

# Occurrence, Origin and Transformation Processes of Geogenic Chromium in Soils and Sediments

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**Abstract** Weathering of ultramafic rocks has been linked to the occurrence of elevated concentrations of hexavalent chromium (Cr(VI)) in soils, sediments, and groundwater. Ultramafic rocks and the derived serpentine soils and sediments are encountered in populated areas around the world and present high Cr concentrations, with an average of 2200 and 2650 mg/kg for rocks and soils, respectively. Groundwater concentrations between 0.2 and 180 µg/L have been reported for Cr(VI) in ultramafic areas, exceeding occasionally the most prevalent drinking water limit of 50 µg/L Cr<sub>tot</sub>, the 5 µg/L Cr(VI) limit established in Italy, and the 10 µg/L Cr(VI) limit proposed in California. Cr release in groundwater occurs through the dissolution of trivalent chromium (Cr(III)) from its mineral hosts, followed by sorption of Cr(III) onto high-valence Mn oxides and oxidation to Cr(VI), which desorbs and is mobile at alkaline pH. Recent findings indicate that hydrogen peroxide and birnessite produced on the surface of Cr(OH)<sub>3</sub> by heterogeneous oxidation are two additional potential mechanisms. Thus, groundwater

concentrations are controlled by a variety of geoenvironmental factors, including climate, soil mineralogy, pH, organic matter, and others. To provide a basis for the evaluation of Cr mobility in ultramafic environments, this paper presents an overview of the mineralogy and geochemistry of Cr-rich rocks, sediments, and soils, along with the weathering and geochemical processes that control the fate and transport in the subsurface.

**Keywords** Hexavalent chromium · Geogenic chromium · Ultramafic rocks · Serpentine soils · Ophiolites

## Introduction

Environmental contamination with hexavalent chromium (Cr(VI)) has typically been attributed to various anthropogenic activities, including industrial processes such as chromium plating, metal finishing, leather tanning, and paint production [1]. However, the presence of Cr(VI) in soil and groundwater has also been linked to geogenic processes, namely, weathering of ultramafic rocks in various areas around the world, such as several countries in Europe (Greece, Italy, France, Serbia, Poland), USA, Canada, Brazil, New Caledonia, Cameroon, Taiwan, and others [2–10]. The synergistic effects of both natural and anthropogenic processes may also result in high Cr(VI) groundwater concentrations. Distinguishing the contribution of each factor is a challenging task and several studies have employed isotope analyses and other geochemical assessments to this end [11–14].

Toxic and carcinogenic effects from industrial Cr(VI) pollution have been demonstrated since the nineteenth century [15]; however, there have been only limited and recent studies on the effects of naturally occurring concentrations that are below the 50 µg/L WHO limit. The state of California has

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primarily led related efforts, given the prevalence of naturally occurring Cr in its geological environment [2, 11]. The Cr(VI) concentration for de minimis lifetime cancer risk has been determined to be 0.2 µg/L based on mouse studies [16]. As of July 1, 2014 the California Department of Public Health established a 10 µg/L limit for Cr(VI) in drinking water, a concentration that is often exceeded in water impacted by ophiolitic systems. Italy is the only country that has set the drinking water limit for Cr(VI) at 5 µg/L, which is also often exceeded in Italian ophiolitic regions. In addition to drinking water limits, the European Union mandates the establishment of groundwater quality criteria, which are often based on natural background values. Thus, the geogenic levels of Cr(VI) in groundwater can have important implications for the allowable uses of water bodies and for necessary remediation measures, which in turn incur cost and resource considerations. Understanding the factors that control geogenic Cr levels is necessary to shape policy and evaluate the economic and health impacts for areas with Cr-rich geologic background. Accordingly, the purpose of this paper is to review the occurrence, origin, and transformations of geogenic Cr in the environment.

Specifically, the following questions will be examined through a critical synthesis of the relevant literature: (1) what are the anticipated Cr levels in the ultramafic environments? (2) In what form does Cr naturally occur and what are the relevant transformation processes for its release? (3) What is the influence of local geological and environmental factors on Cr mobility?

