Chromium Cycling in Redox-Stratified Basins Challenges δ⁵³Cr Paleoredox Proxy Applications

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Abstract Chromium stable isotope composition (δ⁵³Cr) is a promising tracer for redox conditions throughout Earth's history; however, the geochemical controls of δ⁵³Cr have not been assessed in modern redox-stratified basins. We present new chromium (Cr) concentration and δ⁵³Cr data in dissolved, sinking particulate, and sediment samples from the redox-stratified Lake Cadagno (Switzerland), a modern Proterozoic ocean analog. These data demonstrate isotope fractionation during incomplete (non-quantitative) reduction and removal of Cr above the chemocline, driving isotopically light Cr accumulation in euxinic deep waters. Sediment authigenic Cr is isotopically distinct from overlying waters but comparable to average continental crust. New and published data from other redox-stratified basins show analogous patterns. This challenges assumptions from δ⁵³Cr paleoredox applications that quantitative Cr reduction and removal limits isotope fractionation. Instead, fractionation from non-quantitative Cr removal leads to sedimentary records offset from overlying waters and not reflecting high δ⁵³Cr from oxidative continental weathering.

Plain Language Summary Chromium stable isotope composition in sediments has been used extensively to understand changes in oxygen availability throughout Earth’s history. These reconstructions are built on assumptions of chromium (Cr) transfer betweenoxic and anoxic waters such that sediments directly reflectoxic surface waters, and therefore trace redox cycling at Earth’s surface. However, this has not been tested in modern redox-stratified systems. Here, we show that Cr concentrations and stable isotope compositions deviate from these assumptions. Chromium is neither efficiently removed in anoxic waters, nor do sediments faithfully record water column isotopic signatures. A synthesis of new and published observations from euxinic waters indicates these findings appear universal. Previous assumptions of paleo-studies are not supported by modern systems and should be revised.

1. Introduction

Authigenic chromium (Cr) enrichments and Cr stable isotope (δ⁵³Cr) composition in sedimentary deposits are widely used to trace redox conditions throughout Earth’s history (Frei et al., 2009; Planavsky et al., 2014; Reinhard et al., 2013; Wei et al., 2020). These applications, which interpret high δ⁵³Cr to signal elevated oxidative weathering of the continents, are based on the redox control of Cr solubility and stable isotope fractionation in aqueous environments. Reduced Cr (Cr(III)) is particle reactive and can be readily removed from the water column (Richard & Bourg, 1991), while oxidized Cr(VI) is soluble, with isotope fractionation resulting in enrichment of isotopically light Cr in Cr(III) (Ellis et al., 2002; Wanner & Sonnenthal, 2013). As a consequence of Cr reduction and removal, natural systems with strong O₂ deficiency are associated with dissolved Cr depletions as well as elevated dissolved δ⁵³Cr (Huang et al., 2021; Moos et al., 2020; Murray et al., 1983; Nasemann et al., 2020; Rue et al., 1997).

Paleo-reconstructions using sedimentary δ⁵³Cr records apply the assumption that Cr is efficiently sequestered into sediment phases under reducing conditions (anoxia or euxinia). Thus, complete (i.e., quantitative) Cr redox
2. Study Area and Methods

2.1. Study Area

Lake Cadagno, at 1921 m elevation, is a 21 m deep meromictic alpine lake in Switzerland characterized by a permanent chemocline near 13 m depth. The initially oxic lake formed ∼13,500 YBP. A transition phase persisted between 10,00 and 9,000 YBP, followed by euxinic monimolimnion conditions, which have been generally stable until present (Berg et al., 2022). The lake's distinct geochemistry and microbial communities have been well-characterized. Waters below the chemocline are fed by groundwater input from a karstic system composed of dolomite and gypsum, and are therefore rich in Ca$^2+$, Mg$^{2+}$, SO$_4^{2-}$ and HCO$_3^-$ relative to overlying waters (Del Don et al., 2001, Figure 1). In anoxic deep waters, dissolved concentrations reach 10$^2$ μmol kg$^{-1}$ sulfide, ∼3.5 mmol kg$^{-1}$ sulfate, and ∼1 μmol kg$^{-1}$ Fe (e.g., Ellwood et al., 2019, see supplement). High densities of anoxicogenic photoautotrophic green and purple sulfur bacteria are found at the chemocline in summer (Tonolla et al., 2003). These bacteria exert control on geochemical gradients in this zone (e.g., S, Fe; Del Don et al., 2003). These bacteria utilize oxygen and sulfur species to generate energy, leading to the formation of sulfides and sulfuric acid. The lake is therefore characterized by a steep gradient in redox conditions, with oxygen-depleted bottom waters supporting anoxygenic phototrophic bacteria in the chemocline.

