



Behaviour of cadmium isotopes in sulfidic waters and sediments of the Black Sea: Implications for global cadmium cycling and the application of cadmium isotopes as a paleo-oceanographic proxy

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ABSTRACT

The cadmium isotope system has found use as a tracer for biological productivity, redox and organic carbon burial in the oceans. There are, however, very few observational constraints on Cd isotopic behaviour in modern sulfidic marine conditions, limiting our understanding of the modern Cd cycle, and our ability to use Cd isotope measurements of ancient sedimentary deposits as a paleoceanographic proxy. Here we study the behaviour of dissolved Cd in the water column of the Black Sea and its incorporation into sediments on the basin floor. The isotopic composition of dissolved Cd in the upper ~50 m of the Black Sea water column is controlled by a combination of biological uptake and regeneration along with mixing of river water and Mediterranean seawater. Cadmium declines to <2 % of its peak subsurface concentration within the zone of nitrate-reduction but above the sulfide chemocline. The isotopic composition of dissolved Cd below the sulfide chemocline evolves in a manner that is consistent with experimental Cd sulfide fractionation factors, providing field-based support for these earlier studies. In contrast, the stability of the dissolved Cd isotopic signature above the chemocline, despite a large reduction in dissolved Cd concentrations, is explained by diffusion towards the Cd-sulfide sink below the chemocline. Sediments accumulating in the deep Black Sea below the sulfide chemocline have isotopic compositions that are similar to dissolved Cd in its near-surface aqueous concentration maximum. Sediments accumulating at shallower depths have lighter isotopic compositions that are likely affected by non-sulfidic burial pathways mediated by macrofaunal mixing and diagenesis of shallow burial phases. Our study shows that the isotopic composition of bulk sediments accumulating under sulfidic conditions is similar to dissolved Cd in the upper water column, supporting its use as a paleo-chemical proxy for ancient seawater as long as basin-scale controls on open ocean seawater sources are considered. We show that Cd burial in the deep Black Sea, predominantly as CdS, accounts for ~0.5–15 % of total annual Cd burial in the global ocean.

1. Introduction

There has been a growing interest in using the isotopic composition

of cadmium (Cd) as a tracer for oceanic biogeochemical processes (Lacan et al., 2006; Ripperger et al., 2007; Horner et al., 2021), industrial pollution (Martinkova et al., 2016), and the evolution of past ocean

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chemistry (Georgiev et al., 2015; Hohl et al., 2016; Zhang et al., 2018; Viehmann et al., 2019; Sweere et al., 2020a, 2020b; Fredricksen et al., 2022; Dickson et al., 2022; Druce et al., 2022a, 2022b). Cadmium behaves as a nutrient in the oceans, with a distribution similar to that of phosphate, although the causes for the observed deviations from a universal correlation are debated (Horner et al., 2013, 2021; Middag et al., 2018). Its isotopic composition in seawater deeper than ~500–1000 m becomes near-homogenous (~0.2–0.3 ‰) due to the remineralisation of isotopically light organically assimilated Cd with a large component of isotopically light Cd advected along deep-water flow paths from the Southern Ocean (Xie et al., 2017; Janssen et al., 2017; Sieber et al., 2019). Despite the large number of studies that have documented the behaviour of Cd in modern seawater, and the growing number of studies that use Cd isotopes as a tracer of past marine productivity, redox state, or carbon burial, there are still remarkably few direct observations of the isotopic behaviour of Cd as it is buried in modern marine sediments. An incomplete understanding of modern sedimentary fluxes of Cd is problematic for its application as a tracer of past oceanic conditions, which requires quantitative modelling of the various input and output fluxes to arrive at paleoenvironmental interpretations.

Cadmium is removed into marine sediments in association with a few sedimentary phases: organic matter, Fe and Mn oxyhydroxides, carbonates, and sulfides (e.g. Rosenthal et al., 1995; van Geen et al., 1995; Plass et al., 2021). Clay mineral sorption may also act as a removal vector, but its importance is not currently well understood. Each removal phase carries a distinct Cd isotope composition. Cadmium in organic matter is predicted to be isotopically lighter than in coeval seawater, as predicted from isotopic distributions of Cd in near surface waters (Ripperger et al., 2007; Abouchami et al., 2011), from culturing studies (e.g. Horner et al., 2013), and from direct observations of sinking organic particles (Janssen et al., 2019). Cadmium can precipitate as isotopically light sulfide (CdS) in the presence of H₂S, with $\alpha_{\text{Cd}(\text{water} - \text{CdS})}$ experimentally predicted to be between 1.00011–1.00026 depending on the ionic strength of the fluid (Guinoiseau et al., 2018a; Bryan, 2019). This removal phase has been suggested to be a large contributor to Cd burial in marine sediments (Guinoiseau et al., 2018b; Plass et al., 2021), although this view has been contested (de Souza et al., 2022; Tegler et al., 2024). Recent work has suggested that rapid precipitation of CdS in seafloor sediments can quantitatively remove Cd from the dissolved phase and result in sedimentary deposits that are isotopically similar to deep ocean seawater, even underneath a fully oxygenated water column (Bryan et al., 2021). Iron and manganese oxyhydroxides may fractionate Cd by ~ -0.5 ‰ relative to the precipitating fluid at high ionic strength (Wasylenki et al., 2014; Yan et al., 2021; Gao et al., 2021). Nonetheless there are observations from experimental time series (Wasylenki et al., 2014) that fractionation decreases with time, which accords with field measurements of ferromanganese crusts and nodules that are isotopically similar to deep ocean seawater (Horner et al., 2010). Carbonates also appear to preferentially incorporate lighter Cd isotopes, with inorganic calcite and modern carbonate oozes having offsets of ~ -0.5 ‰ from fluid (seawater), while modern foraminifera have smaller offsets from seawater of ~ -0.25 ‰ (Druce et al., 2022a, 2022b).

