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Chromium isotope fractionation during subduction-related metamorphism, black shale weathering, and hydrothermal alteration

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ABSTRACT

Chromium (Cr) isotopes are an emerging proxy for redox processes at Earth's surface. However, many geological reservoirs and isotope fractionation processes are still not well understood. The purpose of this contribution is to move forward our understanding of (1) the Earth's high temperature Cr isotope inventory and (2) Cr isotope fractionations during subduction-related metamorphism, black shale weathering and hydrothermal alteration. The examined basalts and their metamorphosed equivalents yielded δ^{53}Cr values falling within a narrow range of -0.12 ± 0.13‰ (2SD, $n = 30$), consistent with the previously reported range for the bulk silicate Earth (BSE). Compilations of currently available data for fresh silicate rocks (43 samples), metamorphosed silicate rocks (50 samples), and mantle chromites (39 samples) give δ^{53}Cr values of -0.13 ± 0.13‰, -0.11 ± 0.13‰, and -0.07 ± 0.13‰, respectively. Although the number of high-temperature samples analyzed has tripled, the originally proposed BSE range appears robust. This suggests very limited Cr isotope fractionation under high temperature conditions. Additionally, in a highly altered metacarbonate transect that is representative of fluid-rich regional metamorphism, we did not find resolvable variations in δ^{53}Cr, despite significant loss of Cr. This work suggests that primary Cr isotope signatures may be preserved even in instances of intense metamorphic alteration at relatively high fluid–rock ratios. Oxidative weathering of black shale at low pH creates isotopically heavy mobile Cr(VI). However, a significant proportion of the Cr(VI) is apparently immobilized near the weathering surface, leading to local enrichment of isotopically heavy Cr (δ^{53}Cr values up to ~0.5‰). The observed large Cr isotope variation in the black shale weathering profile provides indirect evidence for active manganese oxide formation, which is primarily controlled by microbial activity. Lastly, we found widely variable δ^{53}Cr (-0.2‰ to 0.6‰) values in highly serpentinized peridotites from ocean drilling program drill cores and outcropping ophiolite sequences. The isotopically heavy serpentinites are most easily explained through a multi-stage alteration processes: Cr loss from the host rock under oxidizing conditions, followed by Cr enrichment under sulfate reducing conditions. In contrast, Cr isotope variability is limited in mildly altered mafic oceanic crust.

1. Introduction

Chromium (Cr) isotopes (with abundances of 2.36% ^{54}Cr, 9.50% ^{53}Cr, 83.79% ^{52}Cr, 4.35% ^{50}Cr) have wide utility for tracking planetary formation, environmental contamination, and paleoenvironmental evolution. Over the past few decades, studies have utilized Cr isotope anomalies in different planetary materials to study spatial and/or temporal heterogeneities in the solar system (Birck and Allègre, 1984; Papanastassiou, 1986; Rotaru et al., 1992; Podosek et al., 1997; Shukolyukov and Lugmair, 2006; Trinquier et al., 2007; Qin et al., 2011). In addition, there has been extensive work on using Cr isotopes to quantify the attenuation of environmental Cr contamination (Ellis et al., 2002; Wanner et al., 2011; Izbicki et al., 2012). More recently, there has been a surge of interest in using Cr isotopes as a paleoredox proxy (e.g., Frei et al., 2009; Crowe et al., 2013; Planavsky et al., 2014; Reinhard et al., 2014).

Chromium has two major valence states in nature: reduced, trivalent Cr (denoted as Cr(III) hereafter) and oxidized, hexavalent Cr (denoted as Cr(VI) hereafter). At circumneutral pH, Cr(III) is insoluble and is a trace nutrient, while Cr(VI) is soluble and carcinogenic (Rai et al., 1989). Therefore, in-situ reduction of Cr(VI) to Cr(III) can serve as a means of remediating Cr(VI) contamination. In Earth's early history, before the emergence of oxygenic photosynthesis, Cr was likely present

