



Chromium isotope systematics and the diagenesis of marine carbonates

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ABSTRACT

Stable chromium (Cr) isotopes have emerged as a new tool for tracking broad-scale changes in Earth's surface oxygen levels. Carbonates are one proposed sedimentary Cr isotope archive. In order to contribute to the development of a robust framework for interpreting carbonate Cr isotopic compositions and evaluating their ability to record the global redox state, we explored Cr isotope systematics of modern and Archean carbonate successions—representing end member oxic and anoxic Earth system states. We generated new data from carbonate platform sediments from the Great Bahama Bank with variable post-depositional histories to better understand the effects of diagenetic alteration on carbonate-bound Cr and its isotopic composition in a modern well-oxygenated ocean-atmosphere system. More specifically, we investigated the effects of dolomitization and aragonite-to-calcite neomorphism in marine and meteoric fluids. We also present $\delta^{53}\text{Cr}$ values from three carbonate successions, the ~ 3.0 Ga Chobeni Formation (South Africa), ~ 2.8 Ga Mosher Carbonate Formation (Canada), and ~ 2.65 Ga Cheshire Formation (Zimbabwe), that were deposited under an anoxic atmosphere. We find that modern Bahamian carbonates have a large range of almost exclusively positive $\delta^{53}\text{Cr}$ values (from -0.04 to 2.88‰). The $\delta^{53}\text{Cr}$ values appear to be altered during both meteoric diagenesis and dolomitization but there may also be instances of rock-buffered conditions that may best preserve depositional $\delta^{53}\text{Cr}$ values. These observations provide a baseline for carbonate Cr isotope behavior in a well-oxygenated ocean-atmosphere system. Our Archean carbonate successions contain both positively fractionated and crustal $\delta^{53}\text{Cr}$ values, ranging between -0.37 and 0.89‰ . The Cr isotope fractionation observed in Archean strata is most plausibly linked to either non-redox dependent Cr isotope fractionation, local Cr redox cycling, late-stage diagenetic alteration, or some combination thereof. Given the significant effects of post-depositional alteration on the isotopic composition of carbonate-bound Cr, we suggest that Cr isotope values from ancient carbonate sediments should be generally interpreted with caution and cannot be straightforwardly linked to changes in atmospheric oxygen abundance.

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1. Introduction

Concentration and stable isotopes of redox-sensitive trace elements have played a critical role in shaping the narrative of Earth's

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oxygenation (Anbar and Rouxel, 2007). Among these geochemical proxies, the stable chromium (Cr) isotope system has emerged as a potential promising tool for tracking broad changes in atmospheric oxygenation (e.g., Crowe et al., 2013; Frei et al., 2009; Planavsky et al., 2014a).

Chromium exists in two primary redox states at Earth's surface—oxidized and soluble Cr(VI), and reduced and poorly soluble Cr(III) (Qin and Wang, 2017). In the continental crust, Cr is present predominantly as Cr(III) where it is contained in either mafic silicate minerals (e.g., pyroxene, olivine) or oxides (e.g., chromite, ilmenite). Once mobilized during oxidative weathering, Cr(VI), either as CrO_4^{2-} (under alkaline pH conditions) or HCrO_4^- (acidic pH conditions), enters the oceans via riverine transport (Oze et al., 2007). In the ocean, Cr(VI) is reduced to Cr(III) and can then be captured as authigenic Cr in sediment archives (e.g., Frei et al., 2009; Reinhard et al., 2014). Like other redox-sensitive elements, the transformation between Cr(III) and Cr(VI) causes a large change in the local coordination environment of Cr, leading to a significant isotopic fractionation (Ellis et al., 2002). This potentially provides a means to track the temporal trend of pervasive oxidative Cr redox cycling at Earth's surface (e.g., Cole et al., 2016; Planavsky et al., 2014a).

The Cr redox cycle is thought to be closely linked to the presence of manganese (Mn) oxides at Earth's surface. Manganese oxides act as a catalyst for oxidization and solubilization of Cr(III) from the crust, ultimately allowing the redox cycling of Cr and generating significant isotope fractionations in modern environments (Fendorf and Zasoski, 1992). As Mn oxides are traditionally viewed to form only in the presence of free environmental O_2 (Tebo et al., 2004, for a different view, see Daye et al., 2019; Liu et al., 2020), this inextricably links the redox cycling of Cr with the ambient oxygenation state of Earth's surface environments. Although there is evidence for marine Cr oxidation (Bauer et al., 2019; Murray and Tebo, 2007), many paleoredox studies have assumed Cr oxidation is limited to terrestrial environments—providing a link between Cr isotope fractionations and atmospheric oxygenation (e.g., Canfield et al., 2018; Frei et al., 2009; Planavsky et al., 2014a).

Chromite and unaltered igneous rocks, with limited exceptions, exhibit a narrow range of $\delta^{53}\text{Cr}$ values of $-0.124 \pm 0.101\%$ (Schoenberg et al., 2008). The oxidation of Cr(III) to Cr(VI) can result in both negative and positive isotopic fractionations (from -2.5 to $+1.1\%$), depending on the reaction path (Bain and Bullen, 2005; Zink et al., 2010; Joshi et al., 2011). The reduction of Cr(VI) to Cr(III) in the presence of a range of naturally occurring reductants including organic matter, sulfides, or ferrous iron, has consistently been shown to produce residual Cr(VI) that is enriched in ^{53}Cr , with apparent fractionation factors ranging from -7.6 to -0.4% (e.g., Ellis et al., 2002; Zink et al., 2010; Izbicki et al., 2012). Further, Cr(VI) reduction could also occur in surface seawater and/or the oxygen minimum zone with a fractionation factor up to -8% (e.g., Scheiderich et al., 2015; Paulukat et al., 2016). It should be noted that several redox-independent processes (e.g., Cr(III) complexation by organic matter) are capable of mobilizing Cr(III) in aqueous solutions and may lead to a mobile, strongly fractionated Cr reservoir (e.g., Babechuk et al., 2017; Saad et al., 2017). However, the common occurrence of mobile but unfractionated Cr (e.g., Frei et al., 2009; Planavsky et al., 2014a) suggests that Cr(III) mobilized via these processes is relatively rare.

Within this framework, initial attempts to reconstruct Earth's oxygenation from Cr isotope analysis have primarily focused on banded iron formations (BIFs) (Crowe et al., 2013; Frei et al., 2009), ironstones (Planavsky et al., 2014a), and shales (Wille et al., 2013; Canfield et al., 2018; Cole et al., 2016), given that these archives can develop large authigenic Cr enrichments. Based on these records of Cr isotopes, especially for ironstones and shales, Earth's mid-Proterozoic atmosphere might be characterized by low

oxygen concentrations $<1\%$ of present atmosphere levels (PAL) (Cole et al., 2016; Planavsky et al., 2014a). In contrast, all ancient marine carbonates analyzed thus far—foremost multiple mid-Proterozoic limestone and dolostone successions—have been found to contain fractionated Cr isotopes that point to strongly oxygenated ocean-atmosphere chemistry (Gilleaudeau et al., 2016). These seemingly conflicting records lead to contrasting interpretations of the mid-Proterozoic atmospheric O_2 abundance, which have important downstream ramifications for the potential role of environmental conditions in constraining the evolution of complex life. Although some studies have critically addressed the potential for modern alteration of Cr isotope signals in ancient BIFs (Albut et al., 2018), no study to date has evaluated the potential for diagenetic alterations of Cr isotope signals in carbonate archives. As shown by recent studies (Fang et al., 2020; Farkaš et al., 2018; Föger et al., 2019; Rodler et al., 2015), the actual mechanism of Cr incorporation and redox-controlled isotope fractionation during the formation of abiotic and biotic carbonate rocks is complex and, arguably, still poorly understood, which provides further motivation for a better understanding of Cr isotope values in modern carbonates.

In order to advance our understanding of the significance of carbonate Cr isotope values in carbonate archives, we provide the first systematic constraints on the effects of marine and meteoric diagenesis, including dolomitization, on the Cr isotope composition of extensively studied Neogene to Quaternary aged marine carbonates from the Great Bahama Bank (e.g., Chen et al., 2018; Dellinger et al., 2020; Hardisty et al., 2017; Higgins et al., 2018; Liu et al., 2019; Stewart et al., 2015). We interpret these results in light of downcore changes in carbonate mineralogy associated with well-documented varying styles of post-depositional alteration (Melim et al., 2002, 2004, 1995; Swart and Melim, 2000). We also cast these results in the context of a simple water rock interaction model for carbonate alteration. For comparison, we present $\delta^{53}\text{Cr}$ values of Archean carbonate rocks, which formed under a reducing and anoxic Earth system state (e.g., Catling and Zahnle, 2020).

2. Study sites and samples

We analyzed two sediment cores recovered during the Bahamas Drilling Project (BDP), referred to as Clino and Unda (Ginsburg, 2001). The BDP core materials are late Miocene to late Pleistocene in age and have been well characterized with respect to sedimentology, biostratigraphy, mineralogy, and diagenetic regimes (Eberli et al., 1997; Melim et al., 2002, 2004, 1995; Swart and Eberli, 2005). Details regarding the location and stratigraphy for these two cores are provided in the *Supplementary Materials*.

The Clino and Unda cores sample a prograding carbonate ramp along the western edge of the Great Bahama Bank (Fig. S1). These same samples have been utilized in previous studies to examine the effects of diagenetic alteration on other carbonate-based geochemical proxies (Chen et al., 2018; Dellinger et al., 2020; Hardisty et al., 2017; Liu et al., 2019). Samples collected for this study capture variable admixtures of primary versus diagenetic carbonate minerals, three distinct diagenetic pathways (meteoric diagenesis, marine diagenesis, and dolomitization), and a negative $\delta^{13}\text{C}$ excursion associated with the meteoric zone of the Clino core (Melim et al., 1995). Given the similar depositional history shared by the Clino and Unda cores, we sampled the Clino core at high resolution and targeted specific intervals of dolomite in the Unda core.