In this study we examine the isotopic behaviour of Cd in Black Sea waters and sediments. The Black Sea is considered a natural laboratory for high-sulfide environments that may have characterised periods of the ancient Earth, and which probably exerted a disproportionate influence on global trace metal cycles through metal-sulfide burial fluxes. The isotopic behaviour of metals such as molybdenum, uranium, nickel, iron and zinc in the Black Sea have yielded important insights into their cycling in sulfidic conditions and application as tracers of past oceanic change (Algeo and Lyons, 2006; Neubert et al., 2008; Nägler et al., 2011; Vance et al., 2016; Rolison et al., 2017, 2018). Our study addresses some simple questions: what is the balance of different Cd sources to the Black Sea? What are the mechanisms that remove dissolved Cd from the water column? What is the composition of Cd accumulating in highly sulfidic

sediments below the chemocline? What is the relationship between solid and dissolved phase Cd isotope compositions in this highly sulfidic environment?

2. Study site

The Black Sea is the largest, permanently anoxic basin in the world with a water volume of 423,000 km³, a maximum depth of 2240 m and a sill (at 33 m water depth) that restricts exchange with the Mediterranean Sea through the shallow Bosphorus and Dardanelles Straits and the Sea of Marmara (Gunnerson and Ozturgut, 1974). Other inflows come from rivers including the Danube, Dneper, and Dniestr on the northwest shelf, which have highly variable seasonal and yearly discharges. The overall basin has an estuarine-type circulation and positive water balance (Özsoy and Ünlüata, 1997). The vertical water column has distinct gradients in temperature and salinity. Surface waters are colder and less saline than deep waters, resulting from freshwater runoff at the surface and saline subsurface Mediterranean Sea inflows (Özsoy and Ünlüata, 1997).

The vertical transition from oxic to anoxic waters in the Black Sea is characterised by a relatively stable chemocline between 50 m and 150 m water depth (Algeo and Lyons, 2006). Below the chemocline, anoxic then euxinic conditions persist with low Cd concentrations (Lewis and Landing, 1992). The deep waters and porewaters in the sediments maintain similar levels of H₂S_{aq}, with maximum concentrations of >400 μM (Murray et al., 1989). Sediments in the Black Sea have been divided into three stratigraphic units. The uppermost unit, from which all data in this paper is extracted, started to form ~1.63–2 kyrs ago (Calvert et al., 1987; Arthur et al., 1994) and consists of organic-rich marl containing abundant coccolithophore carbonate. This unit marks the transition to the present salinity conditions in the basin following the re-establishment of exchange with the eastern Mediterranean after the last glacial period. Bulk sediment accumulation rates for unit I range from 10 g m⁻² yr⁻¹ in the deep basin to 200 g m⁻² yr⁻¹ at the basin margin (Algeo and Lyons, 2006).

3. Methods

3.1. Sample collection

Samples were collected during the GEOTRACES MedBlack cruise (64PE373) in July 2013 (waters and sediments) and the Fe-Vici cruise in

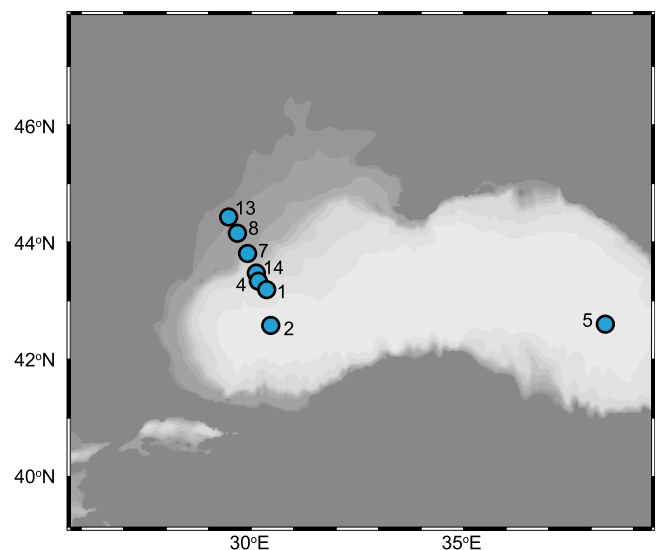


Fig. 1. Location map of stations 1, 2, 4, 5, 7, 8, 13, and 14 in the Black Sea, produced using Ocean Data View (Schlitzer, 2015).

2015 (sediments), both with the R/V/ Pelagia (Fig. 1). Large volume seawater samples (up to 10 L) were obtained from Stations 2 and 5 of the MedBlack cruise (GEOTRACES cruise report 64PE373) (Fig. 1) with ultra-clean PVDF samplers, before being filtered (0.2 μm) and acidified using ultra-pure HCl immediately after collection (Rolison et al., 2017, 2018). Sediments were collected from MedBlack Station 2 using a gravity corer, then sectioned at ~ 1 cm intervals (Rolison et al., 2017, 2018). Sediments were also obtained from seven Stations (1, 2, 4, 7, 8, 13, 14) during the Fe-Vici cruise using an Oktopus multicorer and separated from porewaters by centrifugation and filtration as detailed in Lenstra et al. (2019).

3.2. Cadmium isotope analysis of waters

Seawater samples from the MedBlack cruise were chemically processed and analysed for their Cd concentrations and Cd isotopic compositions at the Centre for Trace Element Analysis, University of Otago using methods adapted from previous studies (Ripperger and Rehkämper, 2007; Gault-Ringold et al., 2012; Rolison et al., 2018; George et al., 2019). In brief, seawaters comprising >5 ng of natural Cd were admixed with a well-calibrated ^{110}Cd - ^{111}Cd double spike (spike: sample ratio of ~ 2) to correct for instrumental mass fractionation during sample processing and analysis. Dissolved Cd was then extracted and purified from seawater using a 3-stage ion exchange procedure with (1) initial pre-concentration using Nobias PA-1 resin (Hitachi High Technologies, Japan) to isolate the trace metal fraction, followed by (2) a two-stage column procedure using AG-MP1 (200–400 mesh) resin (Biorad Technologies, USA) to remove matrix and interfering elements prior to Cd elution.

