



Chromium fluxes and speciation in ultramafic catchments and global rivers



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ABSTRACT

The role of ultramafic rock weathering in global chromium (Cr) budgets and how these may be linked to changes in Earth's climate over geological time was investigated by compiling dissolved Cr speciation and fluxes in (i) 73 of the world's large rivers, representing ~35% of global river discharge to oceans, and in (ii) an ultramafic catchment (Putah Creek watershed) in the California Coast Range Mountains, USA. Weathering of ultramafic rocks creates ideal conditions for Cr release and redox cycling. Alkaline river water draining ultramafic catchments is naturally enriched in Cr (up to 582 nmol/L). Chromium concentrations increase with the extent of rock–water interaction (as indicated by correlations with Mg and HCO_3^- concentrations and pH), whereas Cr cycling depends on the availability of electron donors and acceptors (e.g. Fe(II), organics, Mn(III/IV)-oxides). Thus, dissolved Cr is exported from ultramafic watersheds as both the soluble hexavalent Cr(VI) species (MgCrO_4 , CrO_4^{2-}), and also as trivalent Cr(III) species ($\text{CrOH}(\text{CO}_3)_2^-$, $\text{Cr}(\text{OH})_3$). The latter Cr(III) species were previously thought to have low solubility. Ultramafic catchments have higher area normalized Cr and major ion fluxes for a given runoff when compared to global rivers and may thus have a disproportional impact on global Cr-budgets, long-term carbon cycling and moderation of the Earth's climate over million-year timescales. Riverine export fluxes of Cr are linearly correlated with fluxes of Ca + Mg and alkalinity in both ultramafic catchments and global rivers. This suggests that silicate weathering is a key control on Cr fluxes and that major element weathering fluxes may be a useful proxy for estimating Cr and other trace element fluxes. Globally, present-day riverine dissolved Cr fluxes to oceans are spatially variable and estimated to be 1.7×10^9 mol/yr, three times higher than previously reported. However, when geochemical reactions in estuaries are considered riverine Cr fluxes may be lower. Throughout Earth history, Cr weathering fluxes also may have varied with changes in the global distribution of ultramafic rocks, Cr concentrations in continental rocks, or climatic conditions (e.g. atmospheric CO_2 levels or runoff). Such variation should be considered when interpreting both modern and past Cr seawater isotopic compositions and residence times.

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1. Introduction

Trace elements influence global biogeochemical cycling, moderate redox conditions in water and sediment, reflect human influence on the environment and may have recorded Earth's past environmental conditions. During weathering of rocks, trace elements (e.g., Al, Cr, Mn, Fe, As, Mo, U) are mobilized and transported as dissolved and particulate matter *via* rivers and groundwater to depositional environments such as alluvial plains and ocean basins. Chemical reactions during transport may result in changes in trace element concentration, oxidation state, and aqueous speciation, affecting isotopic composition, mobility, toxicity, bioavailability and ultimately what is recorded in the rock record. Weathering of major elements and large-scale transfer through the Earth's surface to oceans is well understood for many rock

types, but the corresponding weathering fluxes of trace elements have received less attention (Gaillardet and Dupré, 2003). The behavior of chromium (Cr) in rivers is particularly important because Cr riverine fluxes constitute 76–96% of input to oceans (Bonnand et al., 2013), Cr is a possible tracer of paleoredox conditions (Frei et al., 2009), Cr is a widespread contaminant and health hazard (Chatham-Stephens et al., 2013; Oze et al., 2007), and Cr is highly sensitive to biogeochemical transformations under changing environmental conditions.

The main sources of Cr to rivers are rock weathering (crustal rocks typically have Cr concentrations of 100 mg/kg) and anthropogenic discharges (chemicals, tailings, slag, scrap), which are estimated to contribute 5×10^8 mol/yr and 2×10^9 mol/yr, respectively (Nriagu and Nieboer, 1988). For most large rivers, particles transport most of the total Cr load (*i.e.* dissolved plus particulate) (Gibbs, 1977; Kotas and Stasicka, 2000; Pettine et al., 1992). However, the corresponding riverine dissolved Cr concentrations (herein referred to as Cr(TOT)) are crucial to quantify because of toxicity to biota (Nriagu and Nieboer, 1988) and Cr carcinogenicity to humans associated with

