

## Earth and Environmental Sciences

Special Topic: Frontiers of Stable Isotope Research

# Application of chromium isotopes as a proxy for redox processes in present and ancient environments: Promises and pitfalls

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**Abstract:** Chromium (Cr) is a redox-sensitive element, and significant Cr isotope fractionation occurs during redox transformations among its different oxidation states. As a result, the Cr isotopic system has been widely applied as a tracer for redox processes in both present and ancient environments, such as the reductive remediation of hexavalent Cr contamination and the reconstruction of oxygen dynamics in Earth's atmosphere and oceans. Recent studies, however, suggest that the Cr isotopic compositions of aquatic systems and sediments are influenced by more complex processes than previously thought, introducing additional uncertainties in the interpretation of Cr isotopic data. In this review, we first summarize the mechanisms of Cr isotopic fractionation associated with low-temperature processes and the current understanding of the Cr cycle and its isotopic behavior in Earth's surface environments. We then examine the key processes controlling the Cr isotopic compositions of major environmental reservoirs, with a focus on the geochemical interpretation of sedimentary Cr isotope records, their paleoenvironmental implications, and potential directions for future research.

**Keywords:** Cr isotopes, redox processes, Cr(VI) contamination, atmospheric oxygenation

## INTRODUCTION

Chromium (Cr) is a transition metal element in Group VIB of the periodic table, with an electronic configuration of  $[\text{Ar}]3d^54s^1$ . It is a redox-sensitive element that occurs in various oxidation states in natural systems. Trivalent and hexavalent Cr, expressed as Cr(III) and Cr(VI), are the dominant oxidation states in Earth's surface environments. Divalent Cr has also been detected in some meteorites and was suggested to be prevailing in some mantle minerals, such as olivine [1–3]. Cr(III) is almost insoluble in water and represents the primary form of Cr in rocks and minerals, such as chromite. In contrast, Cr(VI) is highly soluble and typically occurs in aqueous systems as chromate ( $\text{CrO}_4^{2-}$ ), hydrogen chromate ( $\text{HCrO}_4^-$ ), and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ).

Transformations between Cr(III) and Cr(VI) are largely controlled by the redox potential of ambient environments, while reaction kinetics also have an important influence. In natural environments, direct

oxidation of Cr(III) by free O<sub>2</sub> is kinetically sluggish, and oxidation of Cr(III) by manganese (Mn) oxides is the primary pathway for the generation of Cr(VI) [4,5]. This process enables the mobilization of Cr from rocks into aquatic systems and its subsequent transport to the oceans [6]. Oxidation of Cr(III) by natural hydrogen peroxide has also been reported. This pathway is mainly associated with serpentinization-related settings and is likely of minor importance to the global Cr cycle [7]. A variety of natural reductants, including ferrous iron, sulfides, and organic matter, can efficiently reduce Cr(VI) to Cr(III), which results in Cr immobilization through precipitation and particle reactivity of Cr(III) [8–10]. However, part of the reduced Cr(III) may remain dissolved through complexation with organic ligands [11].

In addition to natural occurrence in nature, Cr is widely used in industrial activities, including electroplating, leather tanning, and corrosion protection. Cr(VI) is highly toxic and carcinogenic, making it a world-concern environmental contaminant. In contrast, Cr(III) is less toxic and poorly soluble. Therefore, reduction of Cr(VI) to Cr(III) represents an effective strategy for Cr(VI) remediation. In addition to natural reductants, artificial (bio-)materials such as nanoscale zero-valent iron and microorganisms have also been applied to Cr(VI) reduction in contaminated environments [9,12–14].

In terms of Cr isotopes, Cr has four stable isotopes, <sup>50</sup>Cr, <sup>52</sup>Cr, <sup>53</sup>Cr, and <sup>54</sup>Cr, with natural abundances of 4.35%, 83.79%, 9.50%, and 2.36%, respectively. Chromium isotopes have been studied for several decades and have important applications in both geochemistry and cosmochemistry. The short-lived <sup>53</sup>Mn–<sup>53</sup>Cr isotopic system is a key chronometer for dating early solar system processes, and the <sup>54</sup>Cr isotopic anomaly has been widely used to trace nucleosynthetic heterogeneities in the solar nebula [15]. These two applications of Cr isotopes are mass-independent and are discussed elsewhere [15]. In contrast, mass-dependent Cr isotopic fractionation arises from physical and chemical processes that induce small variations in the relative abundances of heavy and light isotopes, such as <sup>53</sup>Cr/<sup>52</sup>Cr ratios for Cr. The mass-dependent Cr isotopic composition of a sample is typically expressed as the deviation of the isotopic ratio from that of a standard reference material. The National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 979 is widely used as the reference. Accordingly, the Cr isotopic composition of a sample is expressed as

$$\delta^{53}\text{Cr} = \left[ \left( ^{53}\text{Cr} / ^{52}\text{Cr} \right)_{\text{sample}} / \left( ^{53}\text{Cr} / ^{52}\text{Cr} \right)_{\text{SRM979}} - 1 \right] \times 1000. \quad (1)$$

During chemical processes, Cr isotopic fractionation can be quantified using the fractionation factor ( $\alpha$ ), defined as

$$\alpha = \left( ^{53}\text{Cr} / ^{52}\text{Cr} \right)_{\text{product}} / \left( ^{53}\text{Cr} / ^{52}\text{Cr} \right)_{\text{reactant}}. \quad (2)$$

For equilibrium isotopic fractionation, such as that between Cr(VI) and Cr(III), the fractionation magnitude can be expressed as

$$\Delta_{\text{Cr(VI)-Cr(III)}} = \delta^{53}\text{Cr} - \delta^{53}\text{Cr} \approx 1000 \ln \alpha. \quad (3)$$

Because  $\alpha$  values typically deviate only slightly from 1, the  $\varepsilon$  notation is often adopted for convenience:

$$\varepsilon = (\alpha - 1) \times 1000. \quad (4)$$

Studies of mass-dependent Cr isotopic fractionation began with its application to quantify the reduction of Cr(VI) contaminants [16]. Subsequent applications to trace atmospheric oxygenation further stimulated research on the geochemical cycling of Cr in natural environments [17]. Detailed description of Cr isotopic fractionation mechanisms and their applications in Cr cycling can be found in several review papers

[4,8,15,18]. However, recent detailed investigations of Cr cycles in both modern and geological times have substantially revised interpretations of Cr isotopic data. In this review, we will focus on the recent advancement in understanding the promises and pitfalls associated with applying Cr isotopes to trace oxygen dynamics in Earth's atmosphere and oceans and to trace the transportation and fate of industrial Cr(VI) contaminants in the environment.

## CR ISOTOPIC FRACTIONATION MECHANISMS IN LOW-TEMPERATURE PROCESSES

A more detailed review on the Cr isotopic fractionation mechanisms can be found in Qin and Wang [15] and thus will be only briefly discussed in the following.

(1) Equilibrium Cr isotopic fractionation. Equilibrium Cr isotope fractionation between Cr(VI) and Cr(III) depends on differences in bonding environments. Both theoretical calculations and laboratory experiments indicate that the equilibrium fractionation between these two redox states can be substantial [19], with laboratory experiments constraints of equilibrium Cr isotopic fractionation (between  $\text{CrO}_4^{2-}$  and  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  at 25 °C,  $\Delta^{53}\text{Cr}_{\text{VI-III}}$ ) to be  $5.8\text{‰} \pm 0.5\text{‰}$  [20]. Isotopic fractionation may also arise among Cr species of the same oxidation state when their ligand environments differ [19]. Isotopic equilibration between Cr(III) and Cr(VI) occurs through multi-step electron exchange reactions that require transient changes in oxidation states and bonding environments. These processes are kinetically sluggish, particularly under room temperature and near-neutral conditions, with equilibration timescales ranging from months to thousands of years [20]. The low solubility of Cr(III) further limits isotope exchange to the surface of Cr(III)-compounds. As a result, equilibrium fractionation rarely dominates Cr isotope fractionation in surface environments, where kinetic effects associated with largely irreversible redox transformations typically prevail.

(2) Reduction of Cr(VI). The most-well studied and pronounced Cr isotopic fractionation is associated with the reduction of Cr(VI) to Cr(III). In natural environments, Cr(VI) can be reduced through both abiotic and biotic pathways. Abiotic reduction is mainly mediated by various inorganic and organic species, including sulfides, Fe(II), zero-valent iron, and natural organic matter [14,21–23]. Biotic reduction is predominantly driven by microorganisms that tolerate Cr toxicity, via co-metabolic processes, whereas in anoxic, organic-rich settings, some metal-reducing bacteria can directly couple Cr(VI) reduction to energy metabolism [24,25]. Reduction may occur intracellularly through enzymatic pathways or extracellularly via electron transfer mechanisms [26].

Reduction of Cr(VI) requires the breaking of Cr–O bonds. Because bonds involving light Cr isotopes have higher zero-point energies and vibrational frequencies, they are more easily broken than those involving heavy isotopes. As a result, light Cr isotopes preferentially participate in reduction reactions and become enriched in the reduced Cr(III) products. The newly formed Cr(III) typically precipitates or is immobilized, limiting back-reaction and rendering the process unidirectional. Consequently, the isotopic fractionation is commonly described by a Rayleigh fractionation model:

$$\delta^{53}\text{Cr} = \left[ \left( \delta^{53}\text{Cr}_0 + 1000 \right) \times f^{(\alpha-1)} \right] - 1000, \quad (5)$$

where  $\delta^{53}\text{Cr}$  and  $\delta^{53}\text{Cr}_0$  represent the Cr isotopic composition at a certain sampling time and the initial isotopic composition of the reactant, respectively, and  $f$  represents the fraction of remaining Cr(VI).

Batch and column experiments investigating abiotic Cr(VI) reduction have reported a broad range of Cr isotopic fractionation factors associated with different reductants, including Fe(II)-bearing minerals, acidified  $\text{H}_2\text{O}_2$ , and humic substances. Reported fractionation factors (expressed as  $\epsilon$ ) span from  $-0.2\text{‰}$  to  $-5\text{‰}$ , with most values clustering between  $-2\text{‰}$  and  $-4\text{‰}$  (Table 1, [9,10,12,14,16,20,27–55]). The results consistently indicate that faster reduction kinetics tend to produce smaller isotopic fractionation. The diversity in fractionation factors among different reductants has been explained by the rate constant of electron transfer, which reflects the free energy of the redox reaction, derived from Marcus electron transfer theory. More specifically, the magnitude of kinetic fractionation should decrease with the standard free energy of the reaction, leading to smaller isotopic fractionation for faster reduction [56,27].

Biotic reduction of Cr(VI) also yields a wide range of isotopic fractionation factors, from  $-0.4\text{‰}$  to  $-7.6\text{‰}$  (Table 1). Variability reflects sensitivity to environmental and biological parameters, including temperature, pH, electron donor type and concentration, initial Cr(VI) concentration, metabolic mode (aerobic versus anaerobic), and microbial species. Additionally, Cr isotopic fractionation during biological reduction does not always follow a simple Rayleigh model. A two-stage fractionation behavior has been identified, in which early stages with high Cr(VI) bioavailability were dominated by enzymatic control and large  $\epsilon$  values, whereas later stages become transport-limited, suppressing fractionation [28].

In natural environments, Cr isotopic fractionation factors are commonly much smaller than those determined under laboratory conditions, largely due to transport-limited suppression effects, also called the reservoir effect [15]. In such settings, the dissolved Cr(VI) pool is separated from the reductant and should be transported across a non-reactive diffusion zone before reduction can occur. Under these circumstances, isotopic discrimination during Cr(VI) reduction is strongly influenced by the effective availability of Cr(VI) at the reaction interface, which leads to partial suppression of isotopic fractionation. As a result, the apparent Cr isotopic fractionation factor decreases with increasing Cr(VI) reduction rates and/or decreasing diffusion rates across the non-reactive zone [10,57,29].