Cadmium isotopic measurements were performed by multi-collector ICP-MS (MC-ICP-MS) at the University of Otago using a Nu Plasma HR instrument following previously reported methods (Gault-Ringold et al., 2012; Gault-Ringold and Stirling, 2012; George et al., 2019; Druce et al., 2022a). Ion beams were monitored simultaneously for masses 110 to 118. The measured $^{110}\text{Cd}/^{111}\text{Cd}$, $^{112}\text{Cd}/^{111}\text{Cd}$, $^{114}\text{Cd}/^{111}\text{Cd}$ ratios were corrected for isobaric interferences from Pd and Sn by monitoring ^{105}Pd and ^{118}Sn , and for instrumental mass fractionation based on the iterative double-spike methods described in Siebert et al. (2001). Following correction, Cd isotopic composition is reported as $^{114}\text{Cd}/^{110}\text{Cd}$, reformulated into delta notation as $\delta^{114}\text{Cd}$ relative to the average of the two bracketing measurements of the primary reference standard NIST3108:

$$\delta^{114}\text{Cd} = \left(\frac{^{114}\text{Cd}/^{110}\text{Cd}_{\text{sample}}}{^{114}\text{Cd}/^{110}\text{Cd}_{\text{NIST3108}}} - 1 \right) * 1000 \quad (1)$$

Uncertainties are reported as 2 S.E.. Dissolved Cd concentrations were determined via isotope dilution using the $^{111}\text{Cd}/^{114}\text{Cd}$ ratio. Typical procedural blanks for seawater analyses were 5 pg. Data quality has been assessed through participation in inter-laboratory comparisons (Boyle et al., 2012; Abouchami et al., 2012) and through analysis of secondary standards over the course of this study: NZ-JMC—Cd yielded a value of -1.67 ± 0.07 ‰ ($n = 12$, 2 S.D.) and Munster Cd yielded a value of 4.56 ± 0.1 ‰ ($n = 6$, 2 S.D.), both within uncertainty of published values (Gault-Ringold and Stirling, 2012; Abouchami et al., 2012; Ripperger and Rehkämper, 2007). External reproducibility assessed using secondary standards was ± 0.06 ‰ for analyte masses >15 ng and $\sim \pm 0.40$ ‰ at 0.5 ng.

3.3. Cadmium isotope analysis of sediments

Dried sediment samples from the Fe-Vici cruise were chemically processed and analysed at the University of Oxford. The sediments were digested using a mixture of perchloric, hydrochloric and hydrofluoric acids as described by Bryan et al. (2021). Aliquots of the sample digests were diluted and measured for minor and major element concentrations using a Perkin Elmer NexION 350D ICP-MS. Cadmium concentration

measurements were performed using ammonia as a reactive cell gas to improve sensitivity and minimise isobars. The obtained Cd concentrations were used to mix an aliquot of the original sample digest containing ~ 100 ng Cd with a ^{111}Cd - ^{113}Cd double spike, to obtain a spike/sample ratio of ~ 1 . Cadmium was subsequently purified from sediment digests using a two-stage column procedure adapted from Ripperger and Rehkämper (2007) and Sweere et al. (2020b) using AG1-X8 anion resin (200–400 mesh) and Tru-spec resin (Eichrom Technologies, USA) to remove matrix elements and Sn.

Cadmium isotope compositions for the Fe-Vici sediments were measured using a Nu Plasma MC-ICP-MS at the University of Oxford. An Elemental Scientific PFA MicroFlow Nebulizer was used for sample introduction with a Nu Instruments DSN-100 desolvation system. Signals were collected simultaneously for ^{110}Cd , ^{111}Cd , ^{112}Cd , ^{113}Cd , ^{114}Cd , along with ^{115}In and ^{117}Sn to correct for isobaric interferences. Signal voltages were recorded over 40x cycles of 10 s integration time. All signals were background corrected by subtracting the voltages measured on an acid blank before each measurement. Measured ratios were deconvolved offline to calculate cadmium isotope compositions using NIST3108 as the zero-delta reference standard according to Eq. (1). Corrections for Sn interferences were small and never resulted in a deviation of isotope compositions of >20 ppm. Measurements of the OXCAD reference solution throughout the course of the study gave a long-term value of -0.95 ± 0.09 ‰ ($n = 139$, 2 S.D.) relative to NIST 3108, similar to values in Abouchami et al. (2012). Procedural blanks were measured using ICP-MS and were near the detection limit of the instrument.

Freeze-dried sediment sub-samples (~ 300 mg) from MedBlack Station 2 were chemically processed and analysed at the Centre for Trace Element Analysis, University of Otago. The sediments were sequentially digested to completion with HF-HNO₃-HCl and the concentrations of a suite of ~ 40 elements were determined by quadrupole ICP-MS (Agilent 7900, USA) (Rolison et al., 2017, 2018). An aliquot of each sediment digest corresponding to ~ 100 ng of Cd was mixed with a ^{110}Cd - ^{111}Cd double spike and chemically processed to isolate and purify Cd from the sample matrix using a two-stage procedure with AG1-X8 and AG-MP1 resins (Bio-Rad Ltd, USA), then analysed for Cd isotopic composition using methods described in Section 3.2. USGS reference material SBC-1 was analysed during the course of the project and yield a composition of -0.08 ± 0.07 ‰ ($n = 4$, 2 S.D.)

The non-detrital Cd isotope compositions of all sediment samples were calculated by mass balance, assuming an upper continental crust Cd/Al ratio of 1.1×10^{-6} and a crustal $\delta^{114}\text{Cd}$ composition of 0 ‰ (Schmitt et al., 2009). Given the high amount of non-detrital Cd in the sediments, this calculation resulted in isotopic compositions for all stations within uncertainty of the measured values. The uncorrected data are therefore used in this paper.