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drinking water high in Cr (Beaumont et al., 2008; World Health Organization, 2012). By extension, understanding the processes that control the dissolved Cr concentration of rivers can lead to improved estimates of metal loading to aquatic ecosystems and drinking water sources. Current estimates of riverine dissolved Cr fluxes to the ocean are based on averages calculated from <15 rivers (Bertine, 1971; Bonnard et al., 2013; Campbell and Yeats, 1984; Gaillardet and Dupré, 2003; Jeandel and Minster, 1984; Martin and Meybeck, 1979), even though more concentration and discharge data are available (GEMS, 2015; Milliman and Farnsworth, 2011). Further, species-specific (*i.e.* Cr(VI), Cr(III)) dissolved Cr fluxes of rivers have not been estimated globally, or for individual rivers, and are necessary to improve understanding of Cr sources, local contamination, oceanic Cr cycling (Scheiderich et al., 2015; Sirinawin et al., 2000), and Cr isotopes as a paleoredox proxy (Crowe et al., 2014; Frei et al., 2009, 2011, 2014; Frei and Polat, 2013; Konhauser et al., 2011).

The majority of research on Cr geochemistry has focused on laboratory studies and individual sites, whereas very little work has focused on large-scale controls on Cr concentrations in surface waters. In rivers, both Cr(III), a vital micronutrient for animals (Nriagu and Nieboer, 1988) and Cr(VI), a toxic carcinogen (Beaumont et al., 2008; World Health Organization, 2012), are detected and thought to cycle through the environment depending on the abundance of electron donors/acceptors, sorbants, competing sorbates and Cr aqueous speciation (Abu-Saba and Flegal, 1995; Comber and Gardner, 2003; Cranston and Murray, 1980; Kaczynski and Kieber, 1993; Pankow et al., 1977; Pettine et al., 1994; Saputro et al., 2014; Shuman and Dempsey, 1977; Stefánsson et al., 2014). Chromium(III) may be oxidized to Cr(VI) by manganese oxides, oxygen or hydrogen peroxide (Richard and Bourg, 1991), whereas Cr(VI) can be reduced under many conditions, primarily by Fe(II), but also by microbes, organic acids and sulfide (Fendorf et al., 2000). Sorption to mineral surfaces will attenuate both Cr(III) and Cr(VI) concentrations, but the extent depends on concentration, pH, specific aqueous speciation, and bulk water composition (Fendorf, 1995; Richard and Bourg, 1991). Typical regulatory limits for Cr in drinking water are 962 nmol/L (50 µg/L) for Cr(TOT) and 192 nmol/L (10 µg/L) for Cr(VI) (California, 2014; World Health Organization, 2012).

Ultramafic rocks have higher Cr concentrations (2400 mg/kg) compared to all other rock types (Nriagu and Nieboer, 1988) and may therefore be a more important source of Cr to natural waters than volcanic, basaltic or sedimentary rocks. Ultramafic rivers (*i.e.* surface water in catchments with ultramafic bedrock) are characterized by high dissolved Cr(TOT) concentrations (13.5 to 4807 nmol/L), which in some cases exceed drinking water limits by a factor of up to five (Farkaš et al., 2013; Gough et al., 1989; Novák et al., 2014; Taylor et al., 1998). Groundwater from aquifers containing ultramafic materials often contains high levels of naturally occurring Cr, mostly as Cr(VI), levels that approach or exceed the drinking water limit for Cr(TOT) of 962 nmol/L (Apollaro et al., 2011; Becquer, 2003; Dawson et al., 2008; Deverel and Millard, 1988; Fantoni et al., 2002; Godgul and Sahu, 1995; Gonzalez et al., 2005; Gray, 2003; Kaprara et al., 2014; Lelli et al., 2013; Manning et al., 2015; Moraetis et al., 2012; Robles-Camacho and Armienta, 2000; Wood et al., 2010). Ultramafic rocks currently compromise ~0.2% of exorheic continental area (Dai and Trenberth, 2003; Dürr et al., 2005) and are generally associated with orogenic belts or ophiolites, which are found along continental margins (Dilek, 2003; Oze et al., 2007) where erosion and weathering rates are higher than cratonic regions (Bluth and Kump, 1991; Stallard, 1988). Throughout Earth's history, the distribution of ultramafic rocks and the Cr content of these rocks have varied (Dilek, 2003; Furnes et al., 2014). Thus, over time, weathering of ultramafic rocks may be important contributors of Cr to surface and groundwater as well as depositional environments including alluvial plains, continental margins and ocean basins.