The top intervals of both Clino and Unda cores – to depths of ~ 150 m and ~ 100 m, respectively – show evidence for early marine diagenesis overprinted by recurring episodes of subaerial exposure and the subsequent infiltration of meteoric waters during the Pleistocene last glacial sea-level lowstand (Melim et al., 2004)

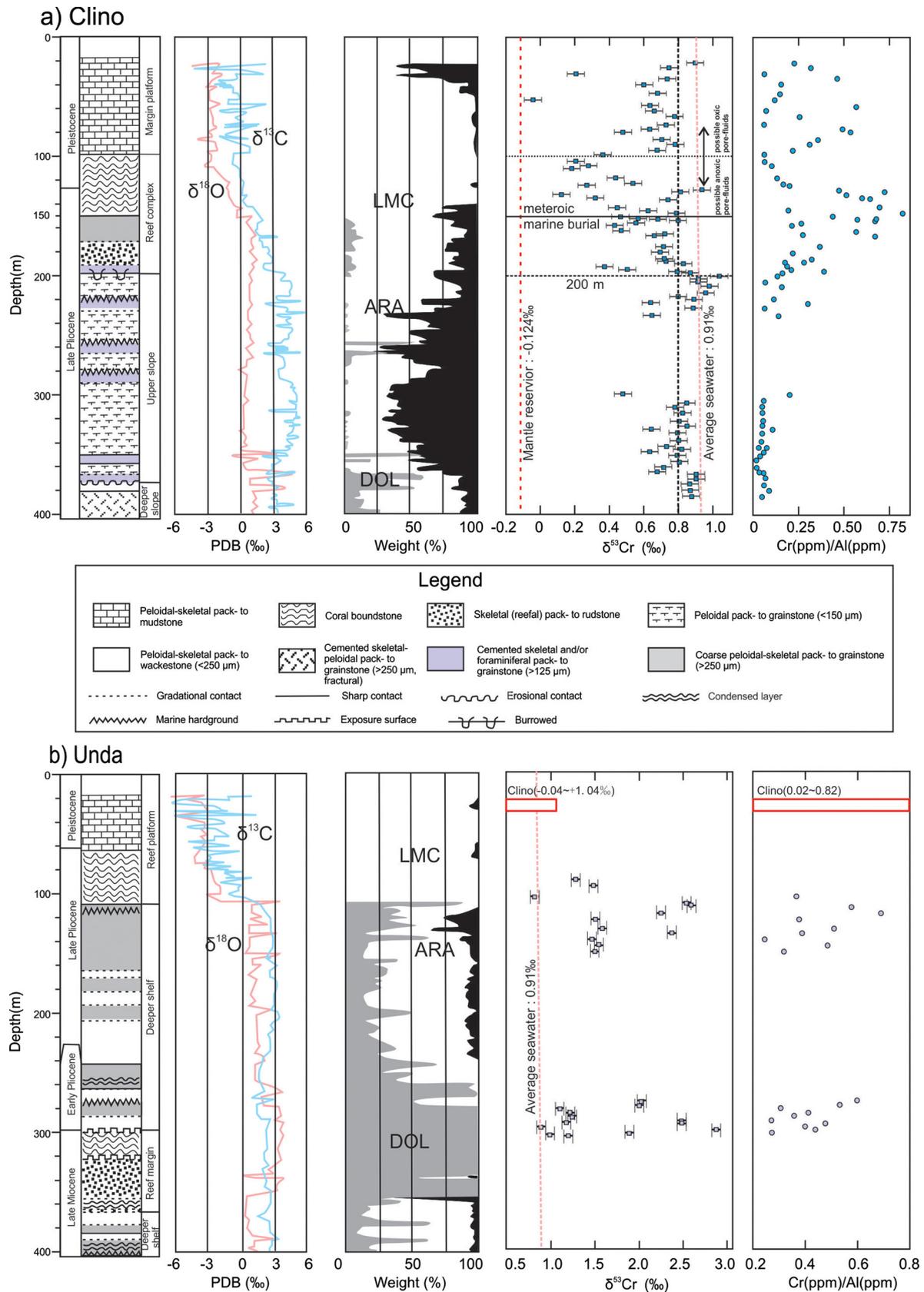


Fig. 1. The facies and lithology, carbonate mineralogy, carbon and oxygen isotopes, $\delta^{53}\text{Cr}$ value, and Cr/Al ratio of the Clino (a) and Unda (b) drill cores, Great Bahama Bank. The facies and lithological data are from Eberli et al. (1997); the mineralogy, and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data are sourced from Melim et al. (1995); the Al data are from Liu et al. (2019). LMC: Low-Mg Calcite; ARA: Aragonite; DOL: Dolomite. The red dotted line denotes igneous-inventory $\delta^{53}\text{Cr}$ values (mean $\delta^{53}\text{Cr}$ value, $-0.124 \pm 0.101\text{‰}$; Schoenberg et al., 2008); the pink line represents average $\delta^{53}\text{Cr}$ values (mean $\delta^{53}\text{Cr}$ value, $0.91 \pm 0.36\text{‰}$) for modern seawater (Bonnand et al., 2013; Farkaš et al., 2018; Frei et al., 2018; Holmden et al., 2016; Paulukat et al., 2016; Scheiderich et al., 2015). (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

(Fig. 1a). Evidence for meteoric diagenesis comes from physical observations of subaerial exposure surfaces (Manfrino and Ginsburg, 2001), the near complete neomorphism of aragonite to low-Mg-calcite (LMC) (Melim et al., 1995), and depleted $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Melim et al., 1995; Swart and Melim, 2000; Swart and Oehlert, 2018).

Below the meteoric alteration zone, the Clino core is characterized by the neomorphism of aragonite to calcite, driven exclusively by marine pore fluids, corresponding to a late Miocene-Pliocene warm world (Fig. 1a) (Melim et al., 1995). This interval consists of a mixture of aragonite, LMC, and minor amounts of dolomite, and is characterized by relatively positive $\delta^{13}\text{C}$ values inherited from aragonite that originated on the platform (Higgins et al., 2018; Swart and Eberli, 2005). Compaction and grain deformation after deposition may have resulted in a tight fabric with low permeability (Melim et al., 1995), restricting ion movement and thus limiting the precipitation of calcite and dolomite (Swart and Melim, 2000). Therefore, this interval is dominated by a relatively low degree of aragonite neomorphism and dolomitization. A recent Ca and Mg isotope study further supported that carbonate recrystallization through sections of the Clino core occurred under fluid-buffered conditions, with a diagenetic fluid similar to seawater (Ahm et al., 2018; Higgins et al., 2018).

Dolomite is found in both Clino and Unda cores, but dolomitization is nearly quantitative in portions of the Unda core (Fig. 1a and b). In each case, the dolomite is diagenetic and results from the post-depositional alteration of aragonite and/or calcite (Swart and Melim, 2000). This implies that dolomitization may have been preceded by either of the meteoric or marine diagenetic regimes described above. Importantly, however, the styles of dolomitization are different between the Clino and Unda cores. Evidence from pore fluid compositions (Swart et al., 2001b), Sr concentrations and isotopes (Swart et al., 2001a; Swart and Melim, 2000), sulfur isotopes in carbonate associated sulfate (CAS; Murray, 2016), and Ca and Mg isotopes (Higgins et al., 2018) indicate that dolomite in the Unda core was largely formed by marine pore fluids that experienced varying degrees of exchange with overlying seawater, whereas Clino dolomites were formed from reducing pore waters with restricted exchange with seawater (Hardisty et al., 2017). Importantly, only bulk samples were analyzed, as opposed to isolated dolomites. As such, samples from the Unda core represent end-member dolomite sediments and are the main focus of our discussions with respect to $\delta^{53}\text{Cr}$ in dolomite.

In addition to our examination of the effects of diagenetic alteration on $\delta^{53}\text{Cr}$ values in the Unda and Clino cores, we also measured $\delta^{53}\text{Cr}$ values, as well as selected major and trace element abundances in carbonate rocks from three Archean sedimentary successions. These Archean data are interpreted in the context from the Clino and Unda cores in order to further discuss possible effects from diagenetic alteration on Cr isotopic fractionations. The Archean successions studied include the ~ 3.0 Ga Chobeni Formation from the Pongola Supergroup in South Africa (Siahi et al., 2018), the ~ 2.8 Ga Mosher Carbonate Formation in south central Canada (Fralick and Riding, 2015), and the ~ 2.65 Ga Cheshire Formation in Zimbabwe (Hofmann et al., 2001). Detailed descriptions of ages, sedimentology, and stratigraphy for each of these formations are provided in the *Supplemental Materials*.

3. Methods

3.1. Sample preparation

Samples that did not show clear indications of secondary alteration (e.g., veins) and weathering were cut in pieces with a diamond-edge rock saw and crushed in an agate mill to a fine powder. ~ 1 g of sample powders were weighed, followed by a

brief leach in 0.5 N HCl for 12 hours in order to specifically target carbonate mineralogical phases. After dissolution, samples were centrifuged to remove insoluble residue and the supernatant was transferred into Teflon beakers and evaporated to dryness. Residues were then refluxed in 5 mL 6 N HCl to produce an archivable sample solution that could then be used for subsequent dilution and analysis.

3.2. Elemental concentration analyses

Major and trace elements were analyzed on a small aliquot of the leachate at the Yale Metal Geochemistry Center by high resolution sector field inductively coupled plasma mass spectrometry (ICP-MS) (ThermoFisher Scientific Element XR) using a standard sample introduction system. Measurement precision was generally better than 5% (2σ). The USGS geostandards BHVO-2 and NOD-A-1 were processed along with samples during each run and are within $\pm 5\%$ of reported values.

3.3. Chromium isotope analyses

A second aliquot containing ~ 100 ng of Cr was purified using the three column procedure described in Wang et al. (2016a). Chromium isotopes were measured on a ThermoFisher Scientific Neptune Plus Multi-Collector ICP-MS (MC-ICP-MS) at the Yale Metal Geochemistry Center using a ^{50}Cr - ^{54}Cr double-spike technique following Cole et al. (2016). The Cr isotope composition is reported as per mil (‰) relative to the standard NIST SRM 979, according to the following equation:

$$\delta^{53}\text{Cr} = \left[\left(\frac{^{53}\text{Cr}/^{52}\text{Cr}}{\text{sample}} / \left(\frac{^{53}\text{Cr}/^{52}\text{Cr}}{\text{NIST SRM 979}} - 1 \right) \right) \times 1000 \right]$$

The total procedural Cr blank was less than 0.15 ng, which is negligible relative to the amount of Cr in the samples. The accuracy and precision of measured $\delta^{53}\text{Cr}$ values was assessed through repeated processing and analysis of the USGS reference material BHVO-2 and NOD-A-1. All standards were subjected to the same processing as the samples. Measured $\delta^{53}\text{Cr}$ values were $-0.12 \pm 0.08\text{‰}$ (2σ , $n = 30$) for BHVO-2 and $0.07 \pm 0.08\text{‰}$ (2σ , $n = 30$) for Nod-A-1, which are within the uncertainty of the accepted values (Schoenberg et al., 2008; Wang et al., 2016a,b). In addition to the standards, five samples were processed in duplicate and all yielded 2σ values $< 0.08\text{‰}$.