4. Results

4.1. Black Sea water column

Data from stations 2 and 5 show similar values and trends, albeit with a slightly deeper chemocline at station 5. The dissolved Cd profiles can be divided into 3 main intervals (Fig. 2). In the first interval, from 0 to 60 m at station 2 and 0–70 m at station 5, dissolved cadmium concentrations [Cd_w] are ~ 50 – 100 pmol kg^{-1} and $\delta^{114}\text{Cd}$ ranges from 0.58 to 0.96 ‰, with a slight increase of $\delta^{114}\text{Cd}$ towards the surface. In interval 2, below ~ 60 m at station 2 and 70 m at station 5, [Cd_w] declines with depth from a peak of 154–165 pmol kg^{-1} to <3 pmol kg^{-1} by 110 m depth at station 2 and 119 m depth at station 5. [Cd_w] is already >98 % lower than its peak concentration before H₂S becomes detectable at ~ 105 m at station 2 and ~ 119 m at station 5. $\delta^{114}\text{Cd}$ remains relatively invariant throughout interval 2, with identical mean values at station 2 (0.35 ± 0.19 ‰, 60–100 m depth, $n = 12$) and station 5 (0.38 ± 0.09 ‰, 70–105 m depth, $n = 8$). $\delta^{114}\text{Cd}$ increases in interval 3, reaching a

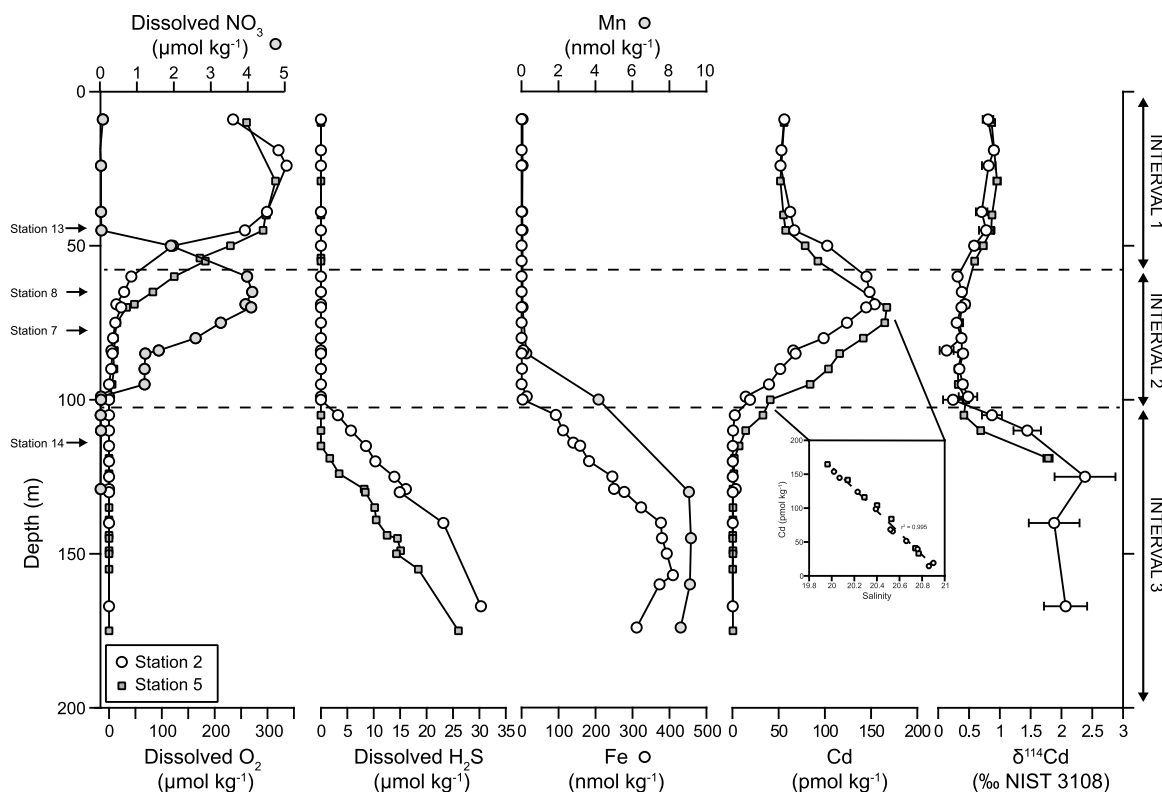


Fig. 2. Concentration and isotopic profiles of dissolved constituents measured at stations 2 and 5 of the GEOTRACES MedBlack cruise. Depths of sediment cores shown in Fig. 3 are marked with arrows to the left of the plot.

maximum of 2.38 ‰ below the H_2S chemocline at station 2. Concentration profiles for $[\text{Cd}_w]$ were similar to previous measurements by Haraldsson and Westerlund (1988) and Lewis and Landing (1992), but with a shallower concentration maximum.

4.2. Black Sea sediments

Sediment Cd concentrations $[\text{Cd}_s]$ and $\delta^{114}\text{Cd}$ at the seven stations range from 0.10 to 2.44 $\mu\text{g g}^{-1}$ and -0.12 – 0.34 ‰ respectively (Fig. 3). Near-surface $[\text{Cd}_s]$ and $\delta^{114}\text{Cd}$ (<5 cm below the sediment-water interface), which are most relatable to the modern water chemistry, both increase basinwards, with $\delta^{114}\text{Cd}$ increasing from a minimum of -0.02 ± 0.07 ‰ at station 13 to 0.24 ± 0.13 ‰ at station 2. There is a notable increase in $[\text{Cd}_s]$ at sites with sediment accumulating below the sulfide chemocline. Where downcore profiles are available, for stations 1, 2, 7, 8, and 13, $\delta^{114}\text{Cd}$ compositions generally do not exhibit variations with depth. The exception is station 13 where $\delta^{114}\text{Cd}$ compositions increase from ~ -0.01 ‰ above 5 cm depth to ~ 0.31 ‰ at ~ 10 cm depth. This increase corresponds to an increase in $[\text{Cd}_s]$ from ~ 0.3 to 1.2 $\mu\text{g g}^{-1}$ across the same depth range (Fig. 3).