## Cr Occurrence in Ultramafic Environments

### *Surface and Ground Water*

There are several reports of elevated Cr(VI) concentrations in surface water, groundwater, and soil solutions from ultramafic and mafic geologic backgrounds, occasionally exceeding the World Health Organization (WHO) maximum contaminant level (MCL) for total Cr in drinking water (50 µg/L). Interestingly, groundwater and surface water data are available for only a subset of the regions with ultramafic geologic background. While some studies report Cr(VI) and some total Cr concentrations, it has been demonstrated in several areas that the correlation between the two parameters is very high (typically  $R^2 > 95\%$ ) and the fraction of Cr(VI) exceeds 80% [7, 17, 18], so that either parameter may be used to evaluate Cr(VI) presence. To facilitate discussion, studies were grouped by country as follows:

- a. *Italy*: In La Spezia, an alpine forested area, Cr(VI) concentrations in groundwater reached 73 µg/L, with 30 out of 58 samples exceeding 5 µg/L [4]. In the southern Apennines, with both forested and agricultural areas, 6 out of 43 springs had Cr(VI) >5 µg/L, with a maximum of 30 µg/L [19]. Lelli et al. [20] reported median groundwater Cr(VI) concentrations in the range 1–9 µg/L in selected areas in Tuscany, while individual samples had a maximum of 47 µg/L. In Calabria, groundwater concentrations of total Cr were below 10 µg/L [21].
- b. *Greece*: Several studies have reported groundwater concentrations for Greece, given its ophiolite-rich geologic background; however, the majority of the studies have concentrated in areas with mixed geogenic and anthropogenic influence. Megremi et al. [17] reported an average Cr(VI) concentration of 25 µg/L in a central Euboea aquifer and attributed concentrations exceeding 50 µg/L (max reported 360 µg/L) to industrial activities. Several studies have been conducted for the Asopos and Thiva basins, in which there is significant industrial activity in addition to a natural ophiolitic background, causing concentrations >200 µg/L [22–27]. The only identified study conducted in the agricultural area of Vergina reported Cr(VI) at 64 µg/L and total Cr at 90 µg/L due to the geologic background alone [7].
- c. *USA*: Ultramafic rocks in the western USA cover a wide area, ranging from Oregon in the north to the Mojave Desert in the southeastern part of California. Concentrations up to 60 µg/L were reported in the Mojave Desert [18], while the maximum reported concentrations decreased going north, to 30 µg/L in Santa Cruz county [28] and to 22 µg/L in the Cazadero area [2]. However, elevated Cr(VI) concentrations up to 46 µg/L, with 10 % of the groundwater samples exceeding 10 µg/L, were reported for groundwater in the Sacramento Valley in the northwestern part of the state [29, 30]. In the vadose zone of these soils, pore water Cr(VI) concentrations were even higher, ranging from 64 to 180 µg/L [29]. Springs in the Napa Valley north of the Sacramento valley were also found to have up to 90 µg/L total Cr [31]. The Santa Cruz, Napa, and Sacramento valleys are mostly agricultural and suburban areas, while Cazadero is a mountainous region and Mojave has some agricultural activity but is mostly desert.
- d. *Mexico*: The presence of ultramafic rocks in San Juan de Otates, in the agricultural area of León Valley, was linked to Cr(VI) concentrations in surface water in the range 11–14 µg/L and in groundwater concentrations up to 12 µg/L [32] and cycling between non-detectable and up to 16 µg/L according to more recent data [12].
- e. *Brazil*: This was the only area where naturally occurring Cr(VI) up to 45 µg/L was reported for groundwater from non-ultramafic parent protoliths, i.e., a sedimentary aquifer consisting of quartzose sandstones. The natural occurrence of aqueous Cr(VI) was attributed to weathering of diopside grains which contained up to 1.2 % of Cr<sub>2</sub>O<sub>3</sub> [33].

f. *New Caledonia*: Even though no data related to groundwater or surface water were identified for the ophiolite-rich New Caledonia region, Becquer et al. [5] reported that phosphate-fertilized soil solutions had Cr(VI) concentrations between 199 and 555  $\mu\text{g/L}$ , with a maximum at 700  $\mu\text{g/L}$ . The elevated concentrations were linked to the presence of phosphate, since non-fertilized soil solutions had Cr(VI) concentrations below 70  $\mu\text{g/L}$ .