2.2. Sampling, Sample Purification and Analysis

Dissolved Lake Cadagno water samples were collected from a floating platform on 28–29 August 2017 and analyzed in the laboratory. Sediments were collected in summer 2019 and summer 2020 (Berg et al., 2022), freeze dried, and hand milled with an agate mortar and pestle. Baltic Sea samples were collected in the central Landsort Deep (site LD1; 435 m water depth, Häusler et al., 2018) onboard RV Poseidon (POS507, 29 October 2016).

Water column sampling and spiking (with a $^{53}$Cr-$^{54}$Cr double spike) followed standard procedures, and are discussed in Section S.1 in Supporting Information S1. Samples were processed through three stages of column chromatography: (i) Fe removal using AG1-X8 resin in 6.4 M HCl (Scheiderich et al., 2015), followed by (ii) anion and (iii) cation chromatography as described elsewhere (Janssen et al., 2020; Nasemann et al., 2020; Rickli et al., 2019). Sediment near-total digests were prepared using inverse aqua regia with H$_2$O$_2$. Authigenic sediment phases (primarily organic matter, potentially also sulfides, Figure 2a) were targeted with a 30% v/v H$_2$O$_2$ leach at pH = 2 following Raquet et al. (1999) (see Section S.1 in Supporting Information S1). Leach and digest subsamples were spiked with a $^{53}$Cr-$^{54}$Cr double spike, dried and processed through steps (i) and (iii). Reagents were either sub-boiling distilled (acids) or Romil UpA and Fisher Optima grade (H$_2$O$_2$). Ancillary data are described in the supplement.
Sediment trap fluxes are calculated with and without corrections for lithogenic contributions (Figures 1 and 2, Table 1). Uncertainties on corrected data (pCr\textsubscript{Auth}) follow standard error propagation using lithogenic Cr/Al (Rudnick & Gao, 2014) and δ\textsuperscript{53}Cr = −0.12 ± 0.1 ‰ (Schoenberg et al., 2008). Such corrections, which rely on normalizations to major crustal elements considered minimally mobile (e.g., Al), are complicated by the authigenic components of these elements in Lake Cadagno (Figures S6 and S7 in Supporting Information S1). Therefore, these corrections underestimate pCr\textsubscript{Auth} and overestimate δ\textsuperscript{53}Cr\textsubscript{Auth}, with true authigenic values lying between the corrected and uncorrected data (See Section S.5 in Supporting Information S1). Detrital corrections...
were not applied to sediment leach data as chemical leaches were more gentle than sediment trap digests (See Section S.1.2 in Supporting Information S1) enhancing the impact of authigenic phases of the normalizing element and exacerbating artifacts from improper corrections (Figures S6 and S7 in Supporting Information S1).

Purified $\delta^{53}$Cr samples were dissolved in 0.7–1 mL 0.5 M HNO$_3$ and analyzed with a Neptune Plus MC-ICP-MS (ThermoFisher) (Rickli et al., 2019). Internal sample uncertainty (2 SEM) and session reproducibility from NIST standards ($n \approx 10$, 2 SD) is typically around 0.02–0.03 ‰. External uncertainty has previously been estimated at ±0.033 ‰ for full sample replicates (Janssen et al., 2020). Pure standard reference materials (Merck Cr(III)
standard, this study: $\delta^{53}\text{Cr} = -0.45 \pm 0.03 \text{\%e}$, $n = 10$; $\delta^{53}\text{Cr} = -0.44 \pm 0.02 \text{\%e}$, Schoenberg et al., 2008) and USGS reference materials (Table S3 in Supporting Information S1) agree with published values.