5. Discussion

5.1. Processes controlling cadmium in the upper water column

Near-surface concentrations of $[\text{Cd}_w]$ at stations 2 and 5 are at the lower end of typical open ocean values that range from 0 to 1.1 nmol kg^{-1} (Middag et al., 2018), but similar to previous measurements of near-surface $[\text{Cd}_w]$ in oligotrophic gyres (George et al., 2019), the Black Sea (Haraldsson and Westerlund, 1988; Lewis and Landing, 1992; Tankéř et al., 2001) and the eastern Mediterranean (50–60 pmol kg^{-1}) (Middag et al., 2022).

The low salinity of the near surface waters at station 2 (18–19) record the mixing of eastern Mediterranean waters with river runoff into the

Black Sea basin. Both sources deliver Cd to Black Sea surface waters. Anthropogenic Cd may also be added to Black Sea surface waters from industrial runoff in the rivers draining into the Black Sea basin or from aerosols (e.g. Middag et al., 2022). These additions may have a significant effect on near-surface Cd isotope compositions: acid mine drainage and industrial smelting waste products, for example, can have isotopic compositions >1 ‰ (Martinkova et al., 2016; Yang et al., 2019). Any such anthropogenic component in the Black Sea data cannot be identified using the current constraints and so we do not account for these in the following discussion.

The inverse relationship between $\delta^{114}\text{Cd}$ and $[\text{Cd}_w]$ in interval 1 (0–55 m) is consistent with biological export from the oxygenated photic zone, since kinetic biological assimilation tends to leave Cd_w enriched in heavier isotopes (Lacan et al., 2006; Ripperger et al., 2007). The slope of $\delta^{114}\text{Cd}$ versus $\log[\text{Cd}_w]$ (Fig. 4) shows a linear data array for interval 1 that lies at the upper end of a range of α fractionation factors previously defined for biological Cd utilisation (1.0001–1.0006; e.g. Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011; George et al., 2019). The peak in subsurface Cd_w in interval 2 reflects remineralisation of sinking biological matter and release of Cd and indicates that a significant proportion of exported Cd is recycled in the upper part of the water column, alongside the ~ 80 % of exported organic carbon that is efficiently recycled in the upper 200 m of the Black Sea (Karl and Knauer, 1991).

The sharp decline in $[\text{Cd}_w]$ observed in interval 2 alongside invariant $\delta^{114}\text{Cd}$ occurs below the zone of biological productivity but above the euxinic water column within the nitrogenous zone coincident with rapidly decreasing NO_3^- . Here, nitrate becomes the dominant organic matter oxidant, lowering NO_3^- concentrations as it is reduced to nitrite. In this interval, we attribute the observed behaviour of Cd to downward diffusion of dissolved Cd to a zone of removal at the top of interval 3 (Figs. 2 and 4, also see below). This process is supported by the near linear decrease of $[\text{Cd}_w]$ within interval 2 that correlates tightly with salinity, indicating conservative mixing (Fig. 2 inset)