4. Results

The measured $\delta^{53}\text{Cr}$ values of our Neogene-Quaternary samples span a broad range from close to bulk silicate Earth (BSE) ($-0.12 \pm 0.1\text{‰}$, Schoenberg et al., 2008) to up to $+2.88\text{‰}$, but the majority of samples are characterized by positive $\delta^{53}\text{Cr}$ values (average of 0.93‰). In the Clino core, where the mineralogy is dominated by aragonite and LMC and the relative abundance of aragonite increases downcore (Fig. 1a and Table S1), $\delta^{53}\text{Cr}$ values range between roughly that of BSE to around $+1.0\text{‰}$. The greatest variability in $\delta^{53}\text{Cr}$ values (from -0.04 to $+0.90\text{‰}$) is observed in shallower intervals of the core, associated with near quantitative neomorphism of aragonite to LMC during meteoric diagenesis. Sediments in the lower portion (> 150 m) of the Clino core show relatively more stable $\delta^{53}\text{Cr}$ values from 0.37 to 1.04‰ compared to those of the upper portion. In contrast, the Unda core samples, which are partially to completely dolomitized, are marked by more scattered and positive $\delta^{53}\text{Cr}$ isotopic compositions, from 0.81 to 2.88‰ , that are largely heavier than modern seawater (average of $0.91 \pm 0.36\text{‰}$) (Bonnand et al., 2013; Farkaš et al., 2018; Frei et al., 2018; Holmden et al., 2016; Paulukat et al., 2016; Scheiderich et

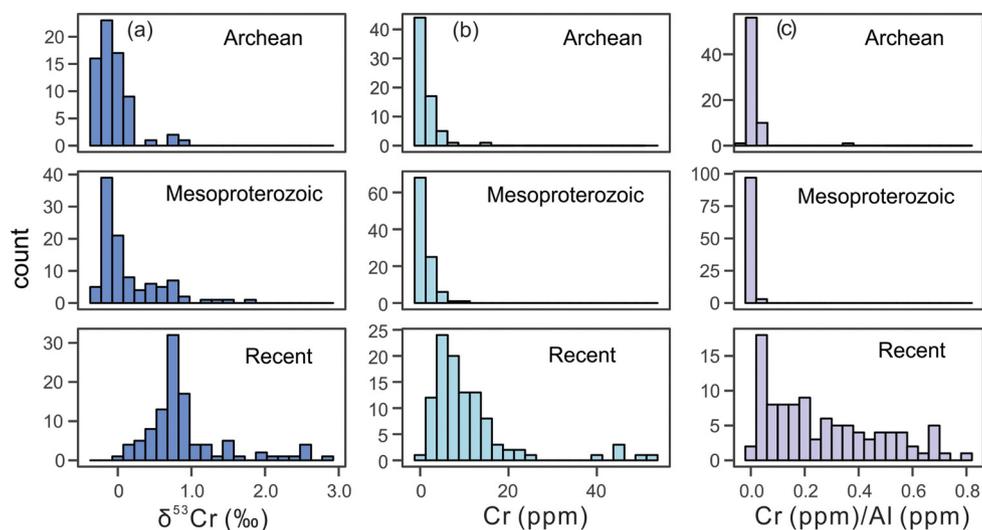


Fig. 2. Histograms of $\delta^{53}\text{Cr}$ values (a), Cr concentrations (b), and Cr/Al ratios (c) in Archean, Mesoproterozoic, and Recent (Clino and Unda) carbonate samples. Mesoproterozoic data are from Gilleaudeau et al. (2016); the Al data of Recent carbonates are from Liu et al. (2019).

al., 2015) or estimates of surface seawater from the Caribbean (Yucatan and Jamaica) ($1.14 \pm 0.06\text{‰}$) (Holmden et al., 2016) (Fig. 1b).

Although the $\delta^{53}\text{Cr}$ values of many Archean carbonate samples overlap within error of BSE $\delta^{53}\text{Cr}$ values, positive $\delta^{53}\text{Cr}$ values were identified in all three formations (Fig. 2a and Table S2). Specifically, the Chobeni carbonates yield a wide range of $\delta^{53}\text{Cr}$ values (from -0.36 to 0.89‰), whereas the Mosher and Cheshire carbonates possess a more limited range of $\delta^{53}\text{Cr}$ values varying from -0.16 to 0.19‰ and from -0.37 to 0.21‰ , respectively. Chromium abundances and Cr/Al ratios of Archean samples are similar to the Mesoproterozoic carbonate samples (Gilleaudeau et al., 2016) but are significantly lower than that of recent (Clino and Unda) samples (Fig. 2b and c). Statistical similarity between the various age groups (Archean, Mesoproterozoic, and the recent Bahama cores) for $\delta^{53}\text{Cr}$ values, Cr concentrations, and Cr/Al ratios can be assessed at a 99% confidence level using a Tukey-Kramer pair-wise comparison (Table S3). Indeed, the ‘recent time’ bin was significantly different when compared to other two time bins for all parameters ($p < 0.01$), whereas Archean and Mesoproterozoic time bins are statistically indistinguishable ($p > 0.01$).

5. Discussion

5.1. Evaluation of detrital contamination

For all of the carbonate samples, low Al and Th contents and a lack of a correlation between Al and $\delta^{53}\text{Cr}$ values (Fig. 3a), suggest little contribution from detrital materials. For the Clino and Unda cores, these observations are generally consistent with the nearly pure carbonate mineralogy (Melim et al., 1995). Any samples with a predominantly detrital Cr source should have Cr/Ti or Cr/Al ratios that are close to either shale composites or average upper continental crust (Cr/Al = 0.001, Rudnick and Gao, 2014). Samples analyzed here are characterized by Cr/Al ratios that are significantly higher than crustal values (Fig. 1 and 2), suggesting that these samples record fluid-derived signals and may be used to trace environmental Cr cycling.

5.2. Chromium cycling during Neogene-Quaternary carbonate diagenesis

5.2.1. Biological process

Based on previous work, and as detailed in the discussion below, we interpret both Cr(VI) and Cr(III) to be incorporated into

the carbonate mineral phase during diagenesis. This interpretation is based on observations from co-precipitation experiments (Tang et al., 2007; Rodler et al., 2015) and XANES spectra analyses (Fang et al., 2020). Previous studies suggest that abiotic carbonates have the potential to reflect the $\delta^{53}\text{Cr}$ value of ambient seawater (Tang et al., 2007; Frei et al., 2011; Rodler et al., 2015). However, more recent work has shown evidence of a pH dependent negative Cr isotope fractionation during abiotic calcite formation at $\text{pH} < 9.4$ (Füger et al., 2019). In addition to potential abiotic fractionations, biological reactions that mediate carbonate production in marine settings, and the corresponding metabolisms of calcifying organisms, may lead to skeletal marine carbonates with $\delta^{53}\text{Cr}$ values lower than contemporaneous seawater (Frei et al., 2018; Holmden et al., 2016; Wang et al., 2017). It is thereby possible that some of the observed scatter in $\delta^{53}\text{Cr}$ values within the Clino core, relative to seawater, could reflect stratigraphic variability in the skeletal content of bulk sediments.

The majority of carbonate sediments from the Clino core yielded similar $\delta^{53}\text{Cr}$ values to previously measured microbial and bulk skeletal marine carbonates gathered near the Bahama Bank (0.62 to 0.77‰ , Bonnand et al., 2013; Holmden et al., 2016). Consistent with this observation, the upper 200 m of Clino sediments are dominated by reefal and shallow-water skeletal deposits (Fig. 1a), whereas nearly 80% of the sediment between 200 and 680 m consists of intervals of skeletal and peloidal sand- and silt-sized grains (Eberli et al., 1997). The upper part of the Clino core (< 200 m), especially between 100 and 200 m, which is dominated by skeletal and coral deposits, have both lighter $\delta^{53}\text{Cr}$ values and higher Cr/Al ratios compared to lower carbonate sediments from the same core (Fig. 1a), consistent with the preferentially incorporated of ^{52}Cr from seawater during biogenic carbonate mineralization.

Previous studies proposed that enrichments in light Cr isotopes in primary biological carbonate sediments could be due to (i) the incorporation of organically complexed and particle-reactive Cr(III) species directly from seawater into CaCO_3 , and/or (ii) biologically mediated redox cycling involving an initial reduction of marine Cr(VI) and subsequent re-oxidation of the Cr(III) reduction products (Farkaš et al., 2018; Paulukat et al., 2016). Given that these carbonates have undergone some degree of diagenesis, and that detailed mechanisms responsible for controlling Cr isotope fractionation during biological precipitation are not well constrained, this only forms a baseline for further investigations and therefore we focus our discussion on the effects of carbonate diagenesis.

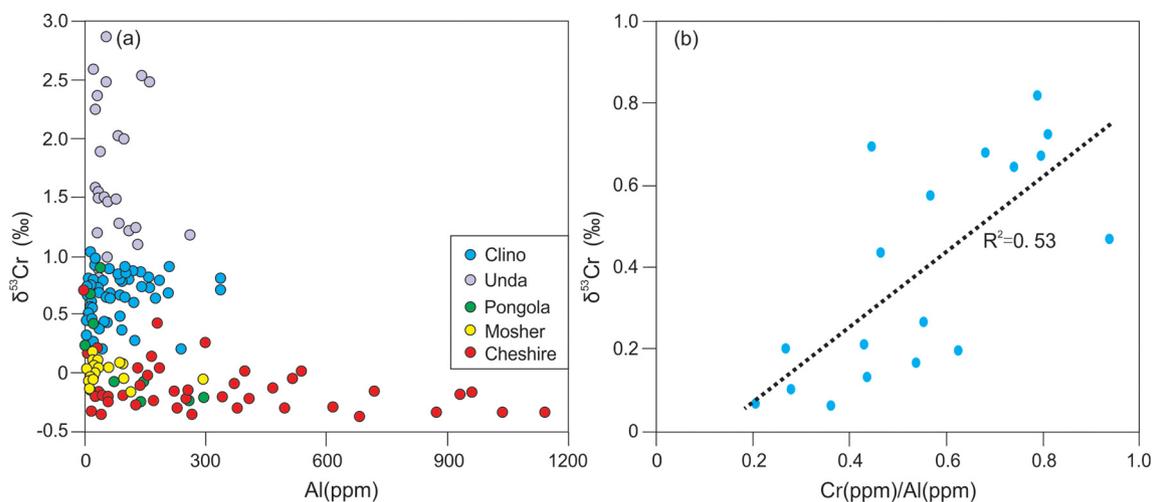


Fig. 3. (a) The Cr isotopic composition compared to the Al concentration of the studied carbonate sediments. The Al data of both Clino and Unda carbonates are from Liu et al. (2019); (b) The Cr/Al ratio versus the $\delta^{53}\text{Cr}$ value of samples from depths ranging from 95 to 160 m in the Clino drill core. The Al data are from Liu et al. (2019). Noted that two outliers (C26 and C27) are not plotted.

Regardless of potential biological isotope fractionations, it is important to note that the $\delta^{53}\text{Cr}$ values for most of the lower (>200 m) carbonates (up to 1.04‰), which are predominantly peloidal packstone and grainstone, are still similar to modern seawater (average of $0.91 \pm 0.36\text{‰}$) (Bonnand et al., 2013; Farkaš et al., 2018; Frei et al., 2018; Holmden et al., 2016; Paulukat et al., 2016; Scheiderich et al., 2015) and values from the Caribbean Sea close to the Bahama Bank ($1.14 \pm 0.06\text{‰}$) (Holmden et al., 2016). Such similarity is consistent with the suggestion that abiotic carbonates may be able to serve as an archive of the Cr isotope signal of contemporaneous seawater (e.g., Frei et al., 2011) and is also expected from a large fraction of primary aragonite in the deeper interval.

5.2.2. Meteoric diagenesis

One of the most striking aspects of our data is the negative excursion in $\delta^{53}\text{Cr}$ values observed between 100 and 160 m of the Clino core, within or close to the zone of meteoric diagenesis (Fig. 1a). This excursion corresponds to an interval of covariance in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and near total conversion of aragonite and high-Mg calcite to LMC.

This anomaly also occurs in the transition zone (approximately from 95 to 160 m) between the typical meteoric and marine-burial environments, as defined by the covarying trend between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Melim et al., 2004; Swart and Oehlert, 2018). Melim et al. (2004) interpreted this transition zone to be the result of alteration within the zone of mixing between meteoric and marine waters based on a positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. Conversely, Swart and Oehlert (2018) concluded that this covariation was a consequence of varying degrees of alteration occurring at the interface between vadose and phreatic zones. In the former scenario, diagenesis occurs in a chemical mixing zone between a meteoric lens and underlying seawater, which would explain the synchronous shifts in Cr concentration and $\delta^{53}\text{Cr}$ values (Fig. 3b). Carbonate sediments above and below this interval, however, have similar $\delta^{53}\text{Cr}$ values (Fig. 1a), suggesting that this zone does not represent mixing between meteoric and marine waters.