3. Lake Cadagno Results and Discussion

3.1. Water Column

Dissolved [Cr] is stable in the surface mixed layer ([Cr] = 0.5 nmol kg$^{-1}$, Figure 1c). A broad [Cr] minimum is found at 8–11 m depth, above the chemocline (~12–13 m in summer 2017, Figure S1 in Supporting Information S1; Sepúlveda Steiner et al., 2021). Particulate Fe and Mn oxides form within and above the chemocline in Lake Cadagno, driven by upward transport of dissolved Fe(II)—a known Cr reductant (Richard & Bourg, 1991; Wanner & Sonnenthal, 2013)—and Mn(II) from the anoxic zone (Ellwood et al., 2019). As these oxides sink below the chemocline, they are reductively dissolved within the anoxic zone, and particulate Fe sulfides are formed (Ellwood et al., 2019). The [Cr] minimum lies within the most stratified portion of the water column (Figure S2 in Supporting Information S1) and corresponds to depths with enhanced formation and sinking of Fe and Mn oxides (see figure 5 in Ellwood et al., 2019). Therefore the [Cr] minimum is mechanistically consistent with Cr reduction coupled to Fe oxidation followed by Cr scavenging onto metal oxides.

Chromium concentrations begin increasing just above the chemocline, exceeding surface concentrations immediately below the chemocline. Dissolved [Fe] and [Mn] also increase over this range, with the [Cr] increase more closely mirroring [Fe] (Figure 1c). Matching [Cr], $\delta^{54}$Cr is stable in the surface mixed layer ($\delta^{54}$Cr = +0.86 \%e) (Figure 1d), with the isotopically heavy dissolved Cr signal likely reflecting surface water input to the lake, consistent with expectations from oxidative terrestrial weathering and global observations of riverine $\delta^{54}$Cr (Wei et al., 2020). $\delta^{53}$Cr decreases with depth, indicating the accumulation of isotopically light Cr in deep waters following Cr release during metal oxide reduction.

Sinking fluxes of authigenic particulate Cr (pCr$_{auth}$) increase near the chemocline, with maximum fluxes observed in the 14 m trap. Exported pCr is isotopically lighter than dissolved Cr, with $\Delta^{53}$Cr$_{particulate-dissolved}$ $\approx -0.6 \pm 0.1 \text{\%e}$ near the chemocline. This is comparable to net fractionations observed in other natural systems, but is much lower than theoretical values observed in lab studies (e.g., Wanner & Sonnenthal, 2013), which likely reflects incomplete removal of reduced Cr resulting in lower apparent fractionation factors for Cr reduction and removal (Huang et al., 2021; Nasemann et al., 2020; Wang, 2021). Isotopically, pCr$_{auth}$ is indistinguishable from the lithogenic background ($\delta^{53}$Cr = −0.12 ± 0.10 \%e, Schoenberg et al., 2008). Export fluxes of pCr$_{auth}$ and pMn decrease with depth in the euxinic zone (Figures 1e and Table 1; Table S2 in Supporting Information S1), while pFe species shift from oxide-dominated above the chemocline to sulfides below (Berg et al., 2022; Ellwood et al., 2019), suggesting an Fe-Mn-oxhydroxide shuttle and resulting in much of the Cr exported across the chemocline being released before the deepest sediment trap (20 m). The behavior of pCr is thus consistent with dissolved data indicating Cr release and accumulation in the euxinic zone following reduction of Fe and Mn oxides. Despite depth-dependent variability in pCr$_{auth}$, exported $\delta^{53}$Cr is uniform within analytical uncertainty, indicating no fractionation during Cr release.

