* [2009]. The samples and bracketing Cd standards displayed a slightly larger range of S/N ratios from 0.4 to 3.7. Nevertheless, the external reproducibility obtained from these standard analyses was determined to be ± 1.1 for $\epsilon^{114/110}\text{Cd}$ ($n = 38$), equivalent to ± 27 ppm AMU^{-1} . This is supported by our triplicate analyses of Nod-P-1, which yield a biased 2 SD of $\pm 0.9 \epsilon^{114/110}\text{Cd}$ (± 22 ppm AMU^{-1}).

[16] The Cd concentration data were obtained using the isotope dilution technique based on the mass bias-corrected $^{111}\text{Cd}/^{114}\text{Cd}$ ratio of the spike-sample mixture for each sample. All concentration data were corrected for a total procedural blank of ~ 5 pg, which represents less than 0.02% of the extant Cd present in the samples. Hence, no blank correction was applied to the isotope data. The epoxy resin that was used to encase several of the Fe-Mn crusts (to retain coherency) was also analyzed and only trace levels of Cd were identified, constraining the resin to contribute < 10 pg of Cd to a sample analysis.

4. Results

[17] The fifteen hydrogenetic Fe-Mn crusts that were analyzed in this study, display Cd concentrations between 1 and 10 ppm and a mean Cd content of 3.5 ppm (Table 2). The two USGS Fe-Mn nodules feature amongst the highest Cd abundances determined in this study, with results of ~ 7 and ~ 21 ppm (Table 2). Taken together, this is consistent with data reported elsewhere [*Hein et al.*, 2000; *Schmitt et al.*, 2009a] and the conclusion that Fe-Mn deposits typically contain 1–10 ppm Cd.

[18] With the exception of one sample, all Fe-Mn crusts and both USGS nodules display a narrow range of Cd isotope compositions between $\epsilon^{114/110}\text{Cd}$ values of 1.8 to 4.6. These Fe-Mn crust data are thus identical to the inferred oceanic deep water mean of $\epsilon^{114/110}\text{Cd} = 3.3 \pm 0.5$ [*Ripperger et al.*, 2007], within the external analytical uncertainty ($\pm 1.1 \epsilon^{114/110}\text{Cd}$). Importantly, our results for the USGS nodules overlap with data reported by *Schmitt et al.* [2009a], when renormalized to $\epsilon^{114/110}\text{Cd}$ and corrected for the offset between the Alfa Cd Zürich and JMC Cd Mainz reference standards. Following renormalization, the *Schmitt et al.* [2009a] analyses yield $\epsilon^{114/110}\text{Cd} = 2.0 \pm 0.2$ and $\epsilon^{114/110}\text{Cd} = 2.4 \pm 0.2$ for Nod-A-1 and Nod-P-1, respectively

(uncertainties are quoted as 2 SE internal), which is identical to our results (Table 2).

[19] No correlations were evident between the Cd isotope data and the Cd contents of the samples, or published literature values for other isotope systems including Pb, Nd, Fe, and Tl.

5. Discussion

[20] The observation that oceanic deep water and the growth surfaces of Fe-Mn crusts have essentially the same Cd isotope compositions supports the view that Fe-Mn crusts record the Cd isotope composition of ambient seawater with no detectable isotopic fractionation. This conclusion is in accord with results obtained for Fe-Mn nodules by *Schmitt et al.* [2009a]. The latter data trend toward slightly “heavier” Cd isotope compositions with decreasing water depth, which is consistent with variations in seawater $\epsilon^{114/110}\text{Cd}$. However, the larger overall variability of $\epsilon^{114/110}\text{Cd}$ in Fe-Mn nodules (Figure 2) may also be related to the addition of a minor sediment-derived Cd component or diagenetic alteration.

[21] The lack of Cd isotope fractionation during incorporation into Fe-Mn crusts is an interesting result, which can be compared to the behavior of other elements for which relevant data are available, particularly Tl and Zn. In the case of Tl, an offset of $\epsilon^{205/203}\text{Tl} \approx 20$ was observed between seawater and hydrogenetic Fe-Mn crusts [*Rehkämper et al.*, 2002, 2004], which was interpreted to reflect equilibrium isotope fractionation between dissolved Tl^+ in seawater and adsorbed Tl^{3+} on Fe-Mn particles. The theoretical study of *Schauble* [2007] corroborated this conclusion, as it predicts large equilibrium Tl isotope fractionations between the two redox states. Further support was provided by the recent study of *Peacock et al.* [2009], which confirmed that Tl isotope fractionation is controlled by surface oxidation of Tl^+ to Tl^{3+} , following sorption onto MnO_2 minerals. Since Cd is dominated by a single (Cd^{2+}) redox state in the marine environment, it lacks a redox mechanism for generating such large isotope effects. However, recent adsorption experiments for Zn, which is almost exclusively present as Zn^{2+} in nature, have shown that “heavy” Zn isotopes preferentially adsorb onto (oxy)hydroxide surfaces [*Pokrovsky et al.*, 2005; *Balistrieri et al.*, 2008; *Juillot et al.*, 2008]. The magnitude of the offset between the dissolved and adsorbed Zn ($\epsilon^{66/64}\text{Zn} \approx 5$) is furthermore consistent with the