Under the latter scenario, the quantitative diagenetic alteration of aragonite to calcite within the meteoric zone would have occurred near the water table (i.e. the boundary between the vadose and freshwater phreatic zones) where organic materials were oxidized (Cooper et al., 2016). This would have added CO_2 to the pore fluids, increasing the dissolved inorganic carbon pool and likely leading to anoxic pore fluids (McClain et al., 1992; Swart

and Oehlert, 2018). The degree of alteration is proposed to decrease with increasing depth from the water table (~100 m). As a result, bulk $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and aragonite content increase with depth while organic material becomes exhausted and carbonate dissolution and precipitation reactions decline.

We propose that the observed negative $\delta^{53}\text{Cr}$ excursion and accompanying decrease in Cr content observed in the Clino core (Fig. 3b) are linked to partial reduction of isotopically heavy Cr(VI) which was expelled from the CaCO_3 lattice during dissolution reactions close to the water table. This is also consistent with decreased I/(Ca+Mg) ratios in this same zone and iodate reduction during recrystallization (Hardisty et al., 2017), which overlaps with Cr reduction on the redox ladder (Rue et al., 1997). The presence of organic carbon and/or H_2S from bacterial sulfate reduction in pore water might have produced favorable conditions for Cr(VI) reduction. Once Cr(VI) is partially reduced to Cr(III), the original Cr concentration of aragonite might be partially lost and isotopically light Cr(III) can be preferentially incorporated into newly-formed LMC precipitates. Therefore, these precipitates would be characterized by lower Cr concentrations and light $\delta^{53}\text{Cr}$ values relative to those of primary aragonite sediments (Fig. 3b). As carbonate dissolution and precipitation reactions diminish with increasing depth, the amount of Cr(VI) expelled from carbonates would decline. After residual Cr(VI) diffuses into dysoxic sediment pore waters, there is likely to be near quantitative reduction of Cr(VI) to Cr(III) and subsequent incorporation of Cr into calcite with negligible Cr isotopic fractionation. Given nearly complete reduction, there could be an insignificant loss of original Cr abundance. Above the water table in the vadose zone (Swart, 2015), O_2 could be sufficiently high to suppress any Cr(VI) reduction or these fluids could also become anoxic. In any oxic portions of the vadose alteration zone, Cr can be readily mobilized out of and into sediments coinciding with the dissolution and precipitation of carbonates. This likely explains the nearly constant $\delta^{53}\text{Cr}$ values with the exception of a few outliers in the upper part (0–100 m) of the Clino core.

5.2.3. Marine diagenesis

The $\delta^{53}\text{Cr}$ values of carbonates from the lower marine diagenetic zone of the Clino core may be divided into two distinct groups: skeletal and non-skeletal (Melim et al., 1995). The skeletal carbonates (150 to 200 m) have lighter $\delta^{53}\text{Cr}$ values of $<0.8\text{‰}$ and higher Cr/Al ratios (>0.2) relative to those of the lower abiotic carbonate sediments (>200 m) (Fig. 1a). Specifically, the heavier $\delta^{53}\text{Cr}$ values (mostly $>0.8\text{‰}$) recorded by the non-skeletal car-

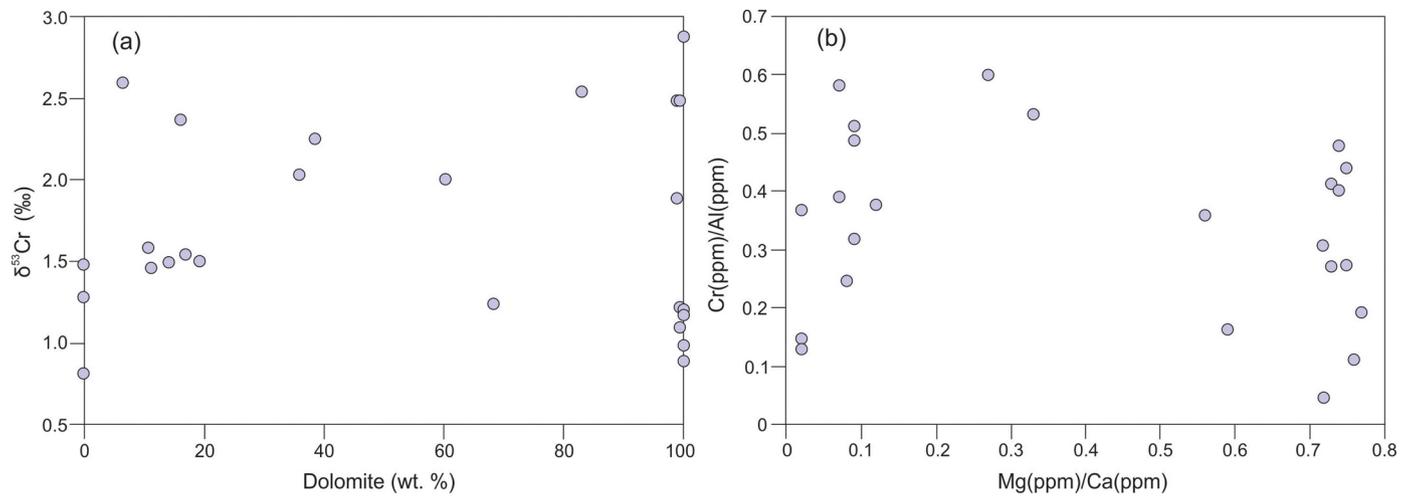


Fig. 4. (a) The abundance of diagenetic dolomite (from Hardisty et al., 2017) versus the $\delta^{53}\text{Cr}$ value of the Unda samples; (b) the Mg/Ca (from Hardisty et al., 2017) versus Cr/Al ratios. The Al data are from Liu et al. (2019).

bonates are close to the reported $\delta^{53}\text{Cr}$ value of contemporaneous seawater (Holmden et al., 2016). These primary values are preserved despite a some degree of aragonite to calcite neomorphism and minor dolomitization by reducing marine pore fluids. This may suggest that marine burial diagenesis does not play a significant role in overprinting primary $\delta^{53}\text{Cr}$ signals within the marine diagenetic zone. However, it is also possible that these sediments may more simply be more unaltered portion of the core, where Cr has not been added during diagenesis.

Previously measured paleoredox proxies, including $I/(\text{Ca}+\text{Mg})$ and $\delta^{34}\text{S}_{\text{CAS}}$, provide evidence for reducing marine pore fluids during diagenesis in the lower Clino core (Hardisty et al., 2017; Murray, 2016). Specifically, the overprinted $I/(\text{Ca}+\text{Mg})$ and $\delta^{34}\text{S}_{\text{CAS}}$ values of these same samples indicate that IO_3^- and SO_4^{2-} were both reduced (Hardisty et al., 2017; Murray, 2016) and that Cr(VI) should also have been quantitatively reduced within the pore waters given the redox potential (Rue et al., 1997). Additional evidences from Sr concentrations and isotopes (Swart et al., 2001a) and Ca and Mg isotopes (Higgins et al., 2018) of dolomite within the lower Clino core suggest that marine diagenesis likely occurred under closed-system, rock-buffered conditions. Although the formation of dolomite requires a supply of Mg^{2+} from incoming fluids, these fluids could be reducing enough to maintain a closed system for Cr. The nearly consistent $\delta^{53}\text{Cr}$ values and Cr/Al ratios in the lower portion of the Clino core, would thereby suggest that these carbonates are rock-buffered under closed-system conditions and thus preserve authigenic Cr isotopic signatures despite diagenetic alteration. Given these observations, we recommend that applications of carbonate Cr isotopes in samples with Ca and Mg isotope evidence for closed-system, rock-buffered diagenesis may be suited for estimating the Cr isotope composition of ancient seawater.

5.2.4. Dolomitization

The samples from the Unda core were specifically selected to provide constraints on $\delta^{53}\text{Cr}$ values in well-characterized dolomites that precipitated from marine pore waters (Fig. 1b and 4a). Previous studies suggest that these carbonates have experienced aragonite to LMC neomorphism in marine pore fluids prior to dolomitization (Swart and Melim, 2000). The dolomitized samples yielded the highest $\delta^{53}\text{Cr}$ values of our entire data set and these values are also significantly heavier than that of any modern seawater (Paulukat et al., 2016). The extent of dolomitization in the core is variable, with the lower section being completely dolomitized. Variations in the extent of dolomitization, however, do not correlate with changes in sample Cr concentration or isotope com-

position (Fig. 4). This would suggest that while $\delta^{53}\text{Cr}$ values in dolomitized samples are somewhat affected by dolomitization, the extent of dolomitization is not the dominant control on resetting Cr isotopes. To date, there has not been a study on the incorporation of Cr(VI) and Cr(III) species into dolomite, or an evaluation of the associated isotope fractionations. Nevertheless, our results indicate that the positive shift in Cr isotopes is not the immediate result of isotopic fractionation during the incorporation of Cr into dolomite, as that the degree of dolomitization does not appear to control the sample Cr concentration or isotope composition.

In the Unda core, there are three non-depositional surfaces at 108.07 m, 270.36 m, and 393.81 m. These non-depositional surfaces correspond to peaks in dolomite concentration, with subsequent downcore decreases in dolomite abundance from the surfaces (Swart and Melim, 2000) (Fig. 1b). In combination with Sr and Ca and Mg isotopic compositions (Swart et al., 2001a; Higgins et al., 2018), these non-depositional surfaces provide evidence for dolomite formation near the sediment-water interface in the presence of a fluid similar in composition to seawater. The Sr concentration of the dolomites increases away from the non-depositional surfaces, as shown in the upper portion (<150 m) of the Unda core near the marine hardground surface (Table S1 and Fig. 1b). To generate such high Sr concentrations in the pore waters from which these dolomites precipitated, there must have been significant depletion of sulfate relative to seawater during dissolution of aragonite, which indicates active sulfate reduction within the pore waters (Swart and Melim, 2000). Such reducing conditions may also have enabled the partial reduction of isotopically heavy Cr(VI) carried by the pore fluids, leading to an increasingly heavier residual Cr(VI) pool in the fluids. Therefore, dolomite precipitated from these fluids would be expected to capture increasingly heavier Cr isotopes.

There is a negative correlation between $\delta^{53}\text{Cr}$ values and Sr abundance in dolomites in the upper portion of the core (Fig. 5a). This tentatively suggests that constraints on the extent of aqueous Cr(VI) reduction in pore fluids can possibly be made based on Sr concentrations of the dolomites. When there is great (near-complete) Cr(VI) reduction, as evidenced by much higher Sr abundances than those of initial fluids, the $\delta^{53}\text{Cr}$ value of dolomites would approach, or be slightly higher than, that of the initial fluids (Fig. 5a). If there is partial Cr(VI) reduction, as shown by slightly higher Sr concentrations compared to that of initial fluids, the $\delta^{53}\text{Cr}$ value would increase dramatically. Dolomites formed under this diagenetic regime would be characterized by highly positive $\delta^{53}\text{Cr}$ values and relatively low Sr abundances (Fig. 5a).