(3) Oxidation of Cr(III). Chromium isotopic fractionation during the oxidation of Cr(III) remains far less well constrained than that of Cr(VI) reduction. Only a few studies have addressed this process, and most of them are conference papers without detailed results. Manganese oxides represent the most important oxidants of Cr(III) in natural environments, with reported experimental Cr isotopic fractionation ranging from  $-2.7\text{‰}$  to  $+3.2\text{‰}$  [30–33,58]. The oxidation of Cr(III) is thought to be a complex process that likely involves transient Cr(IV) or Cr(V) intermediate species [15]. In addition, both isotopic exchange effects, which tend to enrich heavy isotopes in Cr(VI), and kinetic isotope effects, in which lighter isotopes react preferentially and yield isotopically lighter Cr(VI), may operate simultaneously. The net isotopic fractionation during Cr(III) oxidation is therefore sensitive to multiple factors, such as the crystal structures of Mn oxides ( $\beta\text{-MnO}_2$ ,  $\delta\text{-MnO}_2$ ), the Cr(III) species, and pH conditions. Hydrogen peroxide can also oxidize Cr(III) under alkaline conditions, producing Cr isotopic fractionation factors of approximately  $+0.2\text{‰}$  to  $+0.6\text{‰}$  [34].

(4) Redox-independent processes. Although Cr isotopic fractionations during redox transformations between different Cr oxidation states are predominant, non-redox processes have also been shown to result in measurable isotopic fractionation. Dissolution of Cr(III)-bearing solid phases (Cr hydroxides, silicates, chromite) mediated by organic ligands and siderophores can generate both positive and negative  $\Delta^{53}\text{Cr}_{\text{solution–solid}}$  values, ranging from  $-0.96\text{‰}$  to  $2.14\text{‰}$  [35–37]. Kinetic isotopic fractionation has also been reported during transformations of aqueous Cr(III)-Cl- $\text{H}_2\text{O}$  complexes [59]. Adsorption of both Cr(VI) and

**Table 1** Chromium isotopic fractionation induced by different processes determined by laboratory experiments

| Experiment                                                                      | Model                 | Fractionation $\varepsilon$ (‰)                       | Reference |
|---------------------------------------------------------------------------------|-----------------------|-------------------------------------------------------|-----------|
| <b>Isotope exchange</b>                                                         |                       |                                                       |           |
| Aqueous Cr(VI)–Cr(III) (60 °C)                                                  | Equilibrium           | 5.2 ( $\Delta^{53}\text{Cr}$ )                        | [20]      |
| Aqueous Cr(VI)–Cr(III) (40 °C)                                                  |                       | 5.5 ( $\Delta^{53}\text{Cr}$ )                        |           |
| Aqueous Cr(VI)–Cr(III) (25 °C) (extrapolating)                                  |                       | 5.8 ( $\Delta^{53}\text{Cr}$ )                        |           |
| <b>Abiotic Reduction</b>                                                        |                       |                                                       |           |
| Magnetite, sediment slurries                                                    | Rayleigh              | –3.5                                                  | [16]      |
| Sediment slurry                                                                 | Rayleigh              | –2.4 to –3.1                                          | [29]      |
| H <sub>2</sub> O <sub>2</sub>                                                   | Rayleigh              | –4.2 to –5                                            | [34]      |
| H <sub>2</sub> O <sub>2</sub> (Strong acidic)                                   | Equilibrium?          | –3.5                                                  |           |
| Fe(II)-doped goethite                                                           | Rayleigh              | –3.9                                                  | [44]      |
| FeS                                                                             |                       | –2.1                                                  |           |
| Green rust                                                                      |                       | –2.7                                                  |           |
| Siderite                                                                        |                       | –2.8                                                  |           |
| Hanford sediments                                                               |                       | –3.3                                                  |           |
| Dissolved Fe(II)                                                                | Rayleigh              | –1.5 to –3.6                                          | [10]      |
| Dissolved Fe(II)                                                                | Rayleigh              | –4.2                                                  | [9]       |
| Organic acids (Elliot fulvic acid, Waskish humic acid, Mandelic acid)           |                       | –3.1                                                  |           |
| Montmorillonite and nontronite                                                  | Rayleigh              | –1.3 to –4.9                                          | [45]      |
| Fe(II)-organic (citrate, nitrilotriacetate, salicylate)                         | Rayleigh              | –2.8 to –3.6                                          | [27]      |
| Organic carbon                                                                  | Rayleigh              | –3.5                                                  | [46]      |
| Zero-valent iron                                                                | Reactive transport    | –0.2 to –1.5                                          | [14]      |
| <b>Biotic Reduction</b>                                                         |                       |                                                       |           |
| <i>Shewanella oneidensis</i> strain MR-1 (various electron donor conc.)         | Rayleigh              | –1.8 to –4.2                                          | [12]      |
| <i>Pseudomonas stutzeri</i> RCH2 (aerated)                                      | Rayleigh              | –2.0                                                  | [47]      |
| <i>Pseudomonas stutzeri</i> RCH2 (denitrifying)                                 |                       | –0.4                                                  |           |
| <i>Geobacter sulfurreducens</i>                                                 | Rayleigh              | –3.0                                                  | [48]      |
| <i>Shewanella sp. (NR)</i>                                                      |                       | –2.2                                                  |           |
| <i>Pseudomonas stutzeri</i> DCP-Ps1                                             |                       | –3.1                                                  |           |
| <i>Desulfovibrio vulgaris</i>                                                   |                       | –3.0                                                  |           |
| <i>Bacillus sp. QH-1</i> (various glucose conc. and T)                          | Rayleigh              | –1.9 to –7.6                                          | [49]      |
| Methane-based hollow-fiber membrane biofilm reactor                             | Rayleigh              | –2.6                                                  | [50]      |
| <i>Shewanella oneidensis</i> strain MR-1 (different respiratory pathway)        | Rayleigh              | –2.4 to –2.7                                          | [51]      |
| <i>Pseudomonas</i> (various electron donor types and pHs; aerobic or anaerobic) | Rayleigh              | –1.6 to –5.0                                          | [52]      |
| <i>Shewanella</i> with succinate (aerobic or anaerobic)                         |                       | –2.5 to –3.4                                          |           |
| <i>Shewanella oneidensis</i> strain MR-1 (various pH & T)                       | Rayleigh (Two stages) | –2.4 to –3.0 (Early)<br>–0.9 to –1.1 (Late)           | [28]      |
| Extremely thermophilic bacterium <i>Caldicellulosiruptor saccharolyticus</i>    | Rayleigh              | –2.5 to –3.6                                          | [53]      |
| <i>Pseudomonas fluorescens</i> LB 300 with various Fe(II) materials             | Rayleigh              | –3.0 to –4.3                                          | [54]      |
| <i>Shewanella oneidensis</i> MR-1 with various Fe(II) materials                 |                       | –2.1 to –2.3                                          |           |
| <b>Oxidation</b>                                                                |                       |                                                       |           |
| Birnessite ( $\delta$ -MnO <sub>2</sub> )                                       | Unkown                | –2.5 to +0.7 ( $\delta^{53}\text{Cr}_{\text{VI}}$ )   | [30]      |
| Pyrolusite ( $\beta$ -MnO <sub>2</sub> )                                        | Unkown                | up to +1.0 ( $\delta^{53}\text{Cr}_{\text{VI}}$ )     | [55]      |
| Birnessite ( $\delta$ -MnO <sub>2</sub> )                                       | Unkown                | –0.5 to 0 ( $\Delta^{53}\text{Cr}_{\text{VI-III}}$ )  | [32]      |
| H <sub>2</sub> O <sub>2</sub>                                                   | Rayleigh              | +0.2 to +0.6                                          | [34]      |
| Pyrolusite ( $\beta$ -MnO <sub>2</sub> )                                        | Unkown                | +3.2 (equilibrium model)<br>+4.2 (Rayleigh model)     | [33]      |
| Birnessite ( $\delta$ -MnO <sub>2</sub> )                                       | Rayleigh              | +0.3                                                  |           |
| Coupled microbial Mn(II) and Cr(III) oxidation                                  | Unkown                | Up to +0.8 ( $\Delta^{53}\text{Cr}_{\text{VI-III}}$ ) | [31]      |

(To be continued on the next page)

(Continued)

| Experiment                                                      | Model       | Fractionation $\varepsilon$ (‰)                                           | Reference |
|-----------------------------------------------------------------|-------------|---------------------------------------------------------------------------|-----------|
| <b>Adsorption</b>                                               |             |                                                                           |           |
| Cr(VI) onto $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , goethite | Equilibrium | ~0                                                                        | [39]      |
| Cr(VI) onto kaolin (river water)                                | Equilibrium | -0.3 ( $\Delta^{53}\text{Cr}$ )                                           | [38]      |
| Cr(VI) onto $\delta$ -MnO <sub>2</sub>                          | Equilibrium | -0.9 ( $\Delta^{53}\text{Cr}$ )                                           | [40]      |
| Cr(III) onto soils and river sediments                          | Unknown     | -0.1 to -1.0                                                              | [41]      |
| <b>Dissolution</b>                                              |             |                                                                           |           |
| Cr(III)-(oxy)hydroxide by organic acids and siderophores        | Unknown     | -0.2 to +1.2<br>( $\Delta^{53}\text{Cr}_{\text{liquid-starting solid}}$ ) | [35]      |
| Silicates and chromitite leached by DFOB and citric acid        | Unknown     | -0.1 to +2.2<br>( $\Delta^{53}\text{Cr}_{\text{liquid-starting solid}}$ ) | [36]      |
| Soils/sediments by citric and oxalic acids                      | Unknown     | -1.0 to +0.3<br>( $\Delta^{53}\text{Cr}_{\text{liquid-starting solid}}$ ) | [37]      |
| <b>Coprecipitation</b>                                          |             |                                                                           |           |
| Cr(VI) with calcium carbonates (rapid & slow precipitation)     | Unknown     | +0.1 to +0.3<br>( $\Delta^{53}\text{Cr}_{\text{calcite-solution}}$ )      | [43]      |
| Cr(VI) with calcium carbonates (various pH)                     | Unknown     | -0.7 to +0.1<br>( $\Delta^{53}\text{Cr}_{\text{calcite-solution}}$ )      | [42]      |

Cr(III) onto minerals can induce Cr isotopic fractionation. Adsorption of Cr(VI) onto goethite,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and kaolinite produced negligible or small equilibrium fractionation, whereas kinetic effects under non-equilibrium conditions can result in large transient isotopic fractionation  $-0.70\text{‰}$  ( $10^3 \ln \alpha_{\text{adsorb-solution}}$ ) [38,39]. In contrast, adsorption of Cr(VI) onto Mn-oxides represents the only case in which a large equilibrium fractionation has been observed, with  $\Delta^{53}\text{Cr}_{\text{adsorb-solution}}$  values of approximately  $-0.90\text{‰}$  [40]. For Cr(III), preliminary studies indicate that adsorption onto soils and river sediments yields fractionation ranging from  $-0.06\text{‰}$  to  $-0.95\text{‰}$  ( $10^3 \ln \alpha_{\text{adsorb-solution}}$ ), although the underlying fractionation mechanisms require further investigation [41]. In addition, carbonate precipitation can induce Cr isotopic fractionation, with Cr(VI) coprecipitation experiments showing variable fractionation controlled by Cr(VI) concentration and solution pH, resulting in enrichment of either heavy or light Cr isotopes in the solid phase under different conditions ( $\Delta^{53}\text{Cr}_{\text{precipitation-solution}}$  from  $-0.70\text{‰}$  to  $+0.29\text{‰}$ ) [42,43].