Based on the above analysis, Cr(VI) concentrations in ultramafic environments exhibit substantial variability, ranging from non-detectable values ( $<1$   $\mu\text{g/L}$ ) to approximately 70  $\mu\text{g/L}$ . Despite the differences in the geochemical conditions (pH, oxygen, organic matter, weathering stage, and others) in different areas, it appears that geogenic Cr in groundwater generally does not exceed 90  $\mu\text{g/L}$  total Cr or 70  $\mu\text{g/L}$  Cr(VI). Stamatis et al. [26] and Megremi et al. [17] cited an upper limit of 50  $\mu\text{g/L}$  for geogenic Cr(VI) in Central Greece; however, the criterion for establishing the threshold was not discussed. While concentrations exceeding 70–90  $\mu\text{g/L}$  Cr(VI) or total Cr may be globally considered to have at least some anthropogenic origin, the background threshold will vary for individual areas depending on local conditions. Distinguishing the extent of Cr(VI) plumes in areas with high Cr(VI) background on the basis of concentration alone is challenging, and the use of alternative methods such as evaluation of isotopes is recommended [11]. Distinguishing between natural geogenic concentrations and anthropogenic contamination is particularly important from the regulatory standpoint, and evaluating trends in background concentrations is critical for public health considerations.

#### *Soils, Sediments, and Rocks*

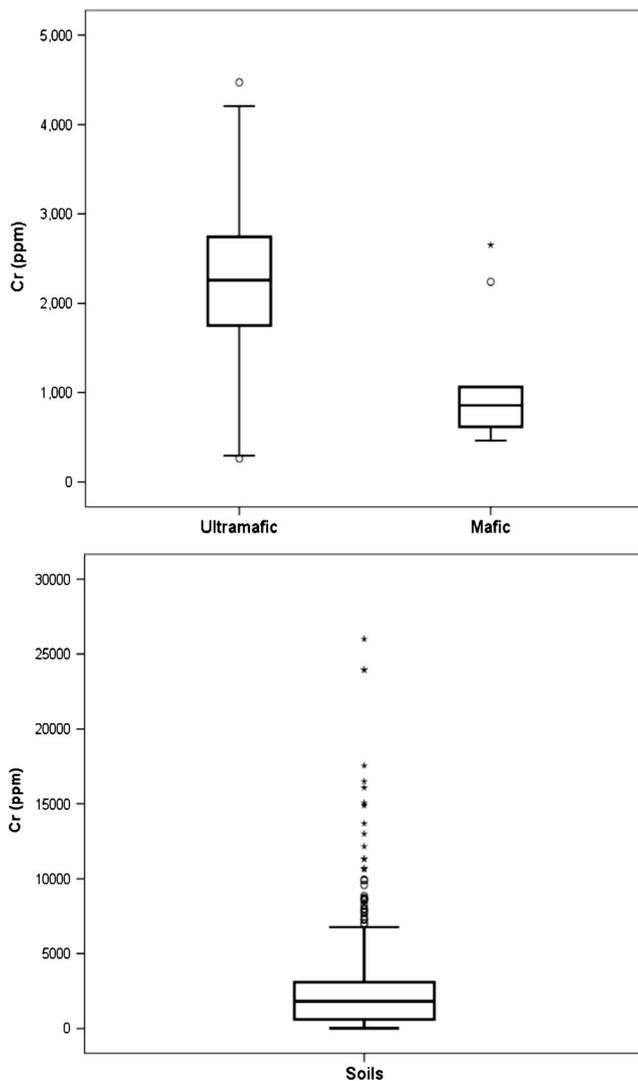
Naturally occurring Cr is typically associated with ultramafic igneous and metamorphic rocks, such as peridotites and serpentinites, and their derived soils. In some cases, mafic rocks and their products may also be linked to elevated Cr concentrations. Figure S1 provides an overview of the rock types encountered in this review, which are distinguished by their chemical and mineralogical composition. Ultramafic rocks are poor in Si rich in Mg and are composed of the primary minerals olivine and pyroxene. The process of serpentinization, i.e., hydration at low temperature and pressure, leads to metamorphic rocks called serpentinites, which are composed mainly of the minerals lizardite, antigorite, and chrysotile, also known as asbestos [34]. From these, ultimately serpentine soils and sediments are developed that are enriched in Cr and other associated elements such as Co and Ni [3, 34]. Some mafic rocks such as gabbro, with higher Si and lower Mg concentrations, have minerals that are also associated with ultramafic rocks, including chlorite and

amphiboles, and also have higher Cr contents compared to the global average of 35 mg/kg in the upper Earth's crust [35].