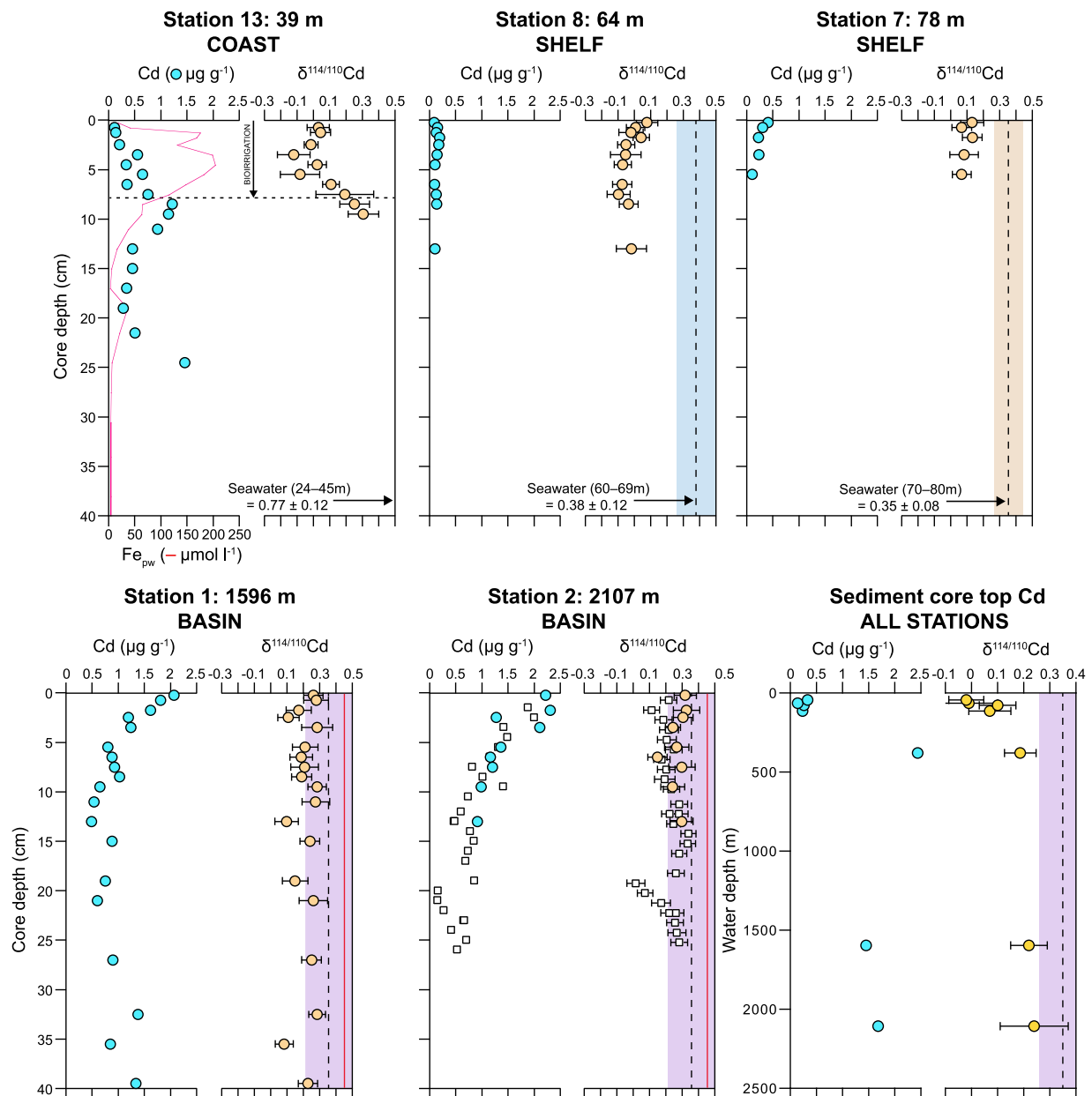


Fig. 3. Sedimentary profiles of $[Cd_w]$ and $\delta^{114}Cd$ at stations 1, 2, 7, 8 and 13. University of Oxford VICI cruise data are shown as blue and yellow circles and University of Otago MedBlack cruise data are shown as white squares. Vertical dashed lines and shaded bands illustrate the mean and 2 S.D. range of dissolved $\delta^{114}Cd$ from the closest three equivalent water depths at station 2. Fe_{pw} : porewater Fe concentrations.

The rapid decrease in $[Cd_w]$ that occurs in tandem with a systematic increase in $\delta^{114}Cd$ at the top of interval 3 has been observed previously and attributed to the precipitation of Cd^{2+} to insoluble CdS (Lewis and Landing, 1992). Experimental precipitation of CdS from synthetic seawater by Guoinseau et al. (2018) and Bryan (2019) showed that isotopically light CdS precipitates with experimentally determined α fractionation factors of 1.00016 and 1.00011 respectively. These lines are superimposed on Fig. 4 and confirm that this process is likely to be responsible for the removal of dissolved Cd below ~ 100 m in the Black Sea, providing a field-based verification of these experimental studies.

The $\sim 98\%$ decrease in $[Cd_w]$ in interval 3 compared to the top of interval 2 implies that the average composition of waters in the upper water column sets the isotopic signature of Cd that is buried in sediments. It is noteworthy that this composition is formed from Cd dissolved in inflowing high salinity waters from the Eastern Mediterranean mixed with Cd presumably sourced from low salinity waters and

atmospheric dust (and potentially anthropogenic inputs). The former source, being of shallow (~ 50 m) origin, is likely to already be fractionated from deeper waters given that Cd does not behave conservatively in seawater (Ripperger et al., 2007; Conway and John, 2015; Xie et al., 2017; Sieber et al., 2023). Unlike other elements such as Mo and U that do behave conservatively in the oxic open ocean, therefore, the isotopic composition of Cd in Black Sea waters is probably not directly representative of the global deep ocean.

5.2. Isotopic composition of sediments accumulating below the chemocline

The quantitative importance of CdS burial on the global burial flux of Cd in marine sediments, and hence on the Cd mass balance in the ocean, was indicated by earlier work that identified Cd burial based on relative depletions of dissolved Cd in seawater relative to P (Rosenthal et al., 1995; Janssen et al., 2014; Guoinseau et al., 2018, 2019; Plass et al.,

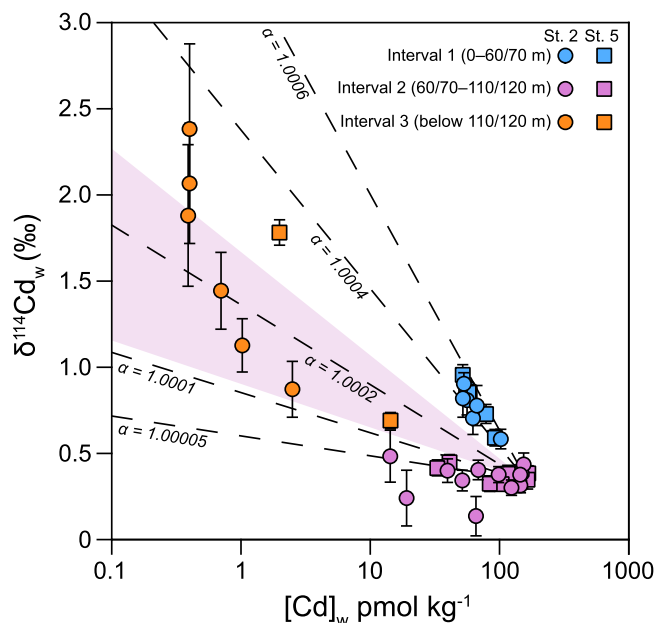


Fig. 4. Dissolved $\delta^{114}\text{Cd}$ versus $\log[\text{Cd}_s]$ for samples from the Black Sea water column. Dashed lines illustrate a range of $\alpha_{\text{Cd}(\text{water} - \text{solid})}$ fractionation factors determined for CdS precipitation and biological assimilation, calculated assuming a starting fluid $\delta^{114}\text{Cd}$ of 0.35 ‰ and a $[\text{Cd}_w]$ of 160 pmol kg^{-1} . The shaded red region indicates $\alpha_{\text{Cd}(\text{water} - \text{solid})}$ values of 1.00011–1.00026 experimentally determined for CdS precipitation (Guinoiseau et al., 2018; Bryan, 2019).