## TRACING THE FATE OF ANTHROPOGENIC CR USING CR ISOTOPES

The first important application of stable Cr isotopes was to trace the reduction and attenuation of anthropogenic Cr(VI) contaminants (Figure 1) [16]. Because Cr(VI) is highly toxic and mobile, evaluating its removal efficiency in aquatic systems is a critical aspect of environmental monitoring and remediation. A wide range of remediation strategies have been implemented at contaminated sites, most of which aim to reduce Cr(VI) to Cr(III), a less toxic and poorly soluble form [60]. Assessing the effectiveness of these reduction-based remediation approaches, however, requires more refined constraints. Traditional monitoring of Cr(VI) contamination relies primarily on measuring Cr(VI) concentrations. Such measurements can be strongly influenced by multiple geochemical processes, including dilution by uncontaminated water and adsorption onto mineral surfaces. Importantly, these processes do not involve redox transformation, and adsorbed Cr(VI) may be readily remobilized or reconcentrated, posing a risk of recurrent environmental

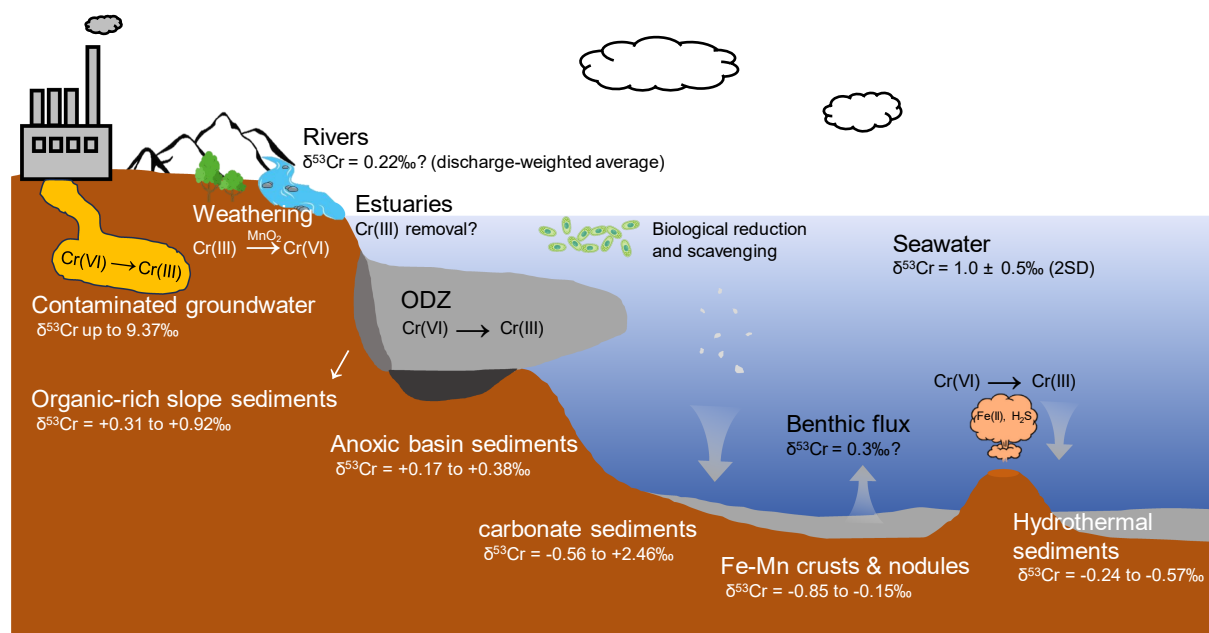


**Figure 1** Schematic illustration of Cr cycling at Earth's surface and the Cr isotopic compositions of major reservoirs. Modified after Janssen *et al.* [4].

contamination. In contrast, the large isotopic fractionation associated with Cr(VI) reduction, combined with negligible to minor fractionation during dilution and adsorption, provides an additional and independent constraint for tracking the fate of anthropogenic, and potentially natural, Cr(VI) in environments [8,16,29,61–69].

### Estimating the reduction degree of Cr(VI) contaminants using Cr isotopes

Estimation of the reduction extent of Cr(VI) contaminants using Cr isotopes is based on the Rayleigh isotopic fractionation model (Eq. (5)). This model has been shown applicable during Cr(VI) reduction by a wide range of natural and artificial reductants under experimental conditions, although additional uncertainties may arise in natural systems. According to the Rayleigh model, if  $\delta^{53}\text{Cr}_0$  and  $\alpha$  are independently constrained, measurements of  $\delta^{53}\text{Cr}$  can be used to quantify the extent of Cr(VI) reduction ( $f$ ).

Anthropogenic Cr(VI) is predominantly associated with industrial activities such as electroplating, leather tanning, and corrosion protection. The Cr used in these applications is commonly derived from chromite ores, and industrial processing generally involves near-complete oxidation of Cr with minimal isotopic fractionation. Analyses of industrial-grade  $\text{CrO}_3$  indicated a mean  $\delta^{53}\text{Cr}$  value close to 0.0‰ [70]. Furthermore, industrial processes including hard plating, decorative plating, chromating, and anodizing typically generate Cr(VI)-bearing solutions with limited isotopic variability, generally yielding  $\delta^{53}\text{Cr}$  values between 0–1‰ [16,70]. This range is therefore considered a reasonable estimate for the initial isotopic composition ( $\delta^{53}\text{Cr}_0$ ) of anthropogenic Cr(VI) contaminants.

Once released into natural environments, Cr(VI) may be reduced by a variety of natural and artificial reductants, including Fe(II)-bearing materials, sulfides, organic matter, and various microbial pathways.

However, isotopic fractionation factors associated with Cr(VI) reduction by these reductants are highly variable (Table 1), introducing significant uncertainty into the estimation of reduction fraction. For site-specific applications, such as contaminated aquifers, laboratory batch experiments using indigenous natural reductants can help constrain intrinsic fractionation factors [16]. A further complication arises from the fact that the Rayleigh fractionation model assumes a closed system, an assumption rarely met in natural contaminated settings. In groundwater systems, reductants are typically heterogeneously distributed, requiring Cr(VI) to be transported by advection or diffusion to reactive zones prior to reduction. Artificial remediation approaches, such as permeable reactive barriers placed across groundwater flow paths [44], represent even more typical examples of non-in-situ reduction. Under such conditions, transport processes preceding reduction can partially mask isotopic fractionation through reservoir effects, resulting in smaller apparent fractionation factors. Consequently, accurate estimation of Cr(VI) reduction extents using Cr isotopes critically depends on the ability to reliably constrain the effective isotopic fractionation factors operating at a given site.

### Applications in natural environments and associated challenges

Pioneering work by Ellis *et al.* [16] analyzed groundwater samples from contaminated sites in California and Connecticut. By combining field observations with isotopic fractionation factors determined from laboratory Cr(VI) reduction experiments, they inferred substantial reduction of Cr(VI) initially present in contaminated groundwater [16]. Direct evidence for the coupled Cr(VI) reduction and enrichment of heavy Cr isotopes was subsequently reported from a comprehensive study of an urban Cr(VI) plume in Berkeley, USA [29]. Multi-year monitoring of groundwater wells surrounding the contaminated plume revealed a systematic increase in  $\delta^{53}\text{Cr}$  values along the flow path, consistent with progressive Cr(VI) reduction. The covariation between Cr(VI) concentrations and Cr isotopic compositions could be described using a Rayleigh isotopic fractionation model with an effective fractionation factor that integrates intrinsic fractionation determined from incubations of indigenous sediments and accounts for reservoir effects [29]. These results support the application of Cr isotopes for quantifying Cr(VI) reduction in natural groundwater systems.

Chromium isotope studies have also demonstrated that decreases in Cr(VI) concentrations in contaminated groundwater can reflect the combined effects of reduction and dilution. By integrating Cr(VI) concentration measurements, Cr isotope analyses, and laboratory incubation experiments to constrain intrinsic fractionation factors, Ceballos *et al.* [71] identified the joint contributions of Cr(VI) reduction and dilution by uncontaminated groundwater to declining Cr(VI) concentrations. Using a Rayleigh fractionation model, they estimated that more than 60% of the Cr(VI) had been reduced at the studied site [71].

In natural environments, oxidative weathering of Cr(III)-bearing minerals and rocks can also generate Cr(VI), which may mix with anthropogenic Cr(VI) inputs, further complicating the monitor of Cr(VI) contamination [69]. In regions dominated by ultramafic rocks and serpentinites, geogenic Cr(VI) concentrations can be sufficiently high to exceed contamination thresholds [72]. In practice, the two-endmember mixing model has been commonly invoked to describe the evolution of both Cr(VI) concentrations and Cr isotopic compositions in such systems [62,73]. However, the isotopic composition of geogenic Cr(VI) itself can be highly variable, reflecting isotopic fractionation during oxidative weathering of Cr(III) minerals as well as partial reduction of Cr(VI) following its formation. For example, Farkaš *et al.* [74] reported  $\delta^{53}\text{Cr}$  values

ranging from 2.48‰ to 3.96‰ in stream waters draining ultramafic rocks, which may reflect some extent of partial Cr(VI) reduction and the associated enrichment of heavy Cr isotopes in the dissolved phase. Izbicki *et al.* [68] conducted a survey of groundwater in the Mojave Desert, USA, revealing a wide range of natural geogenic  $\delta^{53}\text{Cr}$  values (0.7‰–3.1‰, average ~1.7‰), whereas industrial Cr sources typically exhibit near-zero  $\delta^{53}\text{Cr}$  signatures (e.g., ~−0.1‰), allowing source discrimination. In these systems, trends of increasing  $\delta^{53}\text{Cr}$  values coupled with decreasing Cr(VI) concentrations indicate substantial Cr(VI) reduction. However, mixing between natural and anthropogenic Cr sources often obscures the  $\delta^{53}\text{Cr}$ –Cr(VI) concentration relationships, highlighting both the utility and complexity of Cr isotopes in environmental applications. Similarly, diverse  $\delta^{53}\text{Cr}$  values of natural Cr(VI) up to ~3.9‰ have been reported from Central European waters [75]. The study further suggested that anthropogenic Cr(VI) may exhibit systematically higher  $\delta^{53}\text{Cr}$  values than geogenic Cr(VI), potentially reflecting differences in dominant fractionating processes (reduction vs. oxidation). Nevertheless, substantial overlap between the  $\delta^{53}\text{Cr}$  ranges of geogenic and anthropogenic Cr(VI) commonly limits unambiguous source identification and complicates quantitative estimates of Cr(VI) reduction.

Taken together, the evolution of Cr isotopic compositions in anthropogenic Cr(VI)-contaminated systems can be broadly described by three principal processes, as illustrated in Figure 2. First, reduction of Cr(VI) is accompanied by significant Cr isotopic fractionation, resulting in elevated  $\delta^{53}\text{Cr}$  values and decreasing Cr(VI) concentrations. The relationship between them follows the Rayleigh isotopic fractionation model and appears as a linear trend in cross-plots of  $\delta^{53}\text{Cr}$  versus the logarithm of Cr(VI) concentration. Second, dilution of contaminated groundwater by uncontaminated water decreases Cr(VI) concentrations without affecting Cr isotopic compositions. Adsorption of Cr(VI) onto mineral surfaces likely induces negligible isotopic fractionation and therefore produces trends similar to dilution, although short-timescale systems that do not reach isotopic equilibrium (e.g., orders of a few days) may exhibit kinetic effects [39]. Third, mixing between anthropogenic and geogenic Cr(VI) follows a two-endmember mixing line, producing curved trends in  $\delta^{53}\text{Cr}$ –Cr(VI) concentration crossplot (Figure 2). Uncertainties in applying these models mainly arise from difficulties in constraining effective isotopic fractionation factors and from the wide variability in both concentrations and isotopic compositions of natural geogenic Cr(VI).