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almost exclusively as Cr(III) in rocks. After the advent of oxygenic photosynthesis, local and eventually global oxygenated environments passed a critical threshold required for Cr(III) oxidation to Cr(VI), in a process likely linked to manganese redox cycling (Eary and Rai, 1987; Fendorf and Zasoski, 1992; Frei et al., 2009). The oxidized Cr(VI) is carried to the oceans as dissolved oxyanion species and eventually deposited in sedimentary rocks, either as Cr(VI) via adsorption or as Cr(III), typically via reduction by reductants such as ferrous iron and sulfides (Eary and Rai, 1987; Fendorf and Li, 1996; Pettine et al., 1998; Kim et al., 2001). The use of the Cr isotope system as a redox proxy is grounded in the notion that there is up to ~6‰ Cr isotope fractionation during reactions involving electron transfers (Ellis et al., 2002; Schauble et al., 2004; Zink et al., 2010; Wang et al., 2015a), but insignificant Cr isotope fractionations during non-redox-dependent reactions (e.g., Ellis et al., 2004). Studies on modern basaltic weathering profiles have found that isotopically heavy Cr is oxidatively mobilized into rivers, leaving isotopically light Cr in the weathered basalt (e.g., Frei and Polat, 2012). Building on this framework, Cr isotopes have provided a new view of Earth's ocean–atmosphere redox evolution (Frei et al., 2009; Crowe et al., 2013; Planavsky et al., 2014).

Despite the significant potential of Cr isotopes as a redox proxy, there are several notable gaps in current knowledge. The purpose of this contribution is to examine a series of currently unresolved or poorly constrained questions that affect the use of the Cr isotope system as a paleoredox proxy. First, for all Cr isotope work, it is necessary to establish a robust estimate of the Cr isotope inventory of the solid Earth. Only a few studies have been conducted in the past few years for this purpose. For instance, Schoenberg et al. (2008) and Farkas et al. (2013) proposed bulk silicate Earth (BSE) δ^{53}Cr (^{53}Cr/^{52}Cr relative to SRM 979) values of -0.124 ± 0.101‰ and -0.079 ± 0.129‰, respectively. Moynier et al. (2011) reported a bulk Earth (BE) δ^{53}Cr value of -0.32 ± 0.05‰, which is about 0.2‰ lighter than the BSE value. The apparent difference between BE and BSE, and its potential implications for planetary differentiation, provides motivation to expand our current knowledge of the high-T Cr isotope inventory. For this purpose, we explored the δ^{53}Cr systematics of a range of basalt samples (both alkaline and tholeiitic) from different localities.

Second, Cr isotopic systematics in Archean rocks have been used to investigate the earliest emergence of oxygenic photosynthesis (Frei et al., 2009; Crowe et al., 2013). However, most Archean rocks have been subject to various grades of metamorphism. This provides a strong impetus to investigate the magnitude of Cr isotope fractionation associated with metamorphic processes. For this reason, we analyzed a set of subduction-related metamorphosed ultramafic rocks and fluid-altered carbonate rocks. The metamorphic age of these rocks range from Neoproterozoic to Phanerozoic. Although the pattern and depth of subduction may differ on the early and recent Earth, the underlying basic physicochemical processes (e.g., deformation, temperature- or concentration-driven diffusion) are not likely to have varied over time. Furthermore, the Cr isotopic composition of the mantle reservoir has been shown to be the same within error since ~3.5 billion years ago (Ga) (Farkas et al., 2013). Therefore, Cr isotope behavior during high temperature metamorphism derived from recent geological time should be applicable to the Archean.