Deep layers of euxinic water bodies are assumed to remain quiescent given the strong stratification, and therefore the vertical gradient of [Cr] should be smoothed by an upward molecular diffusive flux. However, the pCr$_{auth}$ export ($\sim 6.7 \times 10^3 \text{ng Cr m}^{-2} \text{day}^{-1}$) is orders of magnitude larger than the molecular flux of dissolved Cr (Table 1, Section S.3 in Supporting Information S1) while the observed [Cr] depletion is subtle. Despite the apparent quiescence of the deep interiors of lakes, various physical processes maintain a moderate and intermittent energetic structure (Saggio & Imberger, 2001), including in Lake Cadagno (Wüest, 1994). Here our concurrent microstructure observations indicate that vertical fluxes are sustained by turbulent diffusivity ($K_w$, Osborn & Cox, 1972), with a mean $K_w$ in the layer of interest of $10^{-1} \text{cm}^2 \text{s}^{-1}$ (Figure S2 in Supporting Information S1; four orders of magnitude larger than molecular diffusivity). This results in upward turbulent flux estimates comparable to sinking pCr fluxes, while the authigenic burial flux is comparatively smaller (~25% of turbulent and particulate fluxes, Table 1). The background turbulence thereby explains Cr profiles and, particularly, the lack of a pronounced [Cr] minimum and local $\delta^{53}$Cr maximum above the chemocline, due to the substantial upward turbulent transport of isotopically light Cr. The result is similar to “cryptic” cycles, where rapid and localized
redox cycling masks the expected biogeochemical signals (e.g., Berg et al., 2016), though rather as a larger-scale physical-geochemical transport cycle.

Observed deep water [Cr] enrichments likely reflect the integrated accumulation of Cr released from sinking particles and near-surface sediments as well as the potential contribution from groundwater (Del Don et al., 2001), with concentrations further modified by turbulent mixing. As there is no modification of particulate δ53Cr with depth, released Cr must be of similar isotope composition as the particulates (δ53Cr ≈ 0 ‰). Therefore, any groundwater Cr must be isotopically heavier than 0 ‰ (see Section S.4 in Supporting Information S1). However, while subaquatic springs likely influence specific aspects of Lake Cadagno deep water [Cr] and δ53Cr, other euxinic basins exhibit similar large-scale [Cr] and δ53Cr depth-trends (see below). Therefore, a shared set of geochemical and physical controls likely shape the common large-scale [Cr] and δ53Cr trends across diverse euxinic basins.

3.2. Sediments

Authigenic Cr (CrAuth) in near-surface sediments is isotopically lighter than deep water, with similar δ53Cr as sinking particles (Figure 2). We do not observe strong [CrAuth] enrichments relative to [CrBulk], despite stably euxinic deep waters and large Cr fluxes from the chemocline, and CrAuth burial fluxes are small relative to chemocline particulate fluxes, reflecting significant Cr release from sinking particles (Table 1, Section S.3.3 in Supporting Information S1). Sediment Mn and Fe(III) content is low relative to sinking particles (Figure 1, Ellwood et al., 2019; Berg et al., 2022), supporting a Fe-Mn-oxhydroxide shuttle for Cr, with Cr release following oxide dissolution. Bulk sediment δ53Cr (δ53CrBulk) is indistinguishable from average continental crust (−0.12 ± 0.10 ‰, Schoenberg et al., 2008) at all depths. δ53CrAuth is slightly higher than crustal signatures in the uppermost sediments; however, δ53CrAuth decreases with sediment depth and is indistinguishable from this inventory below 5 cm. δ53CrBulk and δ53CrAuth converge in the upper 10 cm of the sediment, suggesting modification of δ53Cr through early diagenesis (sedimentation rates ~4–6 mm yr⁻¹, Birch et al., 1996), similar to reports of Cr homogenization in black shales (Frank, et al., 2020).