## NATURAL (BIO)GEOCHEMICAL CYCLING OF CR AND ITS ISOTOPIC FRACTIONATION IN EARTH'S SURFACE ENVIRONMENTS

The natural biogeochemical cycling of Cr has recently been comprehensively reviewed by Janssen *et al.* [4], providing a detailed synthesis of Cr pathways from sources to sinks in modern surface environments. Here, we just briefly summarize the key features of natural Cr cycling (Figure 1).

(1) Weathering. In unweathered crustal materials, Cr is predominantly present as Cr(III) within silicates and oxides, where it has very low solubility and mobility. The Cr isotopic compositions of high-temperature igneous reservoirs are remarkably uniform, with compiled values of  $-0.12\text{‰} \pm 0.10\text{‰}$  for bulk silicate Earth (BSE) [76,77]. Oxidative weathering of Cr(III) by the Mn-oxides in soils and regolith is the key process enabling Cr mobilization. Weathering profiles exhibit a wide range of  $\delta^{53}\text{Cr}$  values, from  $-1.29\text{‰}$  to  $0.89\text{‰}$ , reflecting large intra-profile isotopic variabilities [78–85]. Notably, most weathering regolith samples display

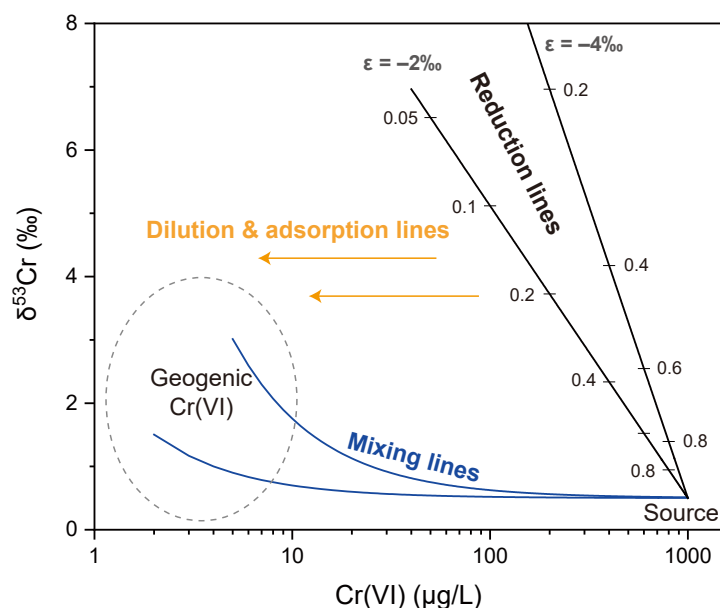


**Figure 2** Cross-plot of  $\delta^{53}\text{Cr}$  values versus the logarithm of  $\text{Cr(VI)}$  concentrations to illustrate the evolution of Cr isotopic compositions in anthropogenic  $\text{Cr(VI)}$ -contaminated systems. The contaminated source water is assumed to have a  $\delta^{53}\text{Cr}$  value of 0.5‰ and a  $\text{Cr(VI)}$  concentration of 1000  $\mu\text{g/L}$ . Reduction of  $\text{Cr(VI)}$  follows a Rayleigh isotopic fractionation model, represented by linear trends in the cross-plot; numbers along the lines indicate the fraction of  $\text{Cr(VI)}$  remaining. Dilution by uncontaminated freshwater and adsorption decrease  $\text{Cr(VI)}$  concentrations with minimal impact on  $\delta^{53}\text{Cr}$  values. Mixing with geogenic  $\text{Cr(VI)}$  produces curved trajectories.

$\delta^{53}\text{Cr}$  values lower than the high-temperature igneous reservoir, showing that the regolith acts as the primary source that generates isotopically heavy dissolved Cr, which is subsequently exported to aquatic systems.

(2) Rivers. Rivers integrate Cr released from the weathering regolith and represent a major external source of Cr to the oceans. Global riverine datasets show  $\delta^{53}\text{Cr}$  values ranging from  $-0.65\text{‰}$  to  $1.73\text{‰}$ , with most values higher than the high-temperature igneous reservoir [79,80,85–88]. This pattern is consistent with the preferential mobilization and export of isotopically heavy Cr during oxidative weathering. Based on currently available data, the discharge-weighted average  $\delta^{53}\text{Cr}$  value of riverine input is approximately  $+0.22\text{‰}$ , although this estimate will likely require revision when additional river datasets become available [4]. Variations in riverine  $\delta^{53}\text{Cr}$  values are controlled by multiple factors, including climate conditions (such as temperature and precipitation), discharge, catchment lithology, and the presence of dissolved organic matter.

(3) Estuaries. Estuaries represent a critical transition zone where riverine Cr is transferred to the ocean and its isotopic composition is further modified. In estuaries, Cr behavior is complex, with both conservative and non-conservative mixing observed.  $\text{Cr(VI)}$  often behaves conservatively during estuarine mixing, while Cr (III) is susceptible to scavenging onto particulates, particularly at low salinities [89,90]. In some settings, estuarine processes involve both  $\text{Cr(VI)}$  reduction and  $\text{Cr(III)}$  removal [91,92]. However, conservative mixing has also been reported [93], and variable riverine endmember compositions can obscure non-conservative signals. Overall, estuaries likely reduce total riverine Cr fluxes to the ocean through preferential removal of  $\text{Cr(III)}$ , which tends to be isotopically lighter, thereby increasing the  $\delta^{53}\text{Cr}$  of the remaining dissolved Cr flux. Despite these insights, the net impact of estuarine processes on global Cr fluxes and isotopic compositions remains poorly constrained, especially for major rivers, causing uncertainties in the marine Cr budget.

(4) Oceans. The Cr isotopic composition of modern seawater is almost exclusively positive, with most reported  $\delta^{53}\text{Cr}$  values clustering between 0.7‰ and 1.2‰ [94–107], which is consistent with the dominant input of isotopically heavy Cr derived from oxidative weathering. Chromium concentrations in the ocean display a nutrient-type vertical profile, with lower concentrations in surface waters and higher concentrations at depth, potentially reflecting biological uptake in the surface ocean and release at depth. At the global scale, seawater  $\delta^{53}\text{Cr}$  values show a clear negative correlation with dissolved Cr concentrations, exhibiting a closed-system Rayleigh-type relationship with an effective fractionation factor ( $\epsilon$ ) of approximately  $-0.7\text{‰}$  [4,97,108]. This relationship does not reflect a single controlling process but rather integrates the combined effects of Cr(VI) reduction in oxygen deficient zones (ODZs), biological uptake, benthic fluxes of Cr from sediments, and large-scale water-mass mixing [4]. Regional redox cycling can generate pronounced local  $\delta^{53}\text{Cr}$  anomalies that deviate from the global  $\delta^{53}\text{Cr}$ –Cr concentration trend [98]. Direct observations have confirmed the reduction of Cr(VI) and sequestration of Cr(III) within ODZ waters, which contribute significantly to Cr isotopic fractionation in the ocean, although neither Cr(VI) reduction nor Cr(III) scavenging is quantitative [103,109]. The global oceanic Cr mass balance remains insufficiently constrained [4]. Rivers are thought to be the largest input; however, the global averaged riverine  $\delta^{53}\text{Cr}$  value is poorly constrained due to limited data from major rivers worldwide. In addition, benthic flux of Cr from the seafloor has recently been identified as an important source of Cr to seawater, although the isotopic composition of this flux also remains poorly constrained [4,110,111]. Other sources, such as atmospheric deposition, contribute minimally to the global Cr inputs. The major sinks of Cr in the modern ocean are suggested to be oxygen-deficient, organic-rich sediments, particularly those associated with ODZs, which together account for  $\sim 98\%$  of total Cr burial [4]. Anoxic basins contribute only  $\sim 2\%$  of the total sink due to their limited spatial extent, whereas other sinks, such as oxic sediments and carbonates, are considered negligible [4]. Detailed calculations and associated uncertainties for the Cr mass balance can be found in Janssen *et al.* [4].

## APPLICATION OF CR ISOTOPES TO THE RECONSTRUCTION OF OXYGEN DYNAMICS IN EARTH’S ANCIENT ATMOSPHERE AND OCEANS

### Framework of the Cr isotopic paleo-proxy for atmospheric oxygenation

The application of Cr isotopes as a paleo-proxy for atmospheric oxygenation is based on the assumption that Cr isotopic fractionation is primarily associated with oxidative Cr cycling [17]. Under sufficiently elevated atmospheric oxygen levels,  $\text{O}_2$  promotes the oxidation of Mn(II) and the formation of Mn-oxides, which can subsequently oxidize Cr(III) in rocks and minerals. Oxidative mobilization of Cr(III), together with potential partial back-reduction of Cr(VI) during transport, results in the enrichment of isotopically heavy Cr(VI) in the dissolved phase. This isotopically fractionated Cr(VI) can be transferred to the oceans and ultimately recorded as elevated  $\delta^{53}\text{Cr}$  values in various marine sediments [17]. Because high-temperature igneous rocks typically exhibit a narrow range of Cr isotopic compositions ( $-0.12\text{‰} \pm 0.10\text{‰}$ ) [76,77], sedimentary rocks with  $\delta^{53}\text{Cr}$  values deviating from this range have been interpreted as reflecting oxidative Cr cycling mediated by manganese oxides and then the presence of free oxygen in the atmosphere [17]. The oxygen threshold required to initiate an oxidative Cr cycle has been constrained using geochemical modeling. Crowe *et al.* [112] indicated that effective transport of Cr(VI) to the oceans requires the absence of Fe(II) in terrestrial

surface environments, as Cr(VI) would otherwise be rapidly and quantitatively reduced; this constraint implied a minimum atmospheric oxygen level of  $\sim 3 \times 10^{-4}$  present atmospheric level (PAL). In contrast, kinetic models of Cr(III) oxidation by Mn-oxides suggest that widespread Cr oxidation requires higher oxygen levels, on the order of  $\sim 0.001$ – $0.01$  PAL [113,114].

Current understanding of modern Cr cycling and associated isotopic fractionation, as summarized above, broadly supports this conceptual framework. However, recent detailed investigations of individual processes within the Cr cycle have revealed substantial complexity, raising questions about the fidelity of Cr isotopic signals preserved in sedimentary rocks. In the following sections, we critically evaluate the key assumptions underlying the Cr isotopic paleo-proxy by integrating insights from experimental simulations, modern environments, and direct assessments of sedimentary Cr isotopic records.