Despite high Cr concentrations, to our knowledge, no studies have quantified Cr aqueous speciation or Cr fluxes in rivers in ultramafic

source regions. Soils, developed from weathering of ultramafic rocks, have been better studied than surface waters in ultramafic regions. Both Cr(VI) and Cr(III) are found to weather from ultramafic soils reaching concentrations of up to 1000 and up to 135 mg/kg soil respectively, constituting a potential source to surface and groundwater (Becquer, 2003; Cooper, 2002; Fandeur et al., 2009; Garnier et al., 2006). However, these studies were mostly conducted in tropical weathering environments where lateritic soils retain Cr(VI) by sorption on Fe-oxides, decreasing Cr mobility. Riverine dissolved Cr concentrations and fluxes may be higher in temperate climates due to differing soil mineralogy (*e.g.* fewer Fe-oxides) and higher pH. Furthermore, more mobile and bioavailable Cr aqueous species (*e.g.* MgCrO₄ and CrOH(CO₃)₂²⁻) may be present in ultramafic water due to high Mg and HCO₃⁻ concentrations, enhancing the solubility of Fe_xCr_{1-x}(OH)₃ solids which are thought to govern Cr(III) concentrations in natural waters (Accornero et al., 2010; Cranston and Murray, 1980; Rai et al., 2007; Sass and Rai, 1987; Stefánsson et al., 2014).

Few studies have quantified the trace element speciation or fluxes associated with rivers draining mafic and ultramafic lithologies (as noted by Gaillardet and Dupré (2003)), despite high trace element concentrations in the rocks (Nriagu and Nieboer, 1988). Moreover, mafic and ultramafic rocks are known to be some of the most reactive materials at the Earth's surface, having elevated weathering fluxes of major ions compared to global rivers (Dupré et al., 2003; Gaillardet et al., 1999, 2011; Schopka et al., 2011). Mafic rock weathering disproportionately contributes to base cation and alkalinity fluxes (Dessert et al., 2003; Dupré et al., 2003; Gaillardet et al., 2011; Hartmann et al., 2009). However, the role of ultramafic rock weathering in setting the global trace metal and major ion weathering fluxes and impacting global geochemical cycles remains to be quantified. Because chemical weathering of Ca- and Mg-silicate rocks is one of the primary mechanisms responsible for removal of atmospheric CO₂ over geologic timescales, the weathering of ultramafic rocks may also play a key role in regulating the long-term carbon cycle and Earth's climate (Berner and Kothavala, 2001; Walker et al., 1981).

This study had four primary research objectives. First, we identified the speciation, fluxes and primary controls on dissolved Cr in surface water from an ultramafic watershed in a temperate climate. Specifically, we collected surface water and spring water samples within a well-characterized ultramafic province along the west coast of North America within the central California Coast Range Serpentine Belt, concurrently measuring discharge and water compositions. Second, we calculated contemporary riverine dissolved Cr flux to oceans by compiling a database of dissolved Cr concentrations, speciation and discharge from 73 rivers globally. Third, we determined whether ultramafic watersheds contribute proportionally to global riverine dissolved Cr fluxes to oceans and to cation and alkalinity fluxes by comparing chemical weathering fluxes from the small uplands ultramafic watershed to fluxes from other ultramafic areas, to Cr fluxes from previous studies in the San Francisco Bay/Estuary, and to Cr fluxes associated with global rivers. Finally, we investigated whether chemical weathering fluxes can be used as a proxy to estimate trace element fluxes by comparing cation and alkalinity fluxes to Cr fluxes.

2. Materials and methods

We present an analysis of two different spatial scales. First, we evaluate the controls on Cr within a small uplands watershed with uniform lithology in central California, USA, based on concentration and discharge data collected from streams and springs over several seasons. Subsequently, we evaluate global Cr concentrations in large rivers obtained from pre-existing databases. These global rivers have mixed lithology, where information is averaged over large areas, providing a complementary approach to investigating riverine Cr cycling. Below we provide an overview of the study area and sampling

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