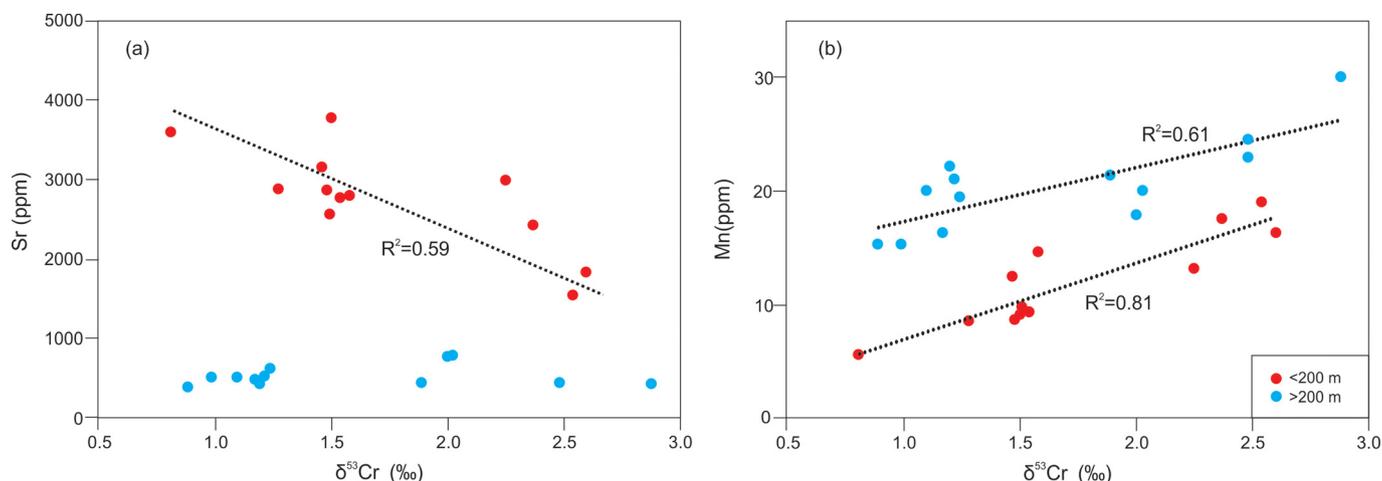


Fig. 5. The Sr (a) and Mn (b) concentrations relative to the $\delta^{53}\text{Cr}$ value of the Unda samples. The Al data are from Liu et al. (2019).

In this scenario, a correlation between $\delta^{53}\text{Cr}$ values and Cr abundances is also expected. However, there is an absence of a relationship between Cr/Al ratios and $\delta^{53}\text{Cr}$ values for these dolomites, which might be explained by a significant amount of aragonite in these carbonate sediments. Primary aragonites possibly have similar $\delta^{53}\text{Cr}$ values but slightly different Cr concentrations. Alternatively, it is also noted that there exists an important positive relationship between $\delta^{53}\text{Cr}$ values and Mn contents (Fig. 5b), indicating local Cr addition likely due to Cr(III) oxidation through Mn oxides into these carbonate sediments, although Mn concentrations are quite low (details for this mechanism see below).

The low Sr content and Sr isotope ratios (Swart et al., 2001a), the Ca–Mg isotope ratios (Higgins et al., 2018), the low $I/(\text{Ca}+\text{Mg})$ ratios (Hardisty et al., 2017), and the $\delta^{34}\text{S}_{\text{CAS}}$ values similar to seawater (Murray, 2016) in the lower massive dolomites (>275 m) of the Unda core provide very narrow constraints on the conditions of dolomitization. Specifically, these proxy values, coupled with these samples developing near the exposure surface (Fig. 1b), are together consistent with dolomitization where pore fluids were in direct advective exchange with seawater and under redox conditions between that promoting iodate and sulfate reduction or at the early onset of sulfate reduction where seawater sulfate still buffered the S isotope signature of pore water sulfate. These conditions are observed together during early burial diagenesis at the onset of reducing conditions, but near the sediment–water interface where oxygen is still available. Based on these constraints, high $\delta^{53}\text{Cr}$ values may indicate local Cr input into dolomites, which could be related to the widespread presence of Mn-oxides in modern marine sediments (Anschutz et al., 2005). Mn-oxides could impact the $\delta^{53}\text{Cr}$ values of dolomites due to positive isotope fractionations during partial oxidation of Cr(III) present in sediments and pore waters, converting Cr(III) and Mn(IV) to more soluble and mobile Cr(VI) and Mn(II) species which would be subsequently incorporated into diagenetic carbonates. Mn reduction is an early diagenetic process that occurs under similar redox conditions to that of iodate reduction. Our interpretation is also consistent with higher Mn contents (generally >20 ppm) observed in these dolomites relative to those of upper dolomites and a significant correlation between Mn contents and $\delta^{53}\text{Cr}$ values (Fig. 5b). Although laboratory studies of Cr(III) oxidation by Mn-oxides show both positive and negative fractionation factors yielding $\delta^{53}\text{Cr}$ values for the produced Cr(VI) ranging from -2.5 to $+1.1\%$ (Bain and Bullen, 2005; Zink et al., 2010; Joshi et al., 2011), the ^{53}Cr -enriched isotopic compositions of the lower Unda core could be attributed to the direct adsorption of isotopically heavy Cr(VI) generated through the partial oxidation of Cr(III) by Mn-oxides (Bauer

et al., 2019). However, there is a poor relationship between Cr/Al ratios and $\delta^{53}\text{Cr}$ values for these pure dolomites, most likely resulted from various Cr contents of earlier carbonate sediments.

An alternative explanation for the highly elevated $\delta^{53}\text{Cr}$ values in Unda dolomites is inheritance of highly positive values during aragonite-to-calcite neomorphism in meteoric waters that preceded dolomitization. For example, groundwater $\delta^{53}\text{Cr}$ values have been demonstrated to be up to $+4\%$ and higher, which could reflect varying source values or local/regional fractionation processes (Ellis et al., 2002; Izbicki et al., 2012). We discuss the potential impacts on meteoric alterations in more detail in the following section using a simple water-rock alteration model, which does demonstrate the potential for elevated $\delta^{53}\text{Cr}$ values relative to seawater depending on the diagenetic fluid. However, we also note that the upper portion of the Clino core has clear evidence for meteoric alterations, but did not display these same highly positive $\delta^{53}\text{Cr}$ values, thus providing some evidence that the elevated $\delta^{53}\text{Cr}$ values relative to seawater in the Unda core are more likely linked to local conditions during deposition and early diagenesis and dolomitization opposed to broader regional groundwater $\delta^{53}\text{Cr}$ values.

5.2.5. A simple model for Cr isotope signals in marine carbonates

To further explore the potential impacts of meteoric diagenesis on Cr isotope signals preserved in carbonate sediments, we employ a modified water-rock interaction model based on that of Banner and Hanson (1990). In this model, we track the concentration and isotopic composition of carbon (C), oxygen (O), and Cr during progressive alteration of a primary marine aragonite precipitate—assumed to record the isotopic composition of ambient seawater for each of the elements considered—in the presence of oxidizing meteoric waters. We specifically consider oxidizing waters for simplicity, as it allows us to avoid consideration of redox-driven Cr isotope fractionations in open vs. closed systems. The concentration of each constituent in the fluid-rock system (o) is given by:

$$C_o^I = F \cdot C_{f,o}^I + (1 - F) \cdot C_{s,o}^I \quad (1)$$

where C terms represent the concentration of an element I within the initial fluid-rock system (o), the initial fluid (f), and the initial solid (s), and F represents the fluid fraction as defined by an assumed porosity and the density of the solid and fluid. By assuming a distribution coefficient for each element (D^I) (e.g., $D_{\text{Cr}} = 4807.69$), we can then calculate the concentration in the solid phase after a single equilibration step (e.g., iteration n):

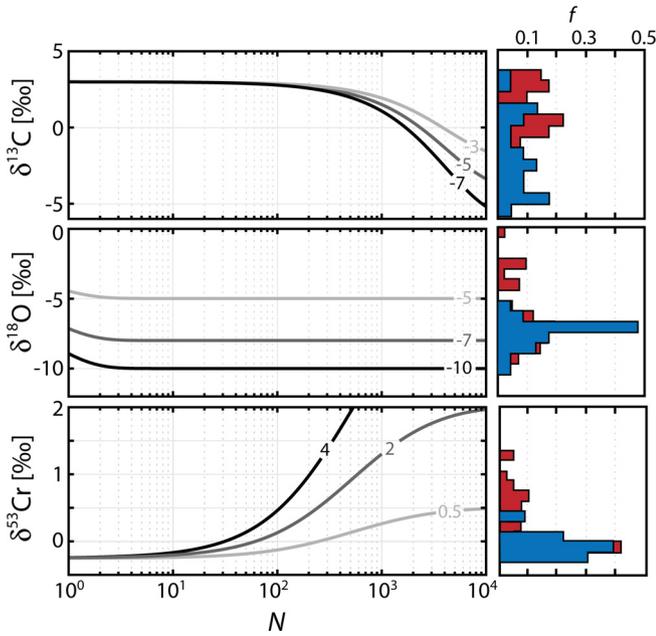


Fig. 6. Representative output from the water-rock interaction model described in the text. From top to bottom, panels show solid carbonate isotopic compositions for carbon, oxygen, and chromium, respectively, as a function of the degree of alteration (N). Curves are labeled according to the assumed initial fluid isotopic compositions. All other parameters as detailed in Table S4. Shown at right are histograms of data from mid-Proterozoic carbonates (Gilleaudeau et al., 2016), with blue bars showing calcite samples and red bars showing dolomitized samples.

$$C_s^I = \frac{C_o^I}{F/D^I + (1-F)} \quad (2)$$

We then calculate the isotopic composition of element I in the solid phase according to:

$$\delta I_s = \frac{\delta I_o \cdot C_o^I \cdot \alpha_{s-f}^I - 1000 \cdot C_f^I \cdot F \cdot (1 - \alpha_{s-f}^I)}{C_s^I \cdot (1-F) \cdot \alpha_{s-f}^I + C_f^I \cdot F} \quad (3)$$

where, in addition to the terms defined above, δI_i represents the isotopic composition of the solid (s) or water-rock system (o) in ‘delta’ notation, and α terms refer to the isotopic fractionation factor between solid (s) and fluid (f) phases. Finally, we can express the degree of water-rock interaction by N , given by:

$$N = n \cdot \left(\frac{F}{1-F} \right) \quad (4)$$

where n is the number of equilibration steps, and F is the fluid fraction defined above. Parameters for our model are given in Table S4.