## Complexity of the Cr isotope paleo-proxy

### *Influence from non-redox Cr isotopic fractionation*

A fundamental assumption for the Cr isotope paleo-proxy framework is that Cr isotopic fractionation is solely caused by redox transformations between Cr(III) and Cr(VI), and therefore reflects the presence of an oxidative Cr cycle. However, as discussed above, redox-independent processes, including dissolution of Cr(III)-bearing solid phases by organic ligands and siderophores, and partial adsorption of Cr(III), can also produce elevated  $\delta^{53}\text{Cr}$  values in the dissolved phase [35,36,59,41]. This raises the possibility that deviations of sedimentary  $\delta^{53}\text{Cr}$  values from the narrow high-temperature igneous range may, in some cases, result from non-redox Cr(III) cycling without involvement of atmospheric oxygenation. Most studies, however, indicate that non-redox Cr isotopic effects are unlikely to generate systematic shifts in Cr isotopic compositions at large spatial or temporal scales [35,41]. First, the majority of Archean and early Proterozoic samples exhibit unfractionated  $\delta^{53}\text{Cr}$  values (Figures 3 and 4), suggesting limited influence from non-redox processes. Second, experimentally determined fractionation factors for non-redox processes are mostly small, with only occasional large fractionations [35–37,59,41]. As a result, their impact on averaged reservoirs, such as the open oceans, is likely limited, and non-redox fractionation may not fundamentally undermine the Cr isotope proxy framework. At the scale of regional profiles or depositional settings, however, non-redox fractionation cannot be neglected. In particular, Rayleigh distillation may amplify Cr isotopic deviations in residual phases even when isotopic fractionation factors are small. This effect may be especially relevant for paleosols, in which ligand-induced Cr isotope fractionation has been proposed to account for unusually high  $\delta^{53}\text{Cr}$  values, such as those reported from the  $\sim 1.85$  Ga Flin Flon paleosol [115].

### *Potential decoupling of Cr isotopic fractionation from oxygenation due to anaerobic formation of Mn oxides*

Early studies linked Cr isotopic fractionation to atmospheric oxygen on the basis that molecular  $\text{O}_2$  oxidizes Cr(III) via the catalysis of Mn oxides [17]. It should be emphasized, however, that Cr(III) is oxidized directly by Mn oxides rather than by  $\text{O}_2$  itself [6]. Although  $\text{O}_2$  and reactive oxygen species are generally considered the primary oxidants driving Mn(II) oxidation, alternative anaerobic pathways have been proposed. These include Mn oxidation mediated by anoxygenic photosynthetic microorganisms and photochemical oxidation

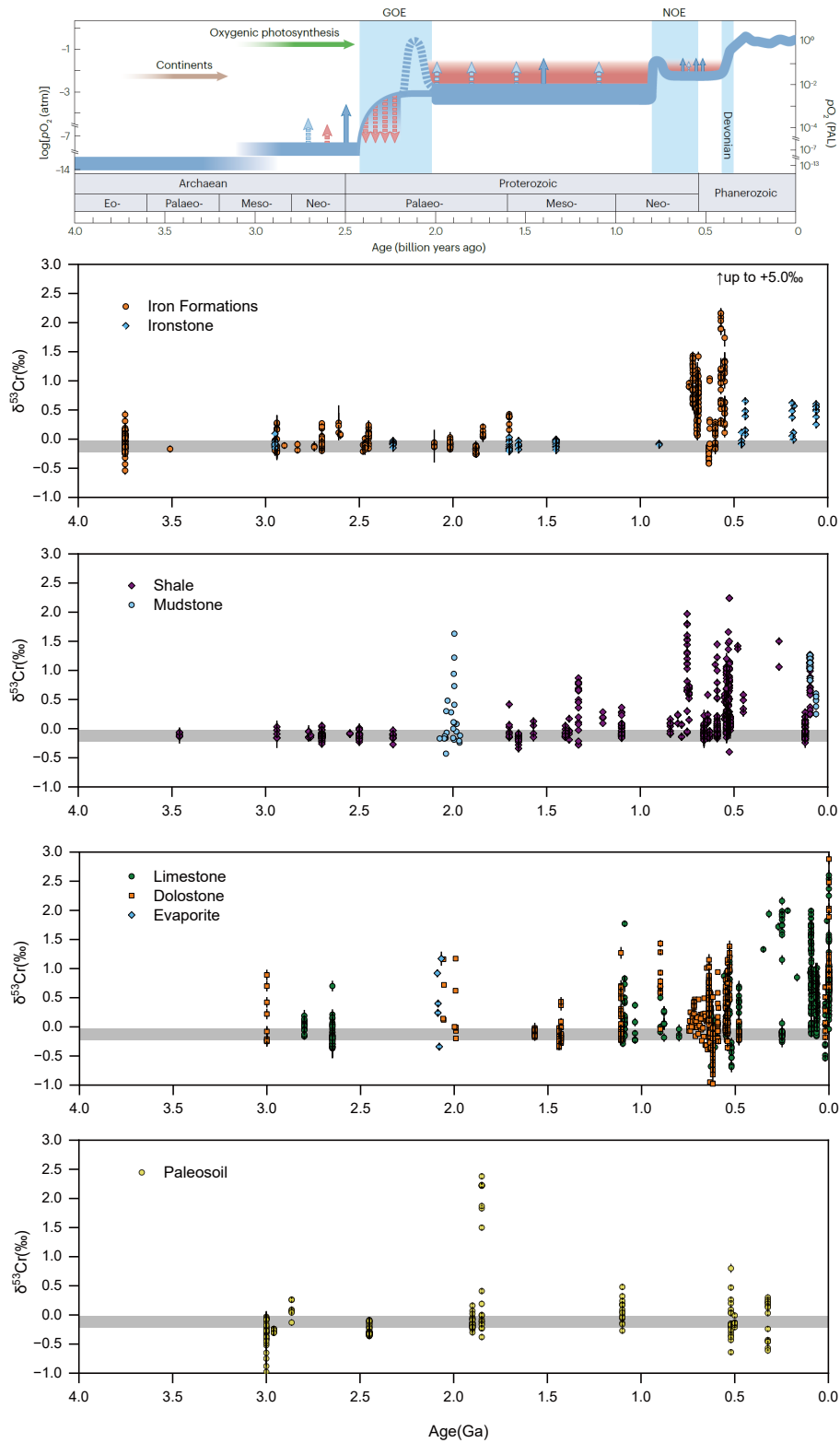


**Figure 3** Compilation of published  $\delta^{53}\text{Cr}$  data for sedimentary rocks [17,94,99,112–173]. The dataset is categorized into four groups: Fe-rich sediments (iron formations and ironstones), shales and mudstones, carbonates (limestones and dolomites) and evaporites, and paleosols. The atmospheric oxygen evolution curve is adopted from Lyons *et al.* [174].

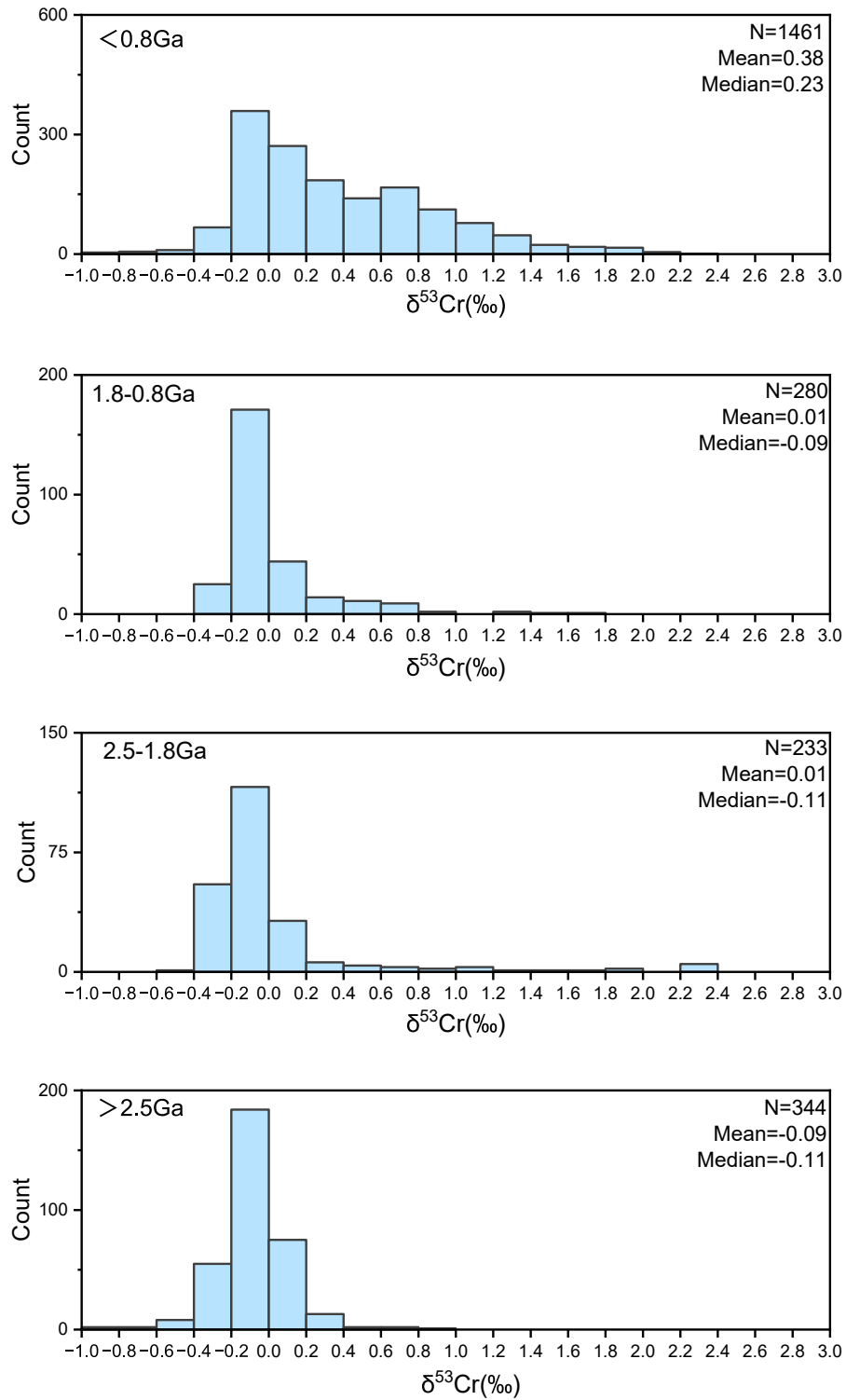


**Figure 4** Histograms of  $\delta^{53}\text{Cr}$  values for Fe-rich sediments, shales/mudstones, and carbonates/evaporites across major geological intervals: pre-GOE (>2.5 Ga), GOE and Paleoproterozoic (2.5–1.8 Ga), Mid-Proterozoic (1.8–0.8 Ga), and Neoproterozoic and beyond (<0.8 Ga). Samples older than 0.8 Ga predominantly cluster within the BSE range ( $\sim -0.2\text{‰}$  to  $0\text{‰}$ ). Note that unfractionated values are also common after 0.8 Ga.

of manganese carbonate minerals (rhodochrosite) [175,176]. Nevertheless, the environmental conditions required for these pathways, such as the widespread presence of rhodochrosite, may not be common on the early Earth [177]. Geochemical evidence from sedimentary successions relevant to early Mn cycling suggested that Mn oxides were most plausibly linked to oxygenated conditions rather than strictly anaerobic processes, although this issue remains an open question [178]. Consequently, the initiation of oxidative Cr cycling is tentatively interpreted to be most likely associated with the presence of O<sub>2</sub>.