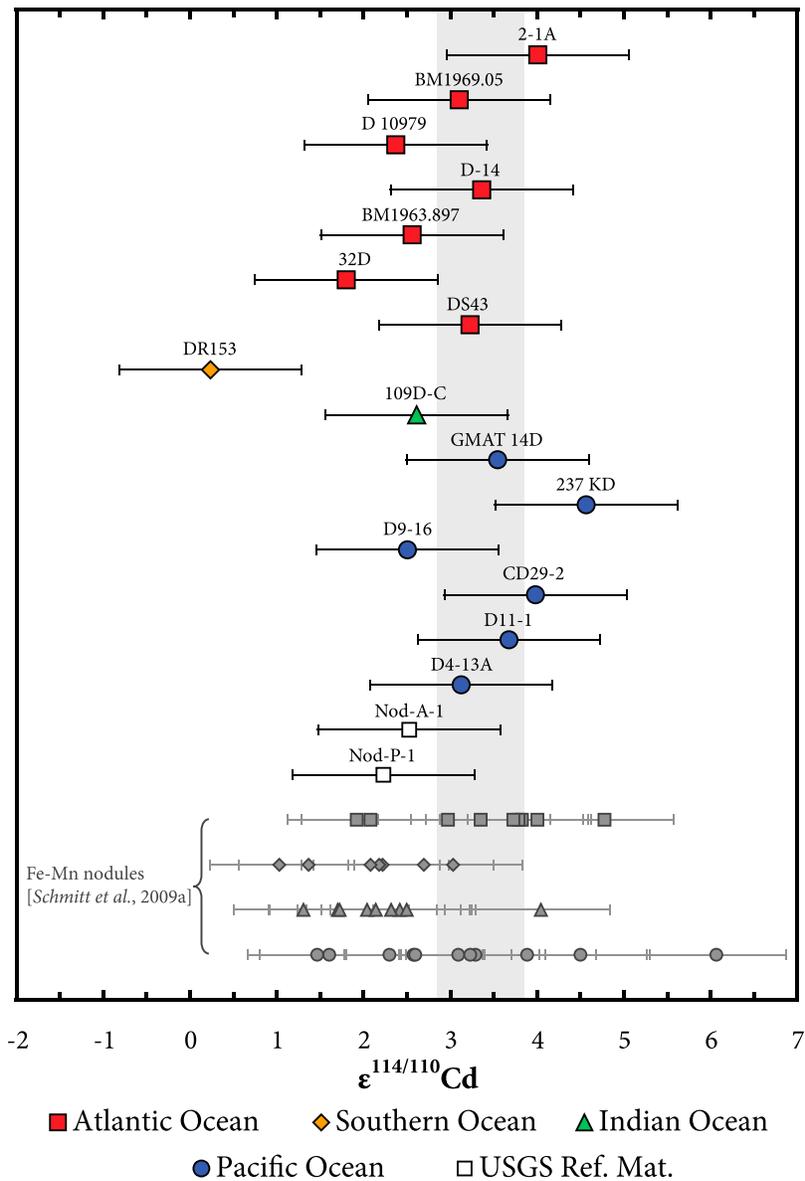


Figure 2. Cd isotope data for the Fe-Mn crust samples analyzed in this study. Samples are grouped by ocean basin (symbols as in Figure 1). Two Fe-Mn nodules, USGS reference materials Nod-A-1 and Nod-P-1, are also included for comparison with results from other laboratories. The light grey band represents the Cd isotope composition of oceanic deep water at $\epsilon^{114/110}\text{Cd} = 3.3 \pm 0.5$ as inferred by Ripperger *et al.* [2007]. Fe-Mn nodule data from Schmitt *et al.* [2009a] are shown at the bottom (all uncertainties are quoted as 2 SD external).

difference in $\epsilon^{66/64}\text{Zn}$ values reported for seawater [Bermin *et al.*, 2006] and Fe-Mn nodules [Maréchal *et al.*, 2000]. The results for Zn demonstrate that future experimental studies are needed for Cd to investigate isotope fractionation during adsorptive scavenging by Fe-Mn (oxy)hydroxides. This conclusion is shared by Schmitt *et al.* [2009a], as the lack of Cd isotope fractionation cannot be simply explained in terms of the smaller mass difference between Cd isotopes compared to Zn. Initial data from Wasylenki *et al.* [2009] suggests that the

magnitude of inorganic Cd isotope fractionation during adsorption onto Mn oxides may be linked to the ionic strength of the dissolved phase, with larger fractionations observed at low ionic strength. The high ionic strength of seawater (~ 0.7 M) may thus explain the lack of a measurable Cd isotope offset between Fe-Mn crusts/nodules and seawater.