Accordingly, the Cr concentrations were evaluated for three groups, as shown in Fig. 1: ultramafic rocks (including igneous and serpentinized rocks), mafic rocks (both igneous and metamorphic), and soils developed in areas with both ultramafic and mafic rocks. While Deschamps et al. [36] provide a comprehensive review on serpentinite rock properties regardless of the geologic setting, this review focused on data available from areas with impacted soils, sediments, and aquifers, i.e., areas with potential human impact. Soils and sediments were grouped in a single category because various pedogenetic processes cause diverse soil and sediment environments with mixed geologic backgrounds. The raw data used to calculate the plots in Fig. 1 are provided in Supplemental Information, along with the descriptive statistics (mean, median, 95 % confidence intervals, variance, etc.). It should be noted here that performing statistical analyses for different types of analytical methods (e.g., X-ray fluorescence versus different types of digestions and ICP-MS) did not yield statistically significant difference in the overall results.

The mean and median values of the Cr concentration for ultramafic rocks are 2215 and 2261 mg/kg, respectively, close to the 2300 mg/kg provided by Alloway [35]. The interquartile range (25–75 percentiles) is 1750 to 2750 mg/kg. Deschamps et al. [36] reviewed the properties of serpentinite rocks from different protoliths and reported average Cr concentrations in the range 1734 to 2907 mg/kg. Subducted serpentinites that are typically associated with ophiolite complexes and serpentine soils had average Cr of 2900 mg/kg regardless of the protolith; the higher concentration is likely due to the fact that most datasets in the Deschamps et al. [36] analysis were from European ophiolite complexes. Isolating the European studies (Poland, Italy, Greece, and Czech Republic) in this analysis yields an almost identical average concentration of 2844 mg/kg. In terms of other geographic patterns, Californian rocks had all total Cr concentrations at or below average. In Mexico, a single available study reported much lower Cr concentrations for several rocks described as serpentinite [32]. Data on Cr rock concentrations in conjunction with soils in tropical areas was scarce and the few values reported for New Caledonia (2053 mg/kg [37]) and Cameroon (1437 mg/kg [9]) were below average, which is particularly interesting given the very high soil concentrations in these areas, as will be discussed subsequently. Additional datasets for rocks in these areas are available in geologic studies cited by Deschamps et al. [36].

Mafic rocks, for which there is much less data available, have lower mean (1100 mg/kg) and median (860 mg/kg) values and the interquartile range is also lower (620–1060 mg/kg). However, it is clear that mafic rocks also have the potential to have substantially higher Cr concentrations compared to the global average. These mafic rocks were



**Fig. 1** Boxplots of total Cr concentrations in ultramafic and mafic rocks (top) and soils and sediments (bottom). Raw data are available in Supplemental Information

encountered in Italy [38], in Poland [39], and in the Mojave Desert [40], and in all cases, they were present in association with ophiolite complexes. Finally, one case was reported in Brazil, in which diopside (pyroxene mineral) grains were present in a quartzite sandstone environment and resulted in Cr concentrations in the range 129–336 mg/kg [41] (these were not included in any statistics).

Soils and sediments presented a wider distribution of concentrations, which reflects the greater variability caused by various pedogenetic processes and contribution of different soil types mixed with the original weathering products of ultramafic rocks. The mean concentration was 2655 mg/kg and median 1810 mg/kg, with the interquartile range between 609 and 3077 mg/kg. Extreme outliers exceeding 10,500 mg/kg (three times higher than the interquartile range) were identified in lateritic soils from tropical areas, including New Caledonia [5, 41], Sri Lanka [42, 43], Brazil [8], and Africa

[9, 44]. Only one extreme outlier was identified in a temperate climate in Vergina, Greece, which also occurred in 100-m deep ophiolitic sediments [7]. Moderate outliers exceeding 6800 mg/kg (1.5 times higher than the interquartile range) were present in France [45] and Greece [7], in addition to tropical areas. The substantial accumulation of Cr in soils in these areas compared to the parent rocks is related to the accelerating weathering that causes leaching of mobile elements such as Mg, the primary element in ultramafic rocks, leaving behind less mobile elements such as Fe and Cr, a well-established process in several studies [5, 37, 45].