### ***Atmospheric or oceanic oxygenation: What do Cr isotopes really reflect?***

Even if O<sub>2</sub> is required for Mn oxidation, its presence does not necessarily imply atmospheric oxygenation. Manganese oxides may form in local oxic marine environments under an anoxic atmosphere, thereby enabling Cr(VI) production independent of atmospheric O<sub>2</sub>. The existence of local oxygen oases, inferred by the presence of Mn oxides, in Archean oceans prior to the Great Oxidation Event (GOE) has been widely proposed and was commonly attributed to locally intense oxygenic photosynthesis [179–182]. Oxidative Cr cycling could therefore have occurred in such environments without a global oxygenated atmosphere. This interpretation is supported by observations from the modern ocean, where benthic fluxes are estimated to be an important Cr input to the ocean [4]. Both Cr(VI) and Cr(III) have been observed in pore water of modern marine sediments. Although there are no direct measurements of the Cr isotopic composition of pore water, geochemical observations suggested oxidative loss of Cr from sediments to bottom water, likely caused by Mn oxides within sediments and pore water [110,111]. In addition, microbial experiments demonstrate that Mn(II)-oxidizing bacteria can mediate coupled Mn(II) and Cr(III) oxidation, producing isotopically heavy Cr(VI) in seawater, although the positive fractionated  $\delta^{53}\text{Cr}$  values were only transiently observed in the experiments [31]. Therefore, positive Cr isotopic fractionation does not necessarily require atmospheric oxygenation and may instead be related to local oxygenation in marine environments.

### ***Sedimentary archives of seawater Cr isotopic composition***

Reconstructing Cr cycling through geological time requires sedimentary archives that reliably preserve the Cr isotopic composition of paleo-seawater. Suitable sedimentary records are therefore critical requirements for applying Cr isotopes as a paleo-redox proxy. Among the Cr isotope studies, banded iron formations (BIFs) or Fe-rich sediments, shales, and carbonates have received the most attention as potential archives of seawater  $\delta^{53}\text{Cr}$  values. However, insights from modern analogues, together with experimental constraints, indicate that none of these sedimentary materials directly and faithfully records the Cr isotopic composition of seawater. Instead, the Cr isotopic signatures preserved in these archives are influenced by complex depositional processes and diagenesis. As a result, deviations from seawater  $\delta^{53}\text{Cr}$  values may be caused by various mechanisms. Despite these complexities, sedimentary records can still provide valuable information on past Cr cycling when interpreted with well-constrained geological and geochemical backgrounds. In the following, we evaluate the strengths and limitations of the three most widely used sedimentary archives for Cr isotopes and discuss how their Cr isotopic records can be used to infer paleo-environmental conditions.

(1) Iron-rich sediments. Iron-rich sediments, particularly banded iron formations (BIFs), were among the first sedimentary archives applied in Cr isotope paleo-redox studies [17]. Early models proposed that, in the

depositional environments of iron formations, abundant dissolved Fe(II) could quantitatively reduce Cr(VI) to Cr(III), which would then be efficiently sequestered through coprecipitation of Fe-Cr hydroxides [17]. Under this assumption, dissolved Cr(VI) would be completely scavenged to sediments, and Cr isotopic fractionation would thereby be negligible, allowing BIFs to directly record the Cr isotopic composition of contemporaneous seawater. A similar mechanism was subsequently extended to other iron-rich sediments, such as Proterozoic and Phanerozoic ironstones [114].

However, observations from modern ferruginous (Fe(II)-rich) environments challenge this assumption. Bauer *et al.* [57] suggested that Cr(VI) reduction and sequestration in Fe-rich sediments are not quantitative, leading to significant isotopic offsets between dissolved Cr and ferruginous sediments, with reported  $\Delta^{53}\text{Cr}_{\text{water-sediments}}$  values ranging from 0.21‰ to 1.81‰. These offsets are influenced by both the Cr(VI) reduction fraction and the isotopic fractionation factor during reduction. Similar results have been reported from paired Cr isotope measurements of waters and sediments in redox-stratified lakes, where authigenic Cr in sediments is isotopically lighter than the overlying waters and falls within the bulk silicate Earth (BSE) range [183]. Quantifying Cr isotopic fractionation during the deposition of ferruginous sediments remains challenging, and experimental constraints derived from laboratory studies of Cr(VI) reduction by Fe(II) [10] cannot be directly applied to natural systems. Bauer *et al.* [57] suggested that the effective fractionation factor may be largely controlled by the oxygen penetration depth below the water-sediment interface, where oxygen penetration creates a non-reduction diffusion zone above the depth at which Cr(VI) reduction occurs. In such settings, reservoir effects may partially mask isotopic fractionation, potentially resulting in near-zero isotopic fractionation if the diffusion zone is sufficiently thick (>10 cm; [57]). Under these highly idealized conditions, ferruginous sediments could approximately record seawater Cr isotopic values. Nevertheless, there are no comparable natural examples reported, and insufficiently reducing conditions under such environments may further limit the accumulation of authigenic Cr, raising other problems such as detrital contamination (see next subsection).

Despite these limitations and uncertainties, the fact that Fe-rich sediments cannot directly record seawater  $\delta^{53}\text{Cr}$  values does not preclude their use as qualitative indicators of oxidative Cr cycling. Although BIFs and other Fe-rich sediments likely record lower  $\delta^{53}\text{Cr}$  values than the contemporaneous seawater, the magnitude of the isotopic offset is unlikely to remain constant, nor to consistently equal the difference between seawater and the BSE range, across different geological settings or over prolonged timescales. The presence of isotopically heavy Cr(VI) in seawater can still be inferred qualitatively from Fe-rich sedimentary rocks, particularly when evaluated across broad stratigraphic intervals rather than relying on limited sample sets. The prevalence of positive  $\delta^{53}\text{Cr}$  values in Phanerozoic and Neoproterozoic BIFs and ironstones, for example, strongly suggests the preservation of signals related to oxidative continental weathering [17,114,116,117].

Finally, the interpretation of Cr isotopic data from BIFs must consider their depositional types [184]. Algoma-type BIFs, which formed in association with submarine volcanism within predominantly anoxic marine settings, likely received minimal Cr from terrestrial weathering. In contrast, Superior-type BIFs, deposited on continental shelves, are more suitable for recording signals related to continental oxidative Cr weathering. These considerations are also applicable to ironstones and other Fe-rich sedimentary archives, particularly when the oceans were predominantly anoxic, as the dissolved Cr(VI) reservoir in anoxic oceans would be much lower and the accumulation of authigenic Cr in pelagic sediments would be likely limited.

(2) Black shales. Black shales are another widely used archive for sedimentary Cr isotope studies and have recorded highly variable  $\delta^{53}\text{Cr}$  values ( $-0.4\text{‰}$  to  $+2.2\text{‰}$ , Figure 3, [9, 10, 12, 14, 16, 20, 27–55, 174]). Black shales are typically deposited under anoxic conditions, where dissolved Fe(II) or sulfide species accumulate in pore waters and even in the overlying water column. These reduced species can act as efficient reductants for Cr(VI), promoting its reduction and the accumulation of authigenic Cr in sediments. Early studies therefore proposed that Cr(VI) reduction in such environments could be quantitative, allowing black shales to faithfully record the  $\delta^{53}\text{Cr}$  value of contemporaneous seawater [185,186].

Currently, paired Cr isotope measurements of seawater and modern anoxic sediments, which are direct precursors to black shales, remain scarce. Available evidence instead suggests that Cr(VI) reduction in anoxic and euxinic settings is commonly non-quantitative and cannot directly record seawater  $\delta^{53}\text{Cr}$  values. For example, authigenic Cr in euxinic sediments from the Cariaco Basin, where hydrogen sulfide accumulates below  $\sim 300$  m water depth, exhibits  $\delta^{53}\text{Cr}$  values ranging from  $\sim 0.3\text{‰}$  to  $0.7\text{‰}$  [185,186], systematically lower than those reported for seawater in the nearby Caribbean Sea and Atlantic ( $1.0\text{‰}$ – $1.7\text{‰}$ ) [97,99,105–107,187]. For those anoxic or hypoxic sediments rich in organic matter, such as sediments from the ODZs along the Peru Margin,  $\delta^{53}\text{Cr}$  values display a large range from  $0.3\text{‰}$  to  $1.0\text{‰}$  [185,188], reflecting complex depositional and early diagenetic controls. In such environments, Cr isotopic signatures are influenced not only by redox conditions but also by the cycling of organic matter. Peru Margin sediments show a strong correlation between total organic carbon (TOC) contents and Cr enrichments, indicating a close coupling between organic matter and Cr accumulation [188]. Chromium uptake and adsorption by phytoplankton have been observed [189], and marine primary productivity has been proposed as an important control on Cr isotope variability in some areas of the modern ocean [101]. Nevertheless, existing data do not support substantial Cr enrichment by phytoplankton in shallow waters [4]. Instead, Cr enrichment in organic-rich continental margin sediments is more likely driven by Cr cycling within ODZ waters and by early diagenesis. Direct Cr isotope measurements of dissolved Cr(VI) and Cr(III) species in ODZ water profiles provide clear evidence for Cr(VI) reduction and Cr(III) removal, although the removal is not quantitative [103]. Such incomplete Cr(VI) reduction and Cr(III) removal have also been observed in redox-stratified bay environment [190]. The reduction of Cr(VI) may be mediated by microbial processes that utilize organic matter as an electron donor. These processes may operate in both the water column and sediment pore waters and could contribute to Cr accumulation in organic-rich sediments. In addition, degradation of organic matter may lead to active Cr recycling in pore water, further complicating the Cr isotopic signatures preserved in anoxic sediments and then black shales [110]. Taken together, observations in modern oceans indicate that the Cr isotopic compositions of the precursor materials of sedimentary black shales do not directly record contemporaneous seawater  $\delta^{53}\text{Cr}$  values and most likely reflect systematically lower values. Moreover, biological and organic matter-related processes can exert a significant influence on Cr cycling and isotopic fractionation, other than oxygen-related processes. Consequently, secular variations in  $\delta^{53}\text{Cr}$  recorded by successive black shale depositions likely reflect a combined effect from redox conditions and biological processes.

Another important control on the  $\delta^{53}\text{Cr}$  values of black shales is the contribution of detrital materials. Chromium in black shales consists of two components: authigenic Cr derived from dissolved seawater Cr, and Cr inherited from terrestrial detritus. Because Cr concentrations in the upper continental crust (UCC) are on the same order of magnitude to most black shales, the influence of detrital contribution cannot be

neglected. Terrestrial detritus generally exhibits BSE-like  $\delta^{53}\text{Cr}$  values, and a high proportion of detrital materials can therefore substantially lower the bulk  $\delta^{53}\text{Cr}$  values of black shales, in some cases completely masking the authigenic Cr signal. Two approaches have been widely applied to correct for detrital contamination [185,186,118–122]. The first method estimates the detrital Cr contribution using elements such as titanium (Ti) or aluminum (Al) that are predominantly hosted in detrital components, allowing calculation of the authigenic Cr concentration and isotopic composition:

$$[\text{Cr}]_{\text{auth}} = [\text{Cr}]_{\text{total}} - [\text{Cr} / \text{Ti}]_{\text{det}} \cdot [\text{Ti}], \quad (6)$$

$$\delta^{53}\text{Cr}_{\text{auth}} \cdot f_{\text{auth}} = \delta^{53}\text{Cr}_{\text{bulk}} - (1 - f_{\text{auth}}) \cdot \delta^{53}\text{Cr}_{\text{det}}, \quad (7)$$