Representative results from our model are shown in Fig. 6. Oxygen isotope compositions are poorly rock-buffered and can be easily altered by strongly ^{16}O -enriched alteration fluids typically of meteoric waters. Chromium isotope compositions are more easily altered than C isotope compositions (Fig. 6), with the degree of alteration at a given water-rock ratio strongly dependent on the Cr isotope composition of the alteration fluid. In natural settings, this isotope composition would be expected to vary widely, with seawater typically around 1‰ (Paulukat et al., 2016). Meteoric fluids are not well characterized but current constraints suggest variable compositions with ground water values as positive as 4‰ or greater (Ellis et al., 2002; Izbicki et al., 2012) and unpolluted riverine water values of -0.59 to $+1.7$ ‰ (D’Arcy et al., 2016; Frei et al., 2014; Goring-Harford et al., 2020; Wu et al., 2017). These compositions depend on a combination of the $\delta^{53}\text{Cr}$ value of weathered source rock and the fractionations associated with Cr-reduction

along the flow path. A simple message from the water-rock interaction model is that in many cases carbonate sedimentary rocks will be poorly rock-buffered with respect to Cr if in an open system. This is tied to the fact that the initial concentrations of Cr in carbonate sediments is low and the isotope compositions of potential alteration fluids are widely variable. In particular, cases in which C isotopes have been clearly overprinted would seemingly be very unlikely to preserve primary seawater Cr isotope compositions (Fig. 6). Further, even in cases where primary C isotope signatures are preserved Cr isotope signatures are likely to have been overprinted (Fig. 6). Moreover, because our calculations assume no isotope fractionation upon incorporation of Cr into primary carbonate mineral phases, we have undoubtedly underestimated the possible Cr isotope fractionations induced by formation, diagenesis, and burial alteration of carbonate sediments.

5.3. Significance of $\delta^{53}\text{Cr}$ variations in Archean carbonates

The three Archean carbonate successions yielded predominantly unfractionated $\delta^{53}\text{Cr}$ values, in line with independent proxies for extremely low atmospheric oxygen levels before Great Oxidation Event (~ 2.4 – 2.2 Ga) including the photochemical mass independent fractionation of sulfur isotopes, which implies less than about 10^{-5} PAL (Farquhar et al., 2011). However, the presence of highly fractionated (positive) $\delta^{53}\text{Cr}$ values—recorded mainly in ~ 3.0 Ga Pongola carbonates (Fig. 2a)—provides some new insights into the long-term Cr isotope record. If primary, these values seem to indicate Archean oxidative Cr cycling. This apparent oxidation could have occurred in benthic and soil oxygen photosynthetic ecosystems (Lalonde and Konhauser, 2015), or in the marine realm (e.g., Planavsky et al., 2014b; Bauer et al., 2019) and need not necessarily track atmospheric oxygenation.

In the Pongola basin, previous rare earth element and Mo-Fe-S isotopic studies (e.g., Planavsky et al., 2014b; Eickmann et al., 2018; Siah et al., 2018) suggested that oxygenic photosynthesis had already produced high enough levels of oxygen to oxidize Mn and Fe in the surface waters. Given that Archean carbonates commonly contain high Mn and Fe concentrations, a result of both the mostly anoxic Archean oceans and the effects of meteoric and burial diagenesis (Siah et al., 2018), the relatively low contents of Mn and Fe in these samples with highly fractionated Cr isotopes (Fig. 7a) could also suggest locally oxic seawater with low Mn and Fe contents. Once Mn oxides were deposited, they might generate mobile Cr(VI) into seawater through oxidation of Cr(III), giving rise to a Cr isotope fractionation. The lack of a correlation between Mn contents and $\delta^{53}\text{Cr}$ values (Fig. 7a) may point towards partial reduction rather than the extent of oxidation of Cr(III) in regulating the Cr isotopic composition given Fe(II) as an effective reductant for Cr(VI) and low Fe contents in these samples. During reduction, the lighter ^{52}Cr is preferentially reduced to Cr(III), further enriching dissolved Cr(VI) residue in the heavy ^{53}Cr isotope (Ellis et al., 2002), which might be incorporated into these carbonates.

Alternatively, it is also possible that these values are linked to secondary processes and represent diagenetic signals. Diagenesis or subsequent alteration is a clear concern for these samples given that secondary processes are likely responsible for the fractionated Cr isotopes within the Pongola BIFs (cf. Albut et al., 2018). The fact that Cr in carbonates is unlikely to be rock-buffered (see above) also means that these signals are susceptible to diagenetic alteration. Further, Siah et al. (2018) argued that dolomitization and burial/meteoric diagenesis indeed played an important role in overprinting the Pongola carbonates. However, those fractionated Cr isotopes are found in samples with a low degree of dolomitization ($\text{Mg}/\text{Ca} < 0.01$) and a weak relationship between $\delta^{53}\text{Cr}$ values and Sr abundances exists for these carbonates (Fig. 7b). These are different from those of Unda dolomites (see above), implying that

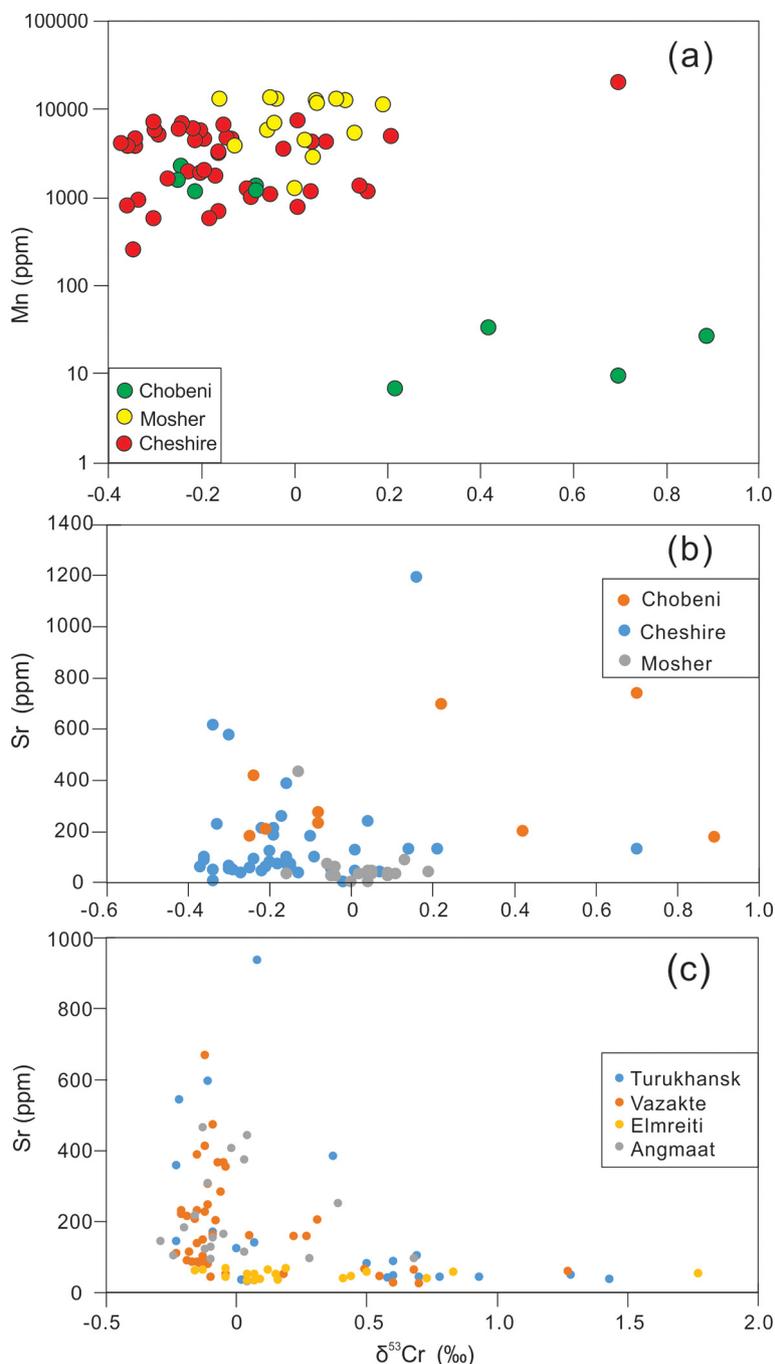


Fig. 7. The $\delta^{53}\text{Cr}$ values relative to Mn (a) and Sr (b) abundances (ppm) of the studied Archean carbonate sediments and Sr (c) abundances (ppm) of the late Mesoproterozoic carbonate sediments (data from Gilleaudeau et al., 2016).

burial/meteoric diagenesis could also lead to the presence of positive Cr isotopes.

The Mosher Carbonate and Cheshire formation carbonates contain fewer and less positive Cr isotope values than the Pongola carbonates (Fig. 7a). However, they do still contain fractionated Cr isotope values. These values again could have multiple origins—they could either be tied to diagenesis or record depositional signals, and thus additional work (e.g., radiogenic isotope work or Ca–Mg diagenetic constraints) is needed to confirm a depositional origin. Nonetheless we can still gain valuable information from all these units—regardless of the origin of the observed Cr isotope variations—they indicate that it is possible to have fractionated Cr isotope values in rocks that initially formed in a low-oxygen Earth

system state (with $p\text{O}_2$ likely consistently below 10^{-5} PAL) (Eickmann et al., 2018; Farquhar et al., 2011).

5.4. Implications for carbonate Cr isotopic records

After screening for detrital contamination, both negative and positive $\delta^{53}\text{Cr}$ values are found in the mid-Proterozoic carbonate Cr isotope dataset (Gilleaudeau et al., 2016). This variability has been attributed to redox heterogeneity at depth and the degree of *in situ* Cr-reduction in shallow water environments and likely atmospheric oxygenation (Gilleaudeau et al., 2016). However, it needs to be noted that highly positive $\delta^{53}\text{Cr}$ values from late Mesoproterozoic carbonates are often found in dolomitized samples (Fig. 6). Additionally, there exists a significant relationship between $\delta^{53}\text{Cr}$

values and Sr abundances for these carbonates (Fig. 7c). These are similar to those we observed in Unda samples (Fig. 5a and 7c) and likely suggest that post-depositional alteration affects primary Cr isotopes likely during dolomitization. Furthermore, other Neoproterozoic and Phanerozoic carbonate successions also record both unfractionated and fractionated $\delta^{53}\text{Cr}$ values (D'Arcy et al., 2017; Frei et al., 2011; Gilleaudeau et al., 2018; Holmden et al., 2016; Rodler et al., 2016). Such a large range of $\delta^{53}\text{Cr}$ values seems inconsistent with an oxic atmosphere, although unfractionated Cr isotopes might be a result of detrital dilution, strong local hydrothermal input, and/or changes in the redox state of seawater. Our Neogene and Archean carbonates provide new insights into the significance of these records. Specifically, the Neogene samples indicate that variations in carbonate Cr isotope values can be caused by differences in where samples were fluid- or rock-buffered during diagenesis. This complicates linking Cr isotope values to chemoclines or atmosphere-seawater redox conditions, especially without independent constraints on the effects of diagenesis (e.g., Ahm et al., 2018; Higgins et al., 2018). The Archean samples from this study indicate that both fractionated and unfractionated Cr isotope values in carbonates are found even in an end member reducing Earth system. There are multiple possible processes—primary and diagenetic—that could have caused these isotope variations. Nonetheless, these records indicate that significant $\delta^{53}\text{Cr}$ variability can arise under a pervasively reducing atmosphere. These observations bolster the case that fractionated Cr isotope values from a single formation or individual samples should not be linked to atmospheric oxygen levels.