Weathering processes are also responsible for the vertical profile of Cr with depth. Oze et al. [2] summarized Cr profiles with depth down to 5 m in serpentine soils in the USA and Canada, and all showed a decreasing trend. Additional soil and sediment profiles across the world are shown in Figure S1. In New Caledonia, Brazil, and France, the trends were also decreasing with depth. This is attributed to mineral weathering processes that result in a net accumulation of immobile elements near the surface, as also observed for Fe and Al. This is also linked to the fact that all reported studies refer to relatively shallow soils, with the underlying bedrock at 1.5–2-m depth. Trends change for soils sampled from slopes and for very deep lateritic sediments, with only a handful of available studies. Dzemua et al. [9] reported Cr concentrations down to 20-m depth in a lateritic regolith developed on serpentinite from Cameroon; Trolard et al. [44] studied laterites developed on peridotite in Burundi down to 40 m; and Dermatas et al. [7] reported Cr concentrations down to a 93-m depth in Vergina, Greece. While Trolard et al. [44] present too few data points to identify specific trends, both Dzemua et al. [9] and Dermatas et al. [7] had similar trends: Cr concentrations decreased in the first 5–7-m depth, followed by a continuous increase up to 20 m in the Cameroon sediment and an overall, but not continuous, increase down to 100 m in the Greek sediment. Pedogenetic and weathering processes that explain trends in shallow soil layers are likely to be quite different in very deep sediments such as laterites. Furthermore, other factors, such as differences in mineralogical and chemical composition of the parent ultramafic rock and the weathering stage/age of the evolved lateritic soil developed on ultramafic rock, are critical factors affecting the worldwide encountered heterogeneities.

The distribution of Cr may also vary when examining the longitudinal behavior (along a toposequence) of these elements. Specifically, in Taiwan, lower concentrations were found on the summit and shoulder positions in contrast to higher concentrations on the backslope and footslope positions of a serpentinitic hill [46]. However, these trends were not similar in slopes studied in Italy [47] and Brazil [8], so that no generalized trend may be inferred for sloped soils. The vertical and lateral trends in Cr concentrations are driven by the mineralogy and the dominant weathering processes in

each locality, which are influenced by climate and topography. Accordingly, speciation and mineralogy will be discussed in the following sections.

## Mineralogy and Speciation

### *Chromium (III) Speciation*

Most of the Cr(III) minerals contain  $\text{Cr}^{3+}$  ions in octahedral coordination with oxygen. The fact that the octahedral radius of Cr(III), 0.615 Å, lies between the values of  $\text{Al}^{3+}$  (0.53 Å),  $\text{Fe}^{3+}$  (0.645 Å),  $\text{Ti}^{4+}$  (0.68 Å), and  $\text{Mg}^{2+}$  (0.72 Å) creates several isostructural possibilities for Cr(III) compounds and minerals with corresponding Al and Fe(III) phases, as well as substitutions between  $\text{Cr}^{3+}$  ions and Al, Fe, Ti, and Mg in octahedral sites. As such, there are several Cr-bearing hosts in ultramafic rocks and serpentine soils and their relative predominance depends on the weathering stage of the rock, sediment, or soil. Figure 2 provides an overview of the mineral groups encountered in rocks and soils/sediments in various weathering stages, while Table S3 contains detailed information about minerals and their chemical formulas. Table S4 summarizes the Cr host minerals reported in various studies worldwide.

The primary sources of Cr in rocks are chromite and Cr-magnetite, as well as other mixed-(Al, Mg, Fe, Cr) composition spinels [2, 5, 36, 46]. Chromite is typically not pure  $\text{FeCr}_2\text{O}_4$  [2] but contains high levels of Cr (>35 %  $\text{Cr}_2\text{O}_3$  in the majority of the data), while Cr-magnetite typically hosts less than 15 %  $\text{Cr}_2\text{O}_3$  in its structure (Table S4). The Cr content of rock-forming spinels reflects the origin of the parent rock, with high Cr values reflecting origin from subduction zones, while low Cr content is indicative of abyssal origin [36]. The #Cr ( $\text{Cr}/(\text{Cr} + \text{Al})$ ) is often used to differentiate between different types of serpentinite rocks [36]. Chromite grains often exhibit a characteristic zonation, in which an Mg–Al–Cr rich core is surrounded by a Fe-rich rim that consists primarily of ferrichromite and ultimately magnetite [32, 37, 48–50]. The significance of this chemical modification is that it can increase labile Cr [32].