[22] Among all samples analyzed, only DR 153 from the Southern Ocean displays a small but well-resolved offset from the inferred global Cd isotope

composition of oceanic deep water [Ripperger *et al.*, 2007]. This sample was dredged from a seamount in the Amundsen Abyssal Plain [Frank *et al.*, 2002], south of the current Polar Front [Moore *et al.*, 1999]. The water depth at the recovery site (~3200 m) is sufficiently deep such that the sample likely records the Cd isotope signal of AABW (Antarctic Bottom Water). Alternatively, the Cd isotope composition of DR 153 may reflect diagenetic overprinting, but this is unlikely as the sample is not otherwise atypical. Ruling out alteration, two explanations for the distinct $\epsilon^{114/110}\text{Cd}$ value of DR 153 are possible:

[23] 1. The sample may faithfully record the distinct Cd isotope composition of deep water at this locality, but this value differs from results obtained at other locations. It is possible, for example, that the isotopically light Cd signal of DR 153 ($\epsilon^{114/110}\text{Cd} = 0.2 \pm 1.1$) reflects remineralization of organic material that presently records incomplete Cd utilization in surface waters [Ripperger *et al.*, 2007]. This interpretation would be in agreement with the low levels of macronutrient and Cd utilization in the Southern Ocean [Nolting and de Baar, 1994] and the water masses (e.g., AABW) that are derived from it.

[24] 2. Sample DR 153 may integrate over a relatively long time period, potentially several 100 kyr given the slow growth rate of $\sim 0.7 \text{ mm Ma}^{-1}$ [Frank *et al.*, 2002] and our sampling resolution (0.5 mm). This sample may therefore provides an average Cd isotope composition that is distinct from the present-day deep water value.

[25] The Circum-Antarctic Fe-Mn nodule data of Schmitt *et al.* [2009a] also show some evidence of light Cd isotope compositions for the Southern Ocean. For example, sample T 1678-117 has a Cd isotope composition of $\epsilon^{114/110}\text{Cd} = 1.0 \pm 0.5$ (2 SE), which is identical, within error, to DR 153. Unfortunately, the presently available Cd isotope database for seawater and marine sediments is too limited to unequivocally rule out either of the above interpretations. With the exception of sample DR 153 however, the Fe-Mn crusts provide a homogeneous Cd isotope signature, which is in accord with the data presently available for seawater [Lacan *et al.*, 2006; Ripperger *et al.*, 2007].

[26] The lack of observable Cd isotope fractionation during incorporation of Cd into Fe-Mn crusts from seawater is encouraging, because it suggests that it may be possible to construct time-resolved records of deep water $\epsilon^{114/110}\text{Cd}$ values from such

samples. For such time series data to be meaningful it is important, however, that the diffusivity of the element in question is sufficiently slow (in Fe-Mn crusts), such that the isotopic history is not destroyed by diffusion over time. The diffusivity of Cd can be estimated using Henderson and Burton [1999, equation 7]:

$$D_{\text{eff}}^{\text{Cd}} = \frac{D_{\text{eff}}^{\text{U}} K_{\text{c}}^{\text{U}}}{K_{\text{c}}^{\text{Cd}}} \quad (3)$$

where $D_{\text{eff}}^{\text{X}}$ is the effective diffusivity of element X in a Fe-Mn crust (in $\text{cm}^2 \text{ yr}^{-1}$) and K_{c}^{X} is the concentration of element X in the Fe-Mn crust, normalized to the concentration in pore water contained within the sample. For simplicity, the pore water is assumed to have the same composition as ambient seawater [Henderson and Burton, 1999]. Based on equation (3) and using values of $D_{\text{eff}}^{\text{U}} = 1 \times 10^{-6} \text{ cm}^2 \text{ yr}^{-1}$ and $K_{\text{c}}^{\text{U}} = 4 \times 10^3$ [Henderson and Burton, 1999], the diffusivity of Cd is estimated to be between 2×10^{-8} and $3 \times 10^{-7} \text{ cm}^2 \text{ yr}^{-1}$, depending on the Fe-Mn crust and ocean basin in question. This implies that Cd and Hf have very similar diffusivity in Fe-Mn crusts [Henderson and Burton, 1999], and Hf isotope data for such samples have been successfully applied to study past changes in the Hf isotope composition of seawater [David *et al.*, 2001]. This indicates that it may be possible to use Fe-Mn crusts to trace long-term variations in the Cd isotope composition of the oceans. A preliminary study [Schmitt *et al.*, 2009a], which reports Cd isotope data for six samples from a single Fe-Mn crust covering a time period of 8 Myr, suggests that such variations may be small. However, additional data are required to further elucidate this issue.

6. Conclusions

[27] New Cd isotope data are presented for the surface sections of a suite of previously well-studied Fe-Mn crusts that cover all major ocean basins. The results are in agreement with data for Fe-Mn nodules from another laboratory [Schmitt *et al.*, 2009a] and corroborate the conclusion that Fe-Mn crusts faithfully record the Cd isotope composition of ambient seawater with minimal isotopic fractionation. Only a single sample from the Southern Ocean records a Cd isotope composition that is lighter than the global deep water average reported by Ripperger *et al.* [2007]. It is possible that this reflects either long-term changes in seawater $\epsilon^{114/110}\text{Cd}$, or a distinct regional sig-

nature that relates to incomplete Cd utilization in the water column.

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