6. Conclusions

Our results shed light on the potential for the carbonate Cr isotope archive to capture contemporaneous seawater signals. They reveal that meteoric alteration and dolomitization of Neogene-Quaternary carbonates can lead to dramatically decreased and increased $\delta^{53}\text{Cr}$ values, respectively. This is consistent with simple water-rock interaction modelling, suggesting that carbonate Cr isotope values, like O isotope values, appear to be overprinted with relatively limited alteration in contrast to carbonate C isotopes and REE patterns (e.g., Banner and Hanson, 1990; Liu et al., 2019) which are rock-buffered. Nevertheless, this study also demonstrates the potential for diagenetic carbonates formed under rock-buffered conditions to retain primary seawater Cr isotope signatures. Additionally, our Archean carbonate Cr record reveals that fractionated $\delta^{53}\text{Cr}$ values can form despite pervasively reducing atmospheric conditions, with important implications for inferred periods of atmospheric oxygenation based on Cr isotopic fractionation of Proterozoic and Phanerozoic carbonates (D'Arcy et al., 2017; Gilleaudeau et al., 2016). More broadly, we suggest that without combined petrographic and independent geochemical indices to assess the potential of carbonates for preserving a depositional signature, the $\delta^{53}\text{Cr}$ values of carbonate sediments, especially dolomites, should be interpreted with great caution. We further suggest that Ca and Mg isotope constraints on fluid- vs rock-buffered diagenetic conditions may be a path forward for determining the likelihood that ancient carbonates preserve Cr isotope compositions reflective of seawater.

CRedit authorship contribution statement

Changle Wang: Conceptualization, Data curation, Investigation, Methodology, Writing – review & editing. **Christopher T. Reinhard:** Investigation, Visualization, Writing – review & editing. **Kyle S. Rybacki:** Investigation, Visualization, Writing – review & editing. **Dalton S. Hardisty:** Investigation, Visualization, Writing – review & editing. **Frantz Ossa Ossa:** Investigation, Visualization, Writing –

review & editing. **Xiangli Wang:** Investigation, Visualization, Writing – review & editing. **Axel Hofmann:** Investigation, Validation, Writing – review & editing. **Dan Asael:** Investigation, Validation, Writing – review & editing. **Leslie J. Robbins:** Investigation, Visualization, Writing – review & editing. **Lianchang Zhang:** Investigation, Visualization, Writing – review & editing. **Noah J. Planavsky:** Investigation, Validation, Writing – review & editing.

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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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.epsl.2021.116824>.

References

- Ahm, A.-S.C., Bjerrum, C.J., Blättler, C.L., Swart, P.K., Higgins, J.A., 2018. Quantifying early marine diagenesis in shallow-water carbonate sediments. *Geochim. Cosmochim. Acta* 236, 140–159.
- Albut, G., Babechuk, M.G., Kleinhanns, I.C., Bengler, M., Beukes, N.J., Steinhilber, B., Smith, A.J., Kruger, S.J., Schoenberg, R., 2018. Modern rather than Mesoarchean oxidative weathering responsible for the heavy stable Cr isotopic signatures of the 2.95 Ga old Ijzermijn iron formation (South Africa). *Geochim. Cosmochim. Acta* 228, 157–189.
- Anbar, A.D., Rouxel, O., 2007. Metal stable isotopes in paleoceanography. *Annu. Rev. Earth Planet. Sci.* 35, 717–746.
- Anschutz, P., Dedieu, K., Desmazes, F., Chaillou, G., 2005. Speciation, oxidation state, and reactivity of particulate manganese in marine sediments. *Chem. Geol.* 218 (3–4), 265–279.
- Babechuk, M.G., Kleinhanns, I.C., Schoenberg, R., 2017. Chromium geochemistry of the ca. 1.85 Ga Flin Flon paleosol. *Geobiology* 15 (1), 30–50.
- Bain, D.J., Bullen, T.D., 2005. Chromium isotope fractionation during oxidation of Cr(III) by manganese oxides. *Geochim. Cosmochim. Acta* 69 (Supplement), A212.
- Banner, J.L., Hanson, G.N., 1990. Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochim. Cosmochim. Acta* 54, 3123–3137.
- Bauer, K.W., Cole, D.B., Asael, D., Francois, R., Calvert, S.E., Poulton, S.W., Planavsky, N.J., Crowe, S.A., 2019. Chromium isotopes in marine hydrothermal sediments. *Chem. Geol.* 529, 119286.
- Bonnand, P., James, R., Parkinson, I., Connelly, D., Fairchild, I., 2013. The chromium isotopic composition of seawater and marine carbonates. *Earth Planet. Sci. Lett.* 382, 10–20.
- Canfield, D.E., Zhang, S., Frank, A.B., Wang, X., Wang, H., Su, J., Ye, Y., Frei, R., 2018. Highly fractionated chromium isotopes in Mesoproterozoic-aged shales and atmospheric oxygen. *Nat. Commun.* 9 (1), 1–11.
- Catling, D.C., Zahnle, K.J., 2020. The Archean atmosphere. *Sci. Adv.* 6 (9), 1420.
- Chen, X., Romaniello, S.J., Herrmann, A.D., Hardisty, D., Gill, B.C., Anbar, A.D., 2018. Diagenetic effects on uranium isotope fractionation in carbonate sediments from the Bahamas. *Geochim. Cosmochim. Acta* 237, 294–311.
- Cole, D.B., Reinhard, C.T., Wang, X., Gueguen, B., Halverson, G.P., Gibson, T., Hodgskiss, M.S., McKenzie, N.R., Lyons, T.W., Planavsky, N.J., 2016. A shale-hosted