While surface sediment δ53CrAuth equals sinking particulate δ53Cr, non-quantitative water column Cr removal results in isotope fractionation and an offset between sediments and dissolved δ53Cr. This fractionation, along with potential early diagenetic modification, leads coincidentally to a δ53CrAuth equivalent to detrital reservoirs (Figure 2). δ53CrAuth is approximately 0.6 ‰ lower than dissolved δ53Cr in Lake Cadagno at the [Cr] minimum; however, variable dissolved δ53Cr results in inconsistent offsets between δ53CrAuth and surface, deep and chemocline dissolved δ53Cr [CrBulk] and δ53CrBulk in sапропел samples, obtained from a sediment core spanning the last ~12 ka (Berg et al., 2022) remain relatively stable with depth. δ53CrBulk is indistinguishable from lithogenic background and δ53CrAuth is indistinguishable from or only slightly heavier than lithogenic background (Figure S5 in Supporting Information S1). Thus, despite deposition in an anoxic basin below an oxidizing atmosphere, sediment δ53CrBulk and δ53CrAuth provide no isotopically heavy Cr record (reflecting oxidative weathering and high dissolved δ53Cr). These data imply that in other redox-stratified settings, an isotopically heavy dissolved δ53Cr pool does not necessarily result in isotopically heavy δ53CrAuth or δ53CrBulk records, and that constraints on water column fractionation are needed to reconstruct dissolved δ53Cr of overlying waters and oxidative weathering processes from sedimentary δ53Cr records.

4. Synthesis of Redox-Stratified Systems

δ53Cr has received significant attention as a paleoproxy for O2 availability, especially in the Proterozoic. While Lake Cadagno is a promising analogue for biogeochemical cycling in the Proterozoic ocean, it remains a small Alpine lake with unique physical and biogeochemical cycling. To assess the relevance of these data to other modern redox-stratified systems and to oceanic systems throughout geologic time, we compiled new dissolved [Cr] and δ53Cr data from the weakly euxinic Landsort Deep site in the Baltic Sea (Häusler et al., 2018), together with published [Cr] data from other redox-stratified basins (Figure 3).

In the Landsort Deep, Cr is removed near the chemocline (Figure 3b, Table S7 in Supporting Information S1), coincident with a maximum in particulate Fe and Mn oxides. High dissolved [Cr] and low δ53Cr are found in underlying waters where dissolved [Fe] and [Mn] reach μM levels, indicating an accumulation of isotopically light Cr in euxinic waters as in Lake Cadagno. These data support isotope fractionation during non-quantitative
Cr reduction and removal via scavenging onto metal oxides slightly above the chemocline, with Cr release following oxide reduction in euxinic waters and/or surface sediments. Data from other redox-stratified basins are similar, despite wide ranges in dissolved H\(_2\)S (10\(^{-10}\)–10\(^{-2}\) μmol kg\(^{-1}\)) and Fe (10\(^{-2}\)–10\(^{-2}\) μmol kg\(^{-1}\)) concentrations and Fe/H\(_2\)S (10\(^{-4}\)–10\(^{-3}\)) (Table S9 in Supporting Information S1). This includes Lake Cadagno and the Landsort Deep, Saanich Inlet (Emerson et al., 1979, BC Canada, see also Davidson et al., 2020), the Black Sea (Mugo, 1997), Esthwaite Water (UK, Achterberg et al., 1997), and Hall Lake (WA USA; Balistrieri et al., 1994) (Figures 3a–3e). These can be more directly compared by normalizing profiles to [Cr]\(_{surface}\) and relative depth above and below the chemocline, creating four quadrants: (I) [Cr] < [Cr]\(_{surface}\) in oxic waters, (II) [Cr] > [Cr]\(_{surface}\) in oxic waters, (III) [Cr] < [Cr]\(_{surface}\) in anoxic waters, and (IV) [Cr] > [Cr]\(_{surface}\) in anoxic waters (Figure 3e). All environments lie within (I) slightly above the chemocline, indicating non-quantitative Cr removal. Anoxic deep waters fall into quadrant (IV) in most settings, indicating Cr accumulation rather than removal. Basins with only seasonal anoxia (Saanich Inlet, Esthwaite Water) differ, showing a