Third, our current understanding of the terrestrial Cr cycle is based largely on the study of oxidative weathering of igneous rocks (Middelburg et al., 1988; Van der Weijden and van der Weijden, 1995; Frei et al., 2009; Frei and Polat, 2012; Crowe et al., 2013). However, igneous rocks represent only a small area of the subaerially exposed continental crust relative to sedimentary rocks (e.g., Bluth and Kump, 1991). Therefore, weathering of sedimentary rocks can potentially contribute significantly to riverine Cr flux to the ocean. Among sedimentary rocks, black shales are of special interest because of their relatively high Cr concentrations. Given that black shale weathering typically occurs at low pH, the framework developed from basalt weathering (e.g., Crowe et al., 2013; Berger and Frei, 2014; Frei et al., 2014) may not apply. Furthermore, previous studies used lack of Cr isotope fractionation in sedimentary rocks to argue for low atmospheric oxygen levels (e.g., Frei et al., 2009; Frei and Polat, 2012; Crowe et al., 2013; Planavsky et al., 2014). However, the absence of Cr isotope fractionation in sedimentary records is not necessarily a robust evidence for absence of oxygen (Planavsky et al., 2014). This is because pyrite oxidation could generate acids and dissolve solid Cr without Cr oxidation, and this process leads to Cr enrichment but no isotope fractionation in sedimentary rocks (Konhauser et al., 2011). To resolve this uncertainty, we targeted a well-studied black shale weathering profile to test whether there is Cr isotope fractionation and Cr(III) oxidation in a high oxygen but low-pH weathering environment.

Lastly, interaction between seawater and oceanic crust is another process that can affect seawater δ^{53}Cr values. Although this process may not be very important on a global scale in the modern oceans (e.g., Reinhard et al., 2013), it may affect local water masses and sediments, given that large Cr isotope variations have been reported for Cr-rich hydrothermal minerals (Schoenberg et al., 2008; Farkas et al., 2013). Hydrothermal alteration may also have been important for global Cr isotope mass balance during the early periods of Earth's history due to higher heat flux and more mafic crust. It is essential to determine if there are significant Cr isotope fractionations in hydrothermal systems before using the Cr isotope composition of marine sediments to track surface oxidative processes. To further our understanding of seawater–oceanic crust interactions, we analyzed the Cr isotopic compositions of mildly altered oceanic crust and serpentinized peridotite samples from a range of localities.

2. Samples

We selected samples where geochemistry and geological context have been previously studied. Samples for metacarbonates, weathered black shales, altered oceanic crusts, serpentinites, Wudangshan basalts, and Dabie eclogites used powders from previous studies (references in Table 1). Below we provide only a short overview of the samples/sites and refer to previous work for more in-depth descriptions.

2.1. Basalts and eclogites

We examined basalt and eclogite samples from the ultra-high pressure Qinling–Tongbai–Dabie Orogenic Belt (QTDOB, Fig. 1). The QTDOB separates the North China Block (NCB) and South China Block (SCB), and itself is divided into the South Qinling (SQ) and North Qinling (NQ) orogens by the Shangdan Fault. There were several major episodes of tectonic activity from mid-Proterozoic to Cenozoic time (e.g., Ratschbacher et al., 2003). The tholeiitic and alkaline basalt samples (~680–755 Ma) were sampled from the SQ, while the eclogite samples (~800 Ma) were sampled from the NQ. The basalts and eclogites are geographically close to each other and have the same source material (Ling et al., 2002; Wang et al., 2013). We examined the Cr isotope composition of tholeiitic and alkaline basalts because of their differing oxygen fugacities during formation (e.g., Carmichael and Ghiorso, 1986), which could potentially influence the redox geochemistry of Cr.

We also examined eclogite, metabasalt and metagabbro samples from Corsica, Greece, USA, and Norway—mafic rocks that experienced typically high pressure or ultrahigh-pressure metamorphism. Alpine Corsica (France) consists mainly of ophiolitic rocks and their sedimentary cover that underwent high-pressure blueschist–eclogite facies metamorphism during the Alpine orogeny Malavieille et al., 1998. One Corsican mafic pillow breccia (CRB) is from the Farinole–Volpajola eclogite unit that experienced metamorphism at ~520 °C and ~2.3 GPa (Vital Brovarone et al., 2011).

Blueschist–eclogite facies can be found in Syros and Tinos islands in Greece. The metamorphism was caused by subduction of the Apulian microplate beneath the Eurasia plate during the Eocene Alpine orogeny (Keiter et al., 2011 and references therein). Peak metamorphic