- Cr isotope record of low atmospheric oxygen during the Proterozoic. *Geology* 44 (7), 555–558.
- Cooper, K.J., Whitaker, F.F., Anesio, A.M., Naish, M., Reynolds, D.M., Evans, E.L., 2016. Dissolved organic carbon transformations and microbial community response to variations in recharge waters in a shallow carbonate aquifer. *Biogeochemistry* 129 (1–2), 215–234.
- Crowe, S.A., Døssing, L.N., Beukes, N.J., Bau, M., Kruger, S.J., Frei, R., Canfield, D.E., 2013. Atmospheric oxygenation three billion years ago. *Nature* 501 (7468), 535–538.
- D'Arcy, J., Babechuk, M.G., Døssing, L.N., Gaucher, C., Frei, R., 2016. Processes controlling the chromium isotopic composition of river water: constraints from basaltic river catchments. *Geochim. Cosmochim. Acta* 186, 296–315.
- D'Arcy, J., Gilleaudeau, G.J., Peralta, S., Gaucher, C., Frei, R., 2017. Redox fluctuations in the Early Ordovician oceans: an insight from chromium stable isotopes. *Chem. Geol.* 448, 1–12.
- Daye, M., Klepac-Ceraj, V., Pajusalu, M., Rowland, S., Farrell-Sherman, A., Beukes, N., Tamura, N., Fournier, G., Bosak, T., 2019. Light-driven anaerobic microbial oxidation of manganese. *Nature* 576 (7786), 311–314.
- Dellinger, M., Hardisty, D.S., Planavsky, N.J., Gill, B.C., Kalderon-Asael, B., Asael, D., Croissant, T., Swart, P.K., West, A.J., 2020. The effects of diagenesis on lithium isotope ratios of shallow marine carbonates. *Am. J. Sci.* 320 (2), 150–184.
- Eberli, G., Swart, P., McNeill, D., Kenter, J., Anselmetti, F., Melim, L., Ginsburg, R., 1997. A synopsis of the Bahamas Drilling Project: results from two deep core borings drilled on the Great Bahama Bank. In: *Proceedings of the Ocean Drilling Program, Initial Reports*, pp. 23–41.
- Eickmann, B., Hofmann, A., Wille, M., Bui, T.H., Wing, B.A., Schoenberg, R., 2018. Isotopic evidence for oxygenated Mesoproterozoic shallow oceans. *Nat. Geosci.* 11 (2), 133–138.
- Ellis, A.S., Johnson, T.M., Bullen, T.D., 2002. Chromium isotopes and the fate of hexavalent chromium in the environment. *Science* 295 (5562), 2060–2062.
- Fang, Z., Qin, L., Liu, W., Yao, T., Chen, X., Wei, S., 2020. Absence of hexavalent chromium in marine carbonates: implications for chromium isotopes as paleoenvironment proxy. *Nat. Sci. Rev.*
- Farkaš, J., Frýda, J., Paulukat, C., Hathorne, E.C., Matoušková, Š., Rohovec, J., Frýdová, B., Francová, M., Frei, R., 2018. Chromium isotope fractionation between modern seawater and biogenic carbonates from the Great Barrier Reef, Australia: implications for the paleo-seawater $\delta^{53}\text{Cr}$ reconstruction. *Earth Planet. Sci. Lett.* 498, 140–151.
- Farquhar, J., Zerkle, A.L., Bekker, A., 2011. Geological constraints on the origin of oxygenic photosynthesis. *Photosynth. Res.* 107 (1), 11–36.
- Fendorf, S.E., Zasoski, R.J., 1992. Chromium (III) oxidation by Δ -manganese oxide (MnO₂). 1. Characterization. *Environ. Sci. Technol.* 26 (1), 79–85.
- Fralick, P., Riding, R., 2015. Steep Rock lake: sedimentology and geochemistry of an Archean carbonate platform. *Earth-Sci. Rev.* 151, 132–175.
- Frei, R., Gaucher, C., Poulton, S.W., Canfield, D.E., 2009. Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. *Nature* 461 (7261), 250–253.
- Frei, R., Gaucher, C., Døssing, L.N., Sial, A.N., 2011. Chromium isotopes in carbonates—a tracer for climate change and for reconstructing the redox state of ancient seawater. *Earth Planet. Sci. Lett.* 312 (1–2), 114–125.
- Frei, R., Poiré, D., Frei, K.M., 2014. Weathering on land and transport of chromium to the ocean in a subtropical region (Misiones, NW Argentina): a chromium stable isotope perspective. *Chem. Geol.* 381, 110–124.
- Frei, R., Paulukat, C., Bruggmann, S., Kläbe, R.M., 2018. A systematic look at chromium isotopes in modern shells—implications for paleo-environmental reconstructions. *Biogeosciences* 15 (16), 4905–4922.
- Füger, A., Bruggmann, S., Frei, R., Leis, A., Dietzel, M., Mavromatis, V., 2019. The role of pH on Cr (VI) partitioning and isotopic fractionation during its incorporation in calcite. *Geochim. Cosmochim. Acta* 265, 520–532.
- Gilleaudeau, G.J., Frei, R., Kaufman, A., Kah, L., Azmy, K., Bartley, J., Chernyavskiy, P., Knoll, A.H., 2016. Oxygenation of the mid-Proterozoic atmosphere: clues from chromium isotopes in carbonates. *Geochim. Perspect. Lett.*
- Gilleaudeau, G.J., Voegelin, A.R., Thibault, N., Moreau, J., Ullmann, C.V., Kläbe, R.M., Korte, C., Frei, R., 2018. Stable isotope records across the Cretaceous–Paleogene transition, Stevns Klint, Denmark: new insights from the chromium isotope system. *Geochim. Cosmochim. Acta* 235, 305–332.
- Ginsburg, R.N., 2001. Subsurface geology of a prograding carbonate platform margin, Great Bahama Bank: results of the Bahamas Drilling Project. In: *Society of Economic Paleontologists and Mineralogists*. Tulsa, OK.
- Goring-Harford, H.J., Klar, J.K., Donald, H.K., Pearce, C.R., Connelly, D.P., James, R.H., 2020. Behaviour of chromium and chromium isotopes during estuarine mixing in the Beaulieu Estuary, UK. *Earth Planet. Sci. Lett.* 536, 116166.
- Hardisty, D.S., Lu, Z., Bekker, A., Diamond, C.W., Gill, B.C., Jiang, G., Kah, L.C., Knoll, A.H., Loyd, S.J., Osburn, M.R., 2017. Perspectives on Proterozoic surface ocean redox from iodine contents in ancient and recent carbonate. *Earth Planet. Sci. Lett.* 463, 159–170.
- Higgins, J.A., Blättler, C., Lundstrom, E., Santiago-Ramos, D., Akhtar, A., Ahm, A.C., Bialik, O., Holmden, C., Bradbury, H., Murray, S., 2018. Mineralogy, early marine diagenesis, and the chemistry of shallow-water carbonate sediments. *Geochim. Cosmochim. Acta* 220, 512–534.
- Hofmann, A., Dirks, P.H., Jelsma, H.A., 2001. Late Archean foreland basin deposits, Belingwe greenstone belt, Zimbabwe. *Sediment. Geol.* 141, 131–168.
- Holmden, C., Jacobson, A., Sageman, B., Hurtgen, M., 2016. Response of the Cr isotope proxy to Cretaceous Ocean Anoxic Event 2 in a pelagic carbonate succession from the Western Interior Seaway. *Geochim. Cosmochim. Acta* 186, 277–295.
- Izbicki, J.A., Bullen, T.D., Martin, P., Schroth, B., 2012. Delta Chromium-53/52 isotopic composition of native and contaminated groundwater, Mojave Desert, USA. *Appl. Geochem.* 27 (4), 841–853.
- Joshi, S., Wang, D.T., Ellis, A.S., Johnson, T.M., Bullen, T.D., 2011. Stable isotope fractionation during Cr(III) oxidation by manganese oxides. In: *AGU Fall Meeting*, EP41B-0622.
- Lalonde, S.V., Konhauser, K.O., 2015. Benthic perspective on Earth's oldest evidence for oxygenic photosynthesis. *Proc. Natl. Acad. Sci.* 112 (4), 995–1000.
- Liu, W., Hao, J., Elzinga, E.J., Piotrowski, P., Nanda, V., Yee, N., Falkowski, P.G., 2020. Anoxic photogeochemical oxidation of manganese carbonate yields manganese oxide. *Proc. Natl. Acad. Sci.* 117 (37), 22698–22704.
- Liu, X.-M., Hardisty, D.S., Lyons, T.W., Swart, P.K., 2019. Evaluating the fidelity of the cerium paleoredox tracer during variable carbonate diagenesis on the Great Bahamas Bank. *Geochim. Cosmochim. Acta* 248, 25–42.
- Manfrino, C., Ginsburg, R.N., 2001. Pliocene to Pleistocene Deposition History of the Upper Platform Margin.
- McClain, M.E., Swart, P.K., Vacher, H.L., 1992. The hydrogeochemistry of early meteoric diagenesis in a Holocene deposit of biogenic carbonates. *J. Sediment. Res.* 62 (6), 1008–1022.
- Melim, L., Westphal, H., Swart, P.K., Eberli, G.P., Munnecke, A., 2002. Questioning carbonate diagenetic paradigms: evidence from the Neogene of the Bahamas. *Mar. Geol.* 185 (1–2), 27–53.
- Melim, L.A., Swart, P.K., Maliva, R.G., 1995. Meteoric-like fabrics forming in marine waters: implications for the use of petrography to identify diagenetic environments. *Geology* 23 (8), 755–758.
- Melim, L.A., Swart, P.K., Eberli, G.P., 2004. Mixing-zone diagenesis in the subsurface of Florida and the Bahamas. *J. Sediment. Res.* 74 (6), 904–913.
- Murray, K.J., Tebo, B.M., 2007. Cr (III) is indirectly oxidized by the Mn (II)-oxidizing bacterium *Bacillus* sp. strain SG-1. *Environ. Sci. Technol.* 41 (2), 528–533.
- Murray, S.T., 2016. The Application of Clumped Isotopes to Dolomites.
- Oze, C., Bird, D.K., Fendorf, S., 2007. Genesis of hexavalent chromium from natural sources in soil and groundwater. *Proc. Natl. Acad. Sci.* 104 (16), 6544–6549.
- Paulukat, C., Gilleaudeau, G.J., Chernyavskiy, P., Frei, R., 2016. The Cr-isotope signature of surface seawater—a global perspective. *Chem. Geol.* 444, 101–109.
- Planavsky, N.J., Asael, D., Hofmann, A., Reinhard, C.T., Lalonde, S.V., Knudsen, A., Wang, X., Ossa, F.O., Pecoits, E., Smith, A.J., 2014b. Evidence for oxygenic photosynthesis half a billion years before the great oxidation event. *Nat. Geosci.* 7 (4), 283–286.
- Planavsky, N.J., Reinhard, C.T., Wang, X., Thomson, D., McGoldrick, P., Rainbird, R.H., Johnson, T., Fischer, W.W., Lyons, T.W., 2014a. Low mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals. *Science* 346 (6209), 635–638.
- Qin, L., Wang, X., 2017. Chromium isotope geochemistry. *Rev. Mineral. Geochem.* 82 (1), 379–414.
- Reinhard, C.T., Planavsky, N.J., Wang, X., Fischer, W.W., Johnson, T.M., Lyons, T.W., 2014. The isotopic composition of authigenic chromium in anoxic marine sediments: a case study from the Cariaco Basin. *Earth Planet. Sci. Lett.* 407, 9–18.
- Rodler, A., Sánchez-Pastor, N., Fernández-Díaz, L., Frei, R., 2015. Fractionation behavior of chromium isotopes during coprecipitation with calcium carbonate: implications for their use as paleoclimatic proxy. *Geochim. Cosmochim. Acta* 164, 221–235.
- Rodler, A., Hohl, S., Guo, Q., Frei, R., 2016. Chromium isotope stratigraphy of Ediacaran cap dolostones, Doushantuo formation, South China. *Chem. Geol.* 436, 24–34.
- Rudnick, R., Gao, S., 2014. Composition of the Continental Crust in *Treatise on Geochemistry* Editors-in-Chief: Heinrich Holland and Karl Turekian.
- Rue, E.L., Smith, G.J., Cutter, G.A., Bruland, K.W., 1997. The response of trace element redox couples to suboxic conditions in the water column. *Deep-Sea Res., Part 1, Oceanogr. Res. Pap.* 44 (1), 113–134.
- Saad, E.M., Wang, X., Planavsky, N.J., Reinhard, C.T., Tang, Y., 2017. Redox-independent chromium isotope fractionation induced by ligand-promoted dissolution. *Nat. Commun.* 8 (1), 1–10.
- Scheiderich, K., Amini, M., Holmden, C., Francois, R., 2015. Global variability of chromium isotopes in seawater demonstrated by Pacific, Atlantic, and Arctic Ocean samples. *Earth Planet. Sci. Lett.* 423, 87–97.
- Schoenberg, R., Zink, S., Staubwasser, M., von Blanckenburg, F., 2008. The stable Cr isotope inventory of solid Earth reservoirs determined by double spike MC-ICP-MS. *Chem. Geol.* 249 (3–4), 294–306.
- Siahi, M., Hofmann, A., Master, S., Wilson, A., Mayr, C., 2018. Trace element and stable (C, O) and radiogenic (Sr) isotope geochemistry of stromatolitic carbonate rocks of the Mesoproterozoic Pongola Supergroup: implications for seawater composition. *Chem. Geol.* 476, 389–406.
- Stewart, J.A., Gutjahr, M., Pearce, F., Swart, P.K., Foster, G.L., 2015. Boron during meteoric diagenesis and its potential implications for Marinoan snowball Earth $\delta^{11}\text{B}$ -pH excursions. *Geology* 43 (7), 627–630.

- Swart, P.K., 2015. The geochemistry of carbonate diagenesis: the past, present and future. *Sedimentology* 62 (5), 1233–1304.
- Swart, P.K., Eberli, G., 2005. The nature of the $\delta^{13}\text{C}$ of periplatform sediments: implications for stratigraphy and the global carbon cycle. *Sediment. Geol.* 175 (1–4), 115–129.
- Swart, P.K., Melim, L.A., 2000. The origin of dolomites in Tertiary sediments from the margin of Great Bahama Bank. *J. Sediment. Res.* 70 (3), 738–748.
- Swart, P.K., Oehlert, A.M., 2018. Revised interpretations of stable C and O patterns in carbonate rocks resulting from meteoric diagenesis. *Sediment. Geol.* 364, 14–23.
- Swart, P.K., Elderfield, H., Beets, K., 2001a. The $87\text{Sr}/86\text{Sr}$ Ratios of Carbonates, Phosphorites, and Fluids Collected During the Bahamas Drilling Project Cores Clino and Unda: Implications for Dating and Diagenesis.
- Swart, P.K., Elderfield, H., Ostlund, G. The Geochemistry of Pore Fluids from Bore Holes in the Great Bahama Bank.
- Tang, Y., Elzinga, E.J., Lee, Y.J., Reeder, R.J., 2007. Coprecipitation of chromate with calcite: batch experiments and X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* 71 (6), 1480–1493.
- Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R., Webb, S.M., 2004. Biogenic manganese oxides: properties and mechanisms of formation. *Annu. Rev. Earth Planet. Sci.* 32, 287–328.
- Wang, X., Planavsky, N.J., Reinhard, C.T., Zou, H., Ague, J.J., Wu, Y., Gill, B.C., Schwarzenbach, E.M., Peucker-Ehrenbrink, B., 2016a. Chromium isotope fractionation during subduction-related metamorphism, black shale weathering, and hydrothermal alteration. *Chem. Geol.* 423, 19–33.
- Wang, X., Reinhard, C.T., Planavsky, N.J., Owens, J.D., Lyons, T.W., Johnson, T.M., 2016b. Sedimentary chromium isotopic compositions across the Cretaceous OAE2 at Demerara Rise Site 1258. *Chem. Geol.* 429, 85–92.
- Wang, X.L., Planavsky, N.J., Hull, P.M., Tripathi, A.E., Zou, H.J., Elder, L., Henehan, M., 2017. Chromium isotopic composition of core-top planktonic foraminifera. *Geobiology* 15 (1), 51–64.
- Wille, M., Nebel, O., Van Kranendonk, M.J., Schoenberg, R., Kleinhans, I.C., Ellwood, M.J., 2013. Mo–Cr isotope evidence for a reducing Archean atmosphere in 3.46–2.76 Ga black shales from the Pilbara, Western Australia. *Chem. Geol.* 340, 68–76.
- Wu, W., Wang, X., Reinhard, C.T., Planavsky, N.J., 2017. Chromium isotope systematics in the Connecticut River. *Chem. Geol.* 456, 98–111.
- Zink, S., Schoenberg, R., Staubwasser, M., 2010. Isotopic fractionation and reaction kinetics between Cr(III) and Cr(VI) in aqueous media. *Geochim. Cosmochim. Acta* 74, 5729–5745.