![Figure 3. Compilation of anoxic basin data with conceptual mechanistic diagram. Chromium, Fe (orange) and Mn (red) concentrations in the dissolved (open circles, dFe and dMn) and particulate (filled circles, pFe and pMn) phases from Lake Cadagno ((a), black, this study, pFe and pMn: Ellwood et al., 2019), Landsort Deep ((b), dark gray, this study), the Black Sea ((c), blue, Cr: Mugo, 1997, Fe and Mn: Lewis & Landing, 1991), and Saanich Inlet ((d), Emerson et al., 1979, light gray, only dissolved data)). (e) combines (a–d) with Esthwaite Water (green, Achterberg et al., 1997) and Hall Lake (white, Balistrieri et al., 1994). In (a–f), the y-axis ranges from the surface to sediments, with the chemocline at the center. In (a–e), [Cr] is normalized to surface concentrations. The orange shading in (a–d) indicates the zone of enhanced Fe and Mn redox cycling above the chemocline. (f–g) show a schematic of metal cycling in this zone, using Landsort Deep data (f) (see Table S8 in Supporting Information S1).

Cr reduction and removal via scavenging onto metal oxides slightly above the chemocline, with Cr release following oxide reduction in eunxic waters and/or surface sediments.

Data from other redox-stratified basins are similar, despite wide ranges in dissolved H\(_2\)S (10\(^{-10}\)–10\(^{-2}\) μmol kg\(^{-1}\)) and Fe (10\(^{-2}\)–10\(^{-2}\) μmol kg\(^{-1}\)) concentrations and Fe/H\(_2\)S (10\(^{-4}\)–10\(^{-3}\)) (Table S9 in Supporting Information S1). This includes Lake Cadagno and the Landsort Deep, Saanich Inlet (Emerson et al., 1979, BC Canada, see also Davidson et al., 2020), the Black Sea (Mugo, 1997), Esthwaite Water (UK, Achterberg et al., 1997) and Hall Lake (WA USA; Balistrieri et al., 1994) (Figures 3a–3e). These can be more directly compared by normalizing profiles to [Cr]\(_{surface}\) and relative depth above and below the chemocline, creating four quadrants: (I) [Cr] < [Cr]\(_{surface}\) in oxic waters, (II) [Cr] > [Cr]\(_{surface}\) in oxic waters, (III) [Cr] < [Cr]\(_{surface}\) in anoxic waters, and (IV) [Cr] > [Cr]\(_{surface}\) in anoxic waters (Figure 3e). All environments lie within (I) slightly above the chemocline, indicating non-quantitative Cr removal. Anoxic deep waters fall into quadrant (IV) in most settings, indicating Cr accumulation rather than removal. Basins with only seasonal anoxia (Saanich Inlet, Esthwaite Water) differ, showing a
slight increase in [Cr]normalized just above the chemocline but remaining in zone (III) at depth. This may indicate insufficient time to allow Cr accumulation through the Fe-Mn shuttle, due to their only seasonally anoxic nature.

This compilation from diverse permanently and seasonally anoxic systems confirms the general trends observed in Lake Cadagno—i) non-quantitative Cr removal above the chemocline (~20–60% of [Cr]surface), suggesting isotope fractionation and the transport of low δ53Cr to anoxic waters, and (ii) Cr accumulation in anoxic deep waters indicating poor sequestration of Cr into sediments. Therefore, reconstructions of water column or weathering δ53Cr signals from sediments deposited in these environments require accounting for fractionation during Cr removal as well as internal cycling resulting in variable water column δ53Cr.

Chromium depletions consistently occur above the chemocline, coincident with elevated dissolved and particulate [Fe] and [Mn] (orange box in Figures 3a–3d). The sharpness of the Cr depletion above and subsequent increase below the chemocline can be explained by natural variability in the systems (see also Dellwig et al., 2012), including absolute depth ranges (10–105 m), the relative width of the Fe-Mn redox zone (orange box height, Figures 3a–3d) and upward diffusive transport. Shallower systems (e.g., Hall and Cadagno Lakes), thicker Fe-Mn redox zones, and elevated diffusivity correspond with broader Cr minima and more gradual Cr increases below the chemocline.