2021). These observations have more recently been explained by large variability in the seawater Cd/P ratio without the need to infer CdS precipitation (de Souza et al., 2022). In the Black Sea there is a very large Cd concentration gradient of three orders of magnitude between waters above and below the chemocline that cannot be explained by mixing of different water mass endmembers. The relationships between $[\text{Cd}_w]$ and $\delta^{114}\text{Cd}$ in intervals 2 and 3 indicate the importance of CdS formation as a removal pathway driving these concentration changes. Organic matter export is unlikely to be as important here: the abundance of sinking organic particles and fecal pellets decline below ~ 60 m depth (Karl and Knauer, 1991), at the same levels where $[\text{Cd}_w]$ decreases at station 2. Carbonate fluxes are dominated by the coccolithophore *Emiliania huxleyi* in the modern Black Sea (Arthur et al., 1994). Nonetheless, carbonates do not contain a large amount of Cd (Horner et al., 2011; Druce et al., 2022a) and are thus also not likely to be responsible for the bulk of Cd export from the sub-surface layers of the Black Sea.

There is a similarity between the $\delta^{114}\text{Cd}$ of sediments accumulating below ~ 100 m (stations 1 and 2) and the average composition of dissolved Cd above ~ 100 m (Fig. 3). This similarity is unsurprising, given the large fraction of dissolved Cd removed to sediments, as shown for other trace metals in the Black Sea (Neubert et al., 2008; Vance et al., 2016). The exact comparison between sediments and dissolved $\delta^{114}\text{Cd}$ is dependent on what seawater ‘source’ composition is used. The difficulty with estimating this composition lies with the fact the upper water column is affected by biological cycling in the vertical domain, advection and mixing in the horizontal domain, and several other processes occurring below the subsurface, all of which affect the signature of inflowing marine waters. The approach used here is to calculate the average $\delta^{114}\text{Cd}$ composition of Cd dissolved in waters in interval 2 where biological remineralisation from the photic zone is probably most pronounced ($\sim 0.36 \pm 0.15$ ‰, stations 2 and 5). The take home message is that under highly sulfidic conditions in the deeper parts of the Black Sea Basin, the isotopic composition of sediments is identical (i.e. within uncertainties) to the composition of dissolved Cd in the upper part of the water column, and thus record that signature. This observation supports

the use of ancient sedimentary deposits that formed under sulfidic conditions to trace the Cd isotope composition of coeval basin waters. Small offsets to lighter sediment compositions below the sediment-water interface may be variably due to the influence of isotopically light Cd in coccolithophore-carbonate (e.g. Horner et al., 2011; Druce et al., 2022b) or the influence of Fe-Mn shuttling of isotopically light Cd to the basin floor followed by the reductive dissolution of these phases, as suggested for organic-rich sediments accumulating in the western Pacific Ocean (Chen et al., 2021).

5.3. Isotopic composition of sediments accumulating above the chemocline

Sediments at coastal, shelf and shelf-edge stations 7, 8 and 13 all have $\delta^{114}\text{Cd}$ compositions lighter than dissolved Cd at comparable depths (extrapolated from the station 2 data assuming approximate uniformity across the basin) (Fig. 3). At stations 7, 8 and 14 these low compositions can be attributable to the burial of Cd adsorbed to Fe/Mn oxides, which can fractionate Cd by up to -0.5 ‰ (Wasylenki et al., 2014; Yan et al., 2021; Gao et al., 2021). Average non-detrital Mn in the upper 5 cm of these stations ranges from 7.7 to 13.2 mg g^{-1} , compared to <0.3 mg g^{-1} below the chemocline in deep basin stations 1, 2 and 4 where reductive dissolution of Mn prevails in the water column (Lenstra et al., 2020). Organic matter accumulation at stations 7, 8 and 14 is relatively low (Lenstra et al., 2019) but may still play a role in burying isotopically light Cd, perhaps alongside non-quantitative formation of authigenic CdS.

Different processes are probably taking place at coastal station 13, where there is almost no non-detrital Mn and Fe accumulation and both elements are reductively recycled back into the water column. These reductive Fe/Mn releases have been attributed the high supply of organic matter to the sediments driven by coastal primary production and nutrient supply from large rivers draining into the western Black Sea, rather than to ambient water column redox conditions (Tankere et al., 2001; Lenstra et al., 2019, 2020). Bioirrigation has a major impact on the release of Fe and Mn at station 13, whereby macrofauna irrigate burrows down to ~ 8 cm (quantified by bromide tracer results) beneath the sediment-water interface, while bioturbation moves iron oxides and organic matter into the sediments and promotes high rates of iron oxide reduction and subsequent loss of Fe^{2+} back to the overlying water column (Lenstra et al., 2019). The effect of bioirrigation on the amount and composition of Cd accumulating at station 13 can be examined by comparing the vertical profiles of porewater [Fe] and solid phase $[\text{Cd}_s]$ in Fig. 3. In this profile $[\text{Cd}_s]$ and $\delta^{114}\text{Cd}$ increase sharply below the peak in [Fe]. This profile could in principle be explained either by the loss of isotopically heavy Cd within the zone of bioirrigation (upper 8 cm), or by the accumulation of isotopically heavy solid phase Cd below 8 cm. The first option is less likely: while oxide dissolution and organic matter oxidation would release Cd back into porewaters, these losses would liberate isotopically light Cd that would tend to elevate the residual solid phase Cd to heavier compositions, opposite to what is observed. The second option, however, would be plausible due to the formation of CdS below the zone of bioirrigation/Fe-reduction (>8 cm) with isotopically heavier compositions resulting from the rapid precipitation of porewater Cd obtained from the dissolution of dissolved mineral phases during early burial, and/or from the diffusion of isotopically heavy seawater Cd into the sediments (aided by bioirrigation). A diffusive seawater source of Cd, perhaps aided by macrofaunal activity, is favoured by the very high $[\text{Cd}_s]$ observed below ~ 8 cm sediment depth, which are an order of magnitude higher than $[\text{Cd}_s]$ seen at the other coastal and shelf locations.