where  $\delta^{53}\text{Cr}_{\text{det}}$  is commonly assumed to be the average BSE value ( $-0.12\text{‰}$ ). Titanium can be replaced by Al or other detrital indicators, and Cr/Ti (or Cr/Al) ratios of UCC or Post-Archean Australian Shales (PAAS) are most frequently adopted. The second approach involves selective extraction of authigenic Cr from bulk samples, most commonly using 3 mol/L nitric acid ( $\text{HNO}_3$ ). It was assumed that authigenic Cr may be primarily hosted in Fe-Cr oxyhydroxides, Fe-S phases, and organic matter, which can be preferentially released by  $\text{HNO}_3$  and analyzed for their Cr isotopic compositions [186]. Although these two approaches yielded comparable results in modern euxinic sediments, such as the Cariaco Basin [186], recent studies have demonstrated that their application to ancient black shales can introduce uncertainties. For detrital corrections based on Ti or Al, the use of UCC or PAAS compositions represents an oversimplification. A compilation of soil compositions across the United States, which are sources of terrestrial detrital materials, revealed large variations in both Cr/Ti and Cr/Al ratios, even at the catchment scale [191]. As a result, detrital Cr/Ti and Cr/Al ratios in sedimentary systems may deviate markedly from UCC or PAAS values, leading to overestimation or underestimation of the authigenic Cr fraction. This complexity has a particularly large impact on samples with low authigenic Cr proportions, potentially resulting in substantial errors in calculated  $\delta^{53}\text{Cr}$  values. The limitations of selective leaching methods are even more pronounced. Compared to marine anoxic sediments, black shales commonly have undergone complex post-depositional diagenesis. Sequential leaching experiments by Frank *et al.* [192] demonstrated that Cr isotopic compositions among different phases in black shales tend toward whole-rock homogenization. More recently, Fang *et al.* [193] showed that post-depositional diagenesis can drive the migration of authigenic Cr from its original host phase—likely organic matter in precursor anoxic sediments—into silicate minerals. Moreover, this process is accompanied by Cr isotopic fractionation ( $10^3\ln\alpha$ ,  $0.02\text{‰}$  to  $0.83\text{‰}$ ), resulting in much lower  $\delta^{53}\text{Cr}$  values in the residual organic phase [193]. Importantly, the commonly used  $\text{HNO}_3$  leaching procedure primarily targets this phase, potentially yielding strongly biased estimates of authigenic Cr isotopic compositions. It is therefore highly recommended that selective leaching, particularly those targeting organic matter, cannot be used to estimate the authigenic Cr isotopic compositions of ancient black shales. Instead, detrital correction is more applicable, but only for those with high fractions of authigenic Cr.

In summary, although reconstructing contemporaneous seawater  $\delta^{53}\text{Cr}$  values from black shales is challenging, qualitative interpretations remain informative. Similar to Fe-rich sediments, highly fractionated  $\delta^{53}\text{Cr}$  values in black shales are most plausibly linked to oxidative Cr cycling. In contrast, unfractionated or weakly fractionated  $\delta^{53}\text{Cr}$  values may arise from multiple processes and should be interpreted in the context of depositional setting and complementary geochemical proxies.

(3) Carbonates. Carbonates are among the most widely distributed chemical sedimentary rocks throughout

Earth's history, and their deposition is commonly continuous. This is in contrast with BIFs and black shales, which are typically deposited episodically. In addition, coprecipitation experiments have demonstrated that Cr(VI) can be directly incorporated into calcite crystals [194]. Therefore, carbonates have attracted considerable interest as potential archives for reconstructing paleo-seawater  $\delta^{53}\text{Cr}$  values [123]. Experimental constraints on Cr isotopic fractionation during Cr(VI) coprecipitation with calcite indicate variable isotopic fractionation magnitudes ( $\Delta^{53}\text{Cr}_{\text{carb-fluid}} = -0.7\text{‰}$  to  $0.3\text{‰}$ ), depending on solution pH, Cr(VI) concentration, and experimental conditions [42,43]. However, the application of these experimental results to natural carbonates is complicated by additional geochemical processes. Modern carbonate sediments, particularly from the Bahama Bank, have  $\delta^{53}\text{Cr}$  values ranging from  $0.63\text{‰}$  to  $1.07\text{‰}$  [94,99,124], generally lower than corresponding seawater values [4,99]. These sediments likely represent mixtures of multiple carbonate components, including ooids, phytoplankton-derived carbonates, and skeletal debris. Larger variability has been reported among specific biogenic carbonates such as foraminifera, corals, and molluscan shells, with  $\delta^{53}\text{Cr}$  values spanning from approximately  $-0.5\text{‰}$  to  $+2.5\text{‰}$  [107,195–197], including substantial intra-species variability [198]. This range is larger than the isotopic variability of modern seawater and cannot be explained solely by inorganic coprecipitation experiments. Biological processes have been invoked to account for the observed variability, although the underlying mechanism remains poorly understood [107,195,197,198].

The Cr isotopic compositions of ancient carbonates are subject to even more complex influences. Direct measurements of Cr species in sedimentary carbonates from different geological periods suggested that Cr(III) is the dominant species, with no clear evidence for the presence of Cr(VI), implying either reduction of Cr(VI) during or after carbonate deposition, or preferential incorporation of Cr(III) into carbonates [125]. Both scenarios imply that carbonate  $\delta^{53}\text{Cr}$  values may not faithfully record contemporaneous seawater compositions and instead reflect either redox overprinting or species-dependent incorporation effects, thereby introducing variable offsets between carbonates and seawater. Further investigations of Cr species in modern, freshly precipitated marine carbonates are needed to distinguish between these possibilities. Studies of drill cores from carbonate platforms have demonstrated that diagenesis can significantly affect the Cr isotopic compositions of carbonates. Variations in  $\delta^{53}\text{Cr}$  values of ODP Leg 166 Site 1003 in the Bahama Bank have been suggested to be largely governed by mineralogical compositions, such as the relative proportions of aragonite and low-Mg calcite, which may also be influenced by lithification and re-crystallization processes [124]. Another study on the nearby drill cores in the Bahama Bank indicated that meteoric alteration can result in substantially lower  $\delta^{53}\text{Cr}$  values [126]. Dolomitization has also been shown to significantly modify carbonate Cr isotopic compositions, producing both higher and lower  $\delta^{53}\text{Cr}$  values, and the extent of dolomitization does not appear to systematically control Cr concentrations or isotopic signatures, making the assessment of dolomitization influence difficult to constrain [126].

A potential origin of post-depositional alteration of Cr isotopes in carbonates is the overprinting of Cr by external sources. Remmelzwaal *et al.* [199] conducted a detailed investigation of Cr in foraminifera in sediments and indicated that much of the Cr may be acquired post-depositionally, recording bottom water or pore water signals rather than seawater at the time of calcification. In addition, diagenetic dissolution of Mn-oxides in pore water has been proposed to control  $\delta^{53}\text{Cr}$  variability in a carbonate drill core from the South China Sea [127]. Benthic Cr fluxes have been recognized in carbonate-rich regions of the modern ocean, largely driven by the re-release of Cr from sinking particles, suggesting an active Cr cycling in sediments and

pore water [111]. Pore water Cr compositions can differ substantially from overlying seawater and can be dominated by either Cr(VI) or Cr(III), depending on sediment types [110]. In contrast to Cr(VI), experimental evidence suggested that Cr(III) is mainly adsorbed on carbonate crystal surfaces rather than incorporated into the crystal lattice, making them more susceptible to later exchange with pore-water Cr from various sources [200]. Taken together, these observations indicate that sedimentary carbonates are highly sensitive to post-depositional modification of Cr isotopic compositions, likely to a greater extent than many other commonly used geochemical proxies for paleo-environments, such as carbon (C) isotopes and cerium (Ce) anomalies.

Previous studies on carbonate geochemistry commonly relied on indicators such as Mn/Sr ratios and O isotopes for diagenetic screening. However, thresholds developed for other geochemical proxies may not be applicable to Cr isotopes, which appear to be far more susceptible to alteration. The studies from the Bahama Bank and the South China Sea demonstrated that carbonate samples meeting conventional criteria for low diagenetic alteration (e.g., very low Mn/Sr ratios) [201] can nonetheless exhibit substantially modified  $\delta^{53}\text{Cr}$  values [126,127]. Therefore, even when diagenetic effects are constrained by widely used indicators of post-depositional alteration, such as Mn/Sr ratios, O isotopes, and Sr isotopes, interpreting Cr isotopic compositions as primary signals may not be very reliable.

In summary, Cr isotopic compositions of carbonates reflect a complex signal integrating depositional processes and subsequent diagenetic overprinting. Consequently, carbonate Cr isotopic data require careful and case-specific evaluation and should ideally be interpreted in conjunction with independent geochemical constraints.

## Deciphering Cr isotopic records in sedimentary rocks

### *Insights on Precambrian oxygen evolution*

Published  $\delta^{53}\text{Cr}$  records from Fe-rich sediments (including BIFs and ironstones), shales/mudstones, carbonates/evaporites, and paleosols throughout Earth history are compiled in Figure 3. Records from Fe-rich sediments and shales/mudstones are further grouped according to major geological intervals (Figure 4). Overall,  $\delta^{53}\text{Cr}$  values span a wide range, from  $-0.98\text{‰}$  to  $+5.00\text{‰}$ . As discussed above, the geochemical significance of these values cannot be evaluated using a universal framework. Instead, they must be interpreted within their specific geological, depositional, and diagenetic backgrounds. Below, we summarize the key Cr isotopic observations from different geological periods, their most plausible interpretations, and associated uncertainties.

(1) Pre-GOE. The Archean Cr isotopic record is dominated by BSE-like values (Figures 3 and 4), consistent with prevailing anoxic atmospheric and oceanic conditions. Sporadic deviations toward slightly positive or negative  $\delta^{53}\text{Cr}$  values require case-by-case evaluation. The oldest reported fractionated Cr isotopic signatures occur in 3.8–3.7 Ga metamorphosed Isua BIFs in Greenland, where  $\delta^{53}\text{Cr}$  values range from  $-0.54\text{‰}$  to  $+0.42\text{‰}$  [128]. Several mechanisms may account for these deviations. Frei *et al.* [128] proposed oxidative Cr cycling driven by reactive oxygen species under low atmospheric oxygen levels. However, alternative explanations, including non-redox Cr isotopic fractionation and metamorphic overprinting, cannot be excluded.

A particularly intriguing signal of potential early oxidative Cr cycling occurred at  $\sim 3.0$  Ga. Crowe *et al.*

[112] reported strongly negative  $\delta^{53}\text{Cr}$  values (down to  $-0.98\text{‰}$ ) in the Nsuzi paleosol, accompanied by slightly positive values (up to  $+0.28\text{‰}$ ) in near-contemporaneous Ijzermyn iron formation of the Pongola Supergroup, South Africa. However, subsequent paired analyses of outcrops and drill-core samples suggested that the positive  $\delta^{53}\text{Cr}$  values in iron formation may reflect modern oxidative weathering rather than primary Archean signals [129]. In addition, the possibility of non-redox Cr isotopic fractionation for the light  $\delta^{53}\text{Cr}$  values of paleosols cannot be ruled out, making the claim of oxygenation inconclusive. Independent evidence for marine oxygenation during this interval has been proposed based on other geochemical proxies from the Pongola Supergroup, including Mo and Fe isotopes [182,202]. Therefore, the atmospheric and oceanic oxygen level at  $\sim 3.0$  Ga remains unresolved and requires further investigation.

Positive  $\delta^{53}\text{Cr}$  values have also been reported from Archean carbonate successions ( $\sim 3.0$ ,  $2.8$ , and  $2.65$  Ga), but these signals were interpreted as likely reflecting post-depositional alteration rather than primary seawater compositions [126]. Other Archean  $\delta^{53}\text{Cr}$  values that deviated from the BSE range are generally muted ( $<0.5\text{‰}$ ) and cannot be exclusively attributed to oxidative Cr cycling. For example, some fractionated values in Algoma-type BIFs have been suggested to arise from kinetic isotope effects during rapid precipitation of Cr(III) [184].