In agreement with previous studies (e.g., Balistrieri et al., 1994; Mugo, 1997), the consistent Cr minimum in the zone of intense Fe-Mn redox cycling supports the widespread control of these metals on Cr removal in anoxic systems, whereby Cr reduction coupled to Fe oxidation and subsequent Cr(III) scavenging on particulate metal oxides drives Cr removal (Figures 3f and 3g), followed by oxide reduction and Cr release in the anoxic zone or near the sediment surface. The broadly similar Cr trends across these diverse freshwater and marine systems indicates that our data from Cadagno are generally relevant to other systems and can be used to revise the interpretational framework of δ53Cr paleoproxy applications. Specifically, these data indicate that:

1. Cr is partially removed above the chemocline, but is not efficiently removed from the water column in anoxic systems, both at and below the chemocline.
2. Dissolved Cr generally accumulates in anoxic deep water.
3. Sediments from redox-stratified basins may not always show high [Crauth] enrichments.
4. Reconstructing water column δ53Cr from δ53Crauth within these settings requires accounting for variable water column δ53Cr, fractionation during Cr removal and early diagenesis.
5. δ53Crauth within these settings may therefore not directly reflect Cr fractionation originating from oxidative subaerial weathering.

5. Conclusions and Implications

Available data across a range of redox-stratified marine and lacustrine settings share fundamental features—namely, local [Cr] minima with non-quantitative Cr removal slightly above the chemocline, and increasing [Cr] below—with permanently anoxic basins showing deep water dissolved Cr accumulation rather than efficient removal. Given the isotope fractionation associated with Cr reduction, non-quantitative removal suggests that sedimentary authigenic δ53Cr should not match the water column, contrasting previous assumptions (e.g., Frei et al., 2009, 2020; Reinhard et al., 2013, 2014; Wei et al., 2020). Instead, sediment δ53Crauth is isotopically offset from the water column, a factor that must be considered for paleoreconstructions. Furthermore, variable water column δ53Cr, as well as potential early diagenetic modification of δ53Crauth, suggests there is no consistent offset between δ53Crauth and water column δ53Cr. Indeed, our Lake Cadagno data show that sinking particulate δ53Cr is isotopically comparable to sediment δ53Crauth, while dissolved δ53Cr decreases from surface waters to euxinic deep waters, and therefore dissolved δ53Cr differs from δ53Crauth by variable extents.

Despite a strongly oxidizing atmosphere throughout the entire history of Lake Cadagno, we find no significantly fractionated sediment δ53Cr auth. Evidently, oxidative weathering does not necessarily result in high δ53Cr auth. To the contrary, the relatively small ranges of dissolved δ53Cr throughout modern systems (surface waters ≈ ±0.2 to +1.2 ‰, Wei et al., 2020; Horner et al., 2021) coupled with effective fractionation for the reduction and removal of Cr (Δ53Cr ≈ −0.4 to −1.3 ‰, this study; Janssen et al., 2020, 2021; Moos et al., 2020; Nasemann et al., 2020; Huang et al., 2021; Wang, 2021) indicate that authigenic sedimentary δ53Cr records could easily be comparable to unfractonated continental crust (δ53Cr ≈ −0.12 ± 0.10 ‰, Schoenberg et al., 2008). In other words, Cr removal from a water column inventory of +0.2 to +1.2 ‰, with a Δ53Crparticle-dissolved of −0.4 to −1.3 ‰ is expected.
to yield an authigenic sedimentary δ54Cr that is, at times, within the range of −0.2 to 0.0 ‰. Consequently, caution should be used in the interpretation of δ54Cr records from redox-stratified basins, which reflect local redox-related fractionation processes superimposed on oxidative subaerial weathering signals.

Data Availability Statement

Data are presented in the Supporting Information S1 and Table 1. Vertical microstructure data for turbulent diffusion estimations is available at https://doi.org/10.5281/zenodo.3507638. Chemical and CTD data are also available in the following open access datasets in the Zenodo repository: http://doi.org/10.5281/zenodo.7125831 and http://doi.org/10.5281/zenodo.7127882, respectively.

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References


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References From the Supporting Information