5.4. Influence of Cd burial in the anoxic Black Sea on the global Cd budget

The global Cd budget has previously been described in terms of input fluxes from rivers, dust, and hydrothermal fluids, and removal fluxes

into variably oxygenated sediments (van Geen et al., 1995; Bryan et al., 2021; Chen et al., 2021). While useful, these representations of the removal fluxes of Cd have the drawback that they aggregate different sedimentary phases in each redox regime (e.g. oxic, suboxic, anoxic etc.) that may have very different isotopic compositions. The exact redox regime in different sedimentary settings is quite hard to characterise in a consistent way, due to the presence of redox zonations that may extend from the sediments into the water column, and which may be compressed at different length scales, thus altering the stability of Cd burial phases. In the deeper portions of the Black Sea, our data clearly point to a dominant removal pathway of CdS formation in the water column, which transfers the isotopic composition of dissolved Cd into the accumulating sediments. The impact of CdS burial in the Black Sea on the global mass balance of Cd can be calculated using a Black Sea anoxic seafloor area (>200 m depth) of $2.675 \times 10^5 \text{ km}^2$ (Djikstra et al., 2014), mass accumulation rates for sediment unit I of $3.6\text{--}25.4 \text{ mg cm}^{-2} \text{ yr}^{-1}$ (Calvert et al., 1987; Arthur et al., 1994), and an average $[\text{Cd}_s]$ of $1.45 \mu\text{g g}^{-1}$ in the upper 5 cm of stations 1 and 2. This calculation suggests that $1.2\text{--}8.8 \times 10^5 \text{ mol yr}^{-1}$ CdS is buried in the sulfidic region of the Black Sea, which is equivalent to just $\sim 0.4\text{--}2.9 \%$ of the total annual input flux to the ocean of $\sim 3 \times 10^7 \text{ mol}$ ('best estimate' of Chen et al., 2021). A lower global ocean input flux of $0.6 \times 10^7 \text{ mol yr}^{-1}$ (van Geen et al., 1995) increases the estimate to 2.1–14.6 % of the total. Our estimate of CdS burial in the Black Sea is much lower than existing estimates of Cd removal globally into continental margin or low-oxygen sediments (van Geen et al., 1995; Rosenthal et al., 1995b; Little et al., 2015; Chen et al., 2021; Bryan et al., 2021). Quantitatively equating the phase-specific estimate presented here with global fluxes is difficult, however, as published estimates tend to group Cd burial fluxes by bathymetric or redox setting, rather than by the phase of Cd being buried. Regardless, our study is clear that CdS burial in the Black Sea plays a moderate role in the overall global mass balance of Cd.

6. Conclusions

Several processes influence the isotope composition of Cd dissolved in Black Sea waters. Surface inputs of Cd come from Mediterranean inflow through the Bosphorus Strait and from riverine and (presumably) atmospheric delivery. Isotopic variations in near-surface waters are affected by biological assimilation and regeneration, with characteristic deviations to heavier $\delta^{114}\text{Cd}$ in the photic zone that follow fractionation trends identified in productive open-ocean settings. Our new isotopic measurements from depths below ~ 100 m essentially confirm fractionation trends predicted from previous experimental CdS precipitation experiments. We note that removal of dissolved Cd begins above the sulfide chemocline, which we attribute to diffusion of dissolved Cd to the depth of CdS precipitation.

Sediments that accumulate below the sulfide chemocline have $\delta^{114}\text{Cd}$ compositions that are similar to the composition of near-surface Black Sea waters. This similarity, which has also been observed for other trace metals in the Black Sea is unsurprising, given the high fraction of dissolved Cd that precipitates as CdS and is presumably then buried into sediments. The situation for sediments above the chemocline is more complicated, with sediment $\delta^{114}\text{Cd}$ offset to lighter values than seawater at the same depth. We surmise that these offsets are due to mixtures of isotopically light organic-bound Cd with other sedimentary phases such as oxyhydroxides and perhaps non-quantitative precipitation of CdS below the sediment-water interface. We also highlight the potential role of biological mixing as an influence on Cd burial in marine sediments.

Our study has some important implications. Firstly, we present strong evidence that Cd precipitation below the sulfide chemocline is dominated by CdS formation, with near-complete water column removal allowing sediments accumulating below this depth to capture the isotopic signature of dissolved Cd in the upper water column. This observation suggests that ancient marine sediments similarly deposited in sulfidic conditions may record paleo-seawater Cd isotope

compositions, and therefore the global balance of input and removal fluxes to and from the oceans. This application comes with the caveat that the Cd isotope composition of seawater in marginal basins such as the Black Sea may be derived from mixtures of upper-ocean water flowing into the basin, and locally-derived inputs, both of which may be isotopically distinct from the global deep ocean composition. Application to ancient sediments should therefore proceed with caution and with a good understanding of the paleo-bathymetric setting. Secondly, we estimate that the accumulation of CdS in Black Sea sediments below ~ 200 m depth accounts for 0.2–14.6 % of all Cd burial in the oceans, suggesting that open-ocean non-euxinic settings probably account for the majority of Cd buried globally.

CRediT authorship contribution statement

Alexander J. Dickson: Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. **Allison L. Bryan:** Writing – review & editing, Methodology, Investigation, Data curation, Conceptualization. **Ejin George:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gideon M. Henderson:** Writing – review & editing, Validation, Resources, Project administration, Conceptualization. **Donald Porcelli:** Writing – review & editing, Validation, Resources, Project administration, Funding acquisition, Conceptualization. **John Rolison:** Writing – review & editing, Validation, Methodology, Investigation, Conceptualization. **Caroline P. Slomp:** Writing – review & editing, Validation, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. **Rob Middag:** Writing – review & editing, Validation, Resources. **Claudine H. Stirling:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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Data availability

Data are freely available as a supplement to this paper and via the UK National Geoscience Data Centre.

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