(2) GOE and Paleoproterozoic. Chromium isotopic data spanning the GOE remain sparse. Most Paleoproterozoic records yield BSE-like or only slightly positive  $\delta^{53}\text{Cr}$  values (Figures 3 and 4), which cannot provide definitive evidence for widespread oxidative Cr cycling. The most compelling evidence for a transition from dominantly non-redox to oxidative Cr cycling comes from the  $\sim 2.1$ – $2.0$  Ga Onega Basin succession in Russia, where systematically positive  $\delta^{53}\text{Cr}$  values (up to  $+1.64\text{‰}$ ) have been reported from mudstones, carbonates, and evaporites [203]. These results indicate that the atmospheric oxygen level following the GOE should have at least exceeded the threshold required to initiate Mn oxide-mediated oxidative Cr cycling, estimated by modelling results to be  $\sim 0.1\%$ – $1\%$  PAL [113,114].

(3) Mid-Proterozoic. The interpretation of Cr isotopic records and their implications for atmospheric oxygen levels during the mid-Proterozoic remains one of the most debated issues. Early works by Planavsky *et al.* [114] and Cole *et al.* [130] reported extensive Cr isotope data from ironstones and shales deposited during  $1.8$ – $0.8$  Ga and found no evidence for highly fractionated  $\delta^{53}\text{Cr}$  values. On this basis, they proposed that atmospheric oxygen levels may have declined following the GOE and remained below  $\sim 0.1\%$  PAL throughout the mid-Proterozoic until  $\sim 0.8$  Ga, potentially prohibiting the evolution of eukaryotes [114,130]. This interpretation has since been challenged by several subsequent studies. Gilleaudeau *et al.* [131] reported  $\delta^{53}\text{Cr}$  values up to  $+1.77\text{‰}$  in carbonates deposited between  $\sim 1.1$  and  $0.9$  Ga, although these carbonate data have been questioned due to the potential effects of post-depositional alterations such as dolomitization [126], given that dolomites record systematically higher  $\delta^{53}\text{Cr}$  values than limestones in that study [131]. Later work also reported highly fractionated  $\delta^{53}\text{Cr}$  values (up to  $\sim 0.9\text{‰}$ ) in  $\sim 1.33$  Ga black shales from the Shennongjia Group [113], providing compelling evidence that oxidative Cr cycling occurred at least episodically during the mid-Proterozoic. In addition, small positive  $\delta^{53}\text{Cr}$  values ( $<0.5\text{‰}$ ) have also been reported from carbonate successions at  $\sim 1.44$  and  $\sim 1.57$  Ga [132,133]. Although such carbonate-hosted signals alone do not provide definitive evidence due to their relatively muted signals and susceptibility to post-depositional alterations, their secular variations have been suggested to covary with other redox proxies, such as Ce anomalies and  $\delta^{34}\text{S}_{\text{CAS}}$ , thereby offering supporting evidence for transient oxygenation events [132,133].

A key unresolved question is whether the dominantly unfractionated Cr isotope values recorded in most mid-Proterozoic sedimentary rocks (Figures 3 and 4) truly reflect the absence of oxidative Cr cycling for much of this period. As emphasized above, no sedimentary archive is expected to faithfully record contemporaneous seawater  $\delta^{53}\text{Cr}$  values. Multiple processes can lead to BSE-like  $\delta^{53}\text{Cr}$  values in sediments even when seawater Cr was isotopically fractionated, which may be applicable to the mid-Proterozoic. This limitation has been revealed by Ediacaran and Phanerozoic examples, during which atmospheric oxygen levels were well above the threshold required for Mn oxide-mediated oxidative Cr cycling. For instance, deep-basin black shales from the Ediacaran Lantian section display continuous unfractionated  $\delta^{53}\text{Cr}$  values, whereas coeval shallow-water deposits record strongly positive values [121]. Similarly, carbonate samples spanning ~120 m of stratigraphy at the Xiakou section, deposited during the Early Triassic, exhibit uniformly BSE-like  $\delta^{53}\text{Cr}$  values [134]. These patterns have been attributed to widespread oceanic anoxia, which may significantly influence Cr cycling in the oceans and result in unfractionated  $\delta^{53}\text{Cr}$  values recorded in sedimentary records (see the next subsection for details). Given that mid-Proterozoic oceans were widely inferred to be predominantly anoxic [204,205], it is therefore possible that oxidative Cr cycling occurred but did not consistently leave a detectable isotopic imprint in sedimentary archives due to oceanic anoxia. This remains speculative and requires further investigation. Overall, existing evidence indicates that highly fractionated  $\delta^{53}\text{Cr}$  values provide more robust indicators of oxidative Cr cycling, while using unfractionated values to infer low-oxygen conditions is inherently more ambiguous, because BSE-like  $\delta^{53}\text{Cr}$  values in sedimentary records can arise from multiple processes other than the absence of oxidative Cr cycling.

(4) Neoproterozoic and beyond. An uncontroversial systematic transition to fractionated Cr isotopic signatures was observed in shales of the Wynnatt Formation at ~0.8 Ga [114]. Since ~0.8 Ga, persistently elevated  $\delta^{53}\text{Cr}$  values recorded in BIFs, shales, and carbonates collectively indicate the establishment of sustained oxidative Cr cycling (Figure 3). Although positive values dominate the Neoproterozoic and Phanerozoic record, a substantial number of samples still exhibit BSE-like values (Figure 4). Such unfractionated signatures may result from several factors, including deposition under oxic conditions that did not efficiently capture authigenic Cr, dilution by high proportions of detrital material, or widespread oceanic anoxia that limited the preservation of fractionated Cr signals at certain periods.

It is important to emphasize that the magnitude of Cr isotopic fractionation in the sedimentary record is not directly linked to oxygen concentrations in either the atmosphere or the oceans. Instead, Cr isotope fractionation primarily reflects the presence or absence of oxidative Cr cycling and thus represents a threshold response to oxygen concentration. The specific  $\delta^{53}\text{Cr}$  values recorded in sedimentary archives are further modulated by Cr(VI) cycling within aquatic systems, which is governed by multiple geochemical processes. Therefore, variations in atmospheric oxygen levels after ~0.8 Ga cannot be quantitatively constrained using Cr isotopes.

### ***Response of Cr isotopes to oceanic anoxia in the Phanerozoic***

Within the conventional framework of marine Cr cycling, the expansion of oceanic anoxia is expected to enhance the reduction and sequestration of Cr(VI) in anoxic settings. Such preferential removal of isotopically light Cr would, in principle, lead to elevated  $\delta^{53}\text{Cr}$  values in the residual seawater. If faithfully recorded by sedimentary archives, this mechanism predicts positive  $\delta^{53}\text{Cr}$  excursions during oceanic anoxic

events (OAEs) [135]. Contrary to this expectation, sedimentary Cr isotope records across several OAEs commonly display negative  $\delta^{53}\text{Cr}$  excursions. For example, Cr isotope records spanning the Cretaceous OAE2 reveal concurrent decreases in both Cr enrichment and  $\delta^{53}\text{Cr}$  values in black shales [122], while coeval carbonate records show increased Cr concentrations accompanied by a decline in  $\delta^{53}\text{Cr}$  values toward BSE-like compositions [99,136]. The latter observation from carbonate signals has been interpreted as reflecting enhanced inputs of volcanogenic or hydrothermal Cr associated with large igneous province (LIP) activity, rather than changes in ocean redox conditions [99,136]. However, this mechanism cannot readily account for the coupled decreases in Cr concentration and  $\delta^{53}\text{Cr}$  observed in black shales, which has been instead interpreted by expansion of euxinia in the oceans compared to hypoxia [122]. Under such conditions, extensive quantitative Cr(VI) reduction in euxinic environments may have suppressed the Cr isotopic fractionation in the oceans, leading to lower seawater  $\delta^{53}\text{Cr}$  values that were recorded in sediments. A similar pattern of coupled decrease in Cr concentration and  $\delta^{53}\text{Cr}$  values was reported in carbonate successions at the Permian-Triassic boundary, when oceanic anoxia was likely pervasive [134]. The BSE-like  $\delta^{53}\text{Cr}$  values persisting throughout the Early Triassic have been attributed to quantitative Cr(VI) reduction and sequestration at the margins of anoxic zones, which would inhibit the transport of  $^{53}\text{Cr}$ -enriched Cr(VI) into the anoxic interior [134]. Similar mechanisms have also been invoked to explain unfractionated  $\delta^{53}\text{Cr}$  values in deep-basin black shales or cherts deposited during the Ediacaran [120,121,137].

It is important to note that these interpretations, either through suppression of isotopic fractionation during quantitative reduction or through near-complete removal of Cr(VI) at redox boundaries that restricts isotopically heavy Cr from reaching deeper waters, rely on the assumption of effectively quantitative Cr(VI) reduction and sequestration in anoxic/euxinic conditions. However, such assumptions are not supported by observations from modern analogues. Studies of modern anoxic environments, including anoxic/euxinic basins, lakes, and ODZs, consistently indicate that neither Cr(VI) reduction nor Cr(III) sequestration is quantitative [4,103,109,183,188,190]. Therefore, Cr cycling in anoxia-dominated oceans remains poorly understood, and the mechanisms responsible for the coupled negative excursions of Cr concentrations and  $\delta^{53}\text{Cr}$  values during Phanerozoic OAEs require further investigations.

## SUMMARY AND OUTLOOK

Since the pioneering applications of Cr isotopes to trace the reduction of anthropogenic Cr(VI) contaminants and to reconstruct the evolution of oxygen throughout Earth's history, extensive investigations of both modern and ancient Cr cycling and isotopic fractionation have greatly advanced our understanding of the Cr isotope system. Although these studies have revealed considerable complexity, the fundamental frameworks underlying the use of Cr isotopes as proxies for monitoring Cr(VI) contamination and reconstructing paleo-redox conditions remain robust, because redox processes still appear to have primarily controlled the Cr cycling and Cr isotopic fractionation in most natural environments.

In modern environmental applications, Cr isotopes have proven to be a powerful tool for distinguishing Cr(VI) reduction from other processes such as dilution and adsorption. However, quantitatively estimating the extent of Cr(VI) reduction remains challenging. This difficulty arises mainly from uncertainties in constraining the apparent Cr isotopic fractionation factors and from the large variability in both concentrations

and isotopic compositions of natural geogenic Cr(VI), particularly in ultramafic catchments where natural Cr inputs cannot be neglected.

For paleoenvironmental reconstructions, the most critical limitation is that most sedimentary archives do not directly record contemporaneous seawater  $\delta^{53}\text{Cr}$  values. Instead, variable isotopic offsets exist between sediments and seawater, introducing uncertainty in reconstructions of past Cr cycling and redox conditions. This issue may be mitigated by expanding datasets from modern environments, developing a more comprehensive understanding of Cr isotope systematics, and integrating Cr isotopes with complementary geochemical proxies that better constrain depositional settings and diagenetic histories. Another potential direction is looking for alternative sedimentary archives that may faithfully preserve ancient seawater  $\delta^{53}\text{Cr}$  values. We tentatively assume that evaporites may represent such a candidate. To date, only a limited number of Cr isotope data have been reported for evaporites, from the ~2.1–2.0 Ga Onega Basin [203]. Evaporites are typically deposited in isolated, shallow marginal basins that likely received terrestrial Cr inputs, while their formation processes, such as evaporation and precipitation of halite and gypsum, do not involve redox reactions that could induce Cr isotopic fractionation between dissolved and solid phases. Moreover, evaporites can be dissolved in pure water during laboratory Cr isotope analyses, which largely eliminates detrital contamination. If their ability to record seawater (or lacustrine water, when applied to atmospheric oxygen reconstructions)  $\delta^{53}\text{Cr}$  values can be validated through modern analogues, evaporites may open a new avenue for the application of Cr isotopes as a paleo-redox proxy.

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## Conflict of interest

The authors declare no conflict of interest.

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