Cr-bearing spinels persist to some degree in soils and sediments. The contribution of spinels to the total Cr content of soils is usually difficult to establish due to a lack in quantitative data for the abundance of either the amount of spinels or their Cr content. Morrison et al. [49] reported a spinel content (including magnetite and chromite) between 4 and 7 % for serpentine soils in California, and the chromite Cr content was 25–30 %, while magnetite rims had no measurable Cr. One percent of chromite with 30 % Cr content corresponds to 3000 mg/kg total Cr, while the total Cr of the soil was reported at 2000 mg/kg, which means that almost all Cr could be accounted for by a Cr-rich spinel. Taking the average  $\text{Cr}_2\text{O}_3$  concentrations reported in all individual studies (Figure S3),

chromite grains contain 38 %  $\text{Cr}_2\text{O}_3$  in rocks and 43 % in soils which corresponds to 2600 mg/kg Cr for 1 % of chromite in rocks and 2940 mg/kg Cr in soils. Comparing these values to the total Cr concentrations found in most rocks, soils, and sediments, it follows that Cr-bearing spinels likely account for the vast majority of Cr mass.

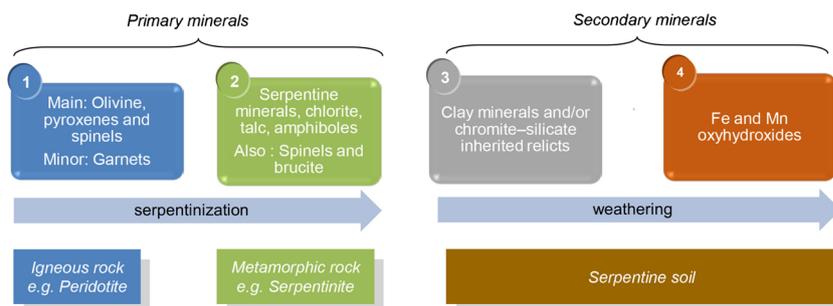
Typically, Cr concentrations are enriched in the sand-size fraction which corresponds to the size of most chromite grains inherited from the serpentinite [36, 51]. Comparing the chromite grain concentrations between an ultramafic bedrock and the derived soil, the soil chromite grains contained significantly higher concentrations of Cr in two regions with available data, Greece and California [51, 52]. Kelepertzis et al. [52] and Fandeur et al. [37] observed an accompanying reduction in the Al content of the relict chromite grains in soil compared to bedrock, which is likely due to incongruent dissolution that preferentially releases  $\text{Al}^{3+}$  vs.  $\text{Cr}^{3+}$  into solution. Magnetite presented the same trend of Cr enrichment in the soil vs. the rock in California [51], but this was not the case in the rock and soil from Poland [6].

Of the remaining rock-forming minerals (groups 1 and 2 in Fig. 2), pyroxenes and chlorite are the most important Cr hosts. Pyroxenes, mostly enstatite and augite, incorporate 0.1–1.5 % of  $\text{Cr}_2\text{O}_3$  in their structure in rock studies from several localities (Greece, Czech Republic, Poland, California, New Caledonia). Pyroxenes are generally depleted from the parent rock during the serpentinization process and thus occur in soils and sediments only as trace phases in isolated cases [52, 53]. Chlorite abundance has been reported at 15 % in rock [51] and between 2 % [49] in serpentine soil and 9 % in deep serpentine sediment [7]. Its  $\text{Cr}_2\text{O}_3$  content in soils is typically in the range of 0.4–1 %, so that 1 % chlorite may account for approximately 40–100 mg/kg total Cr.

Serpentine minerals, which are the major phases in serpentine rocks (up to 70 % [51]) and are still present in substantial amounts in serpentine soils (e.g., 34–37 % in California [49]), typically contain less than 1 %  $\text{Cr}_2\text{O}_3$  in their structure. Oze et al. [51] found no Cr in serpentine minerals in Californian serpentinite, while Fandeur et al. [37] determined that lizardite was the primary Cr-bearing phase in New Caledonia. While the Cr content of serpentine minerals may be low, their abundance renders them important phases for Cr release on a mass basis. For example, 30 % of lizardite with 0.5 %  $\text{Cr}_2\text{O}_3$  in its structure can account for 1000 mg/kg of total Cr in the soil. Assessing a true average Cr content in a large serpentine mass using microscopy methods is, however, a challenge, as typically, studies present results of isolated grains and point analyses.

Garnets and epidotes, which are typically minor phases in ultramafic rocks, have the capacity to bind high amounts of Cr (up to 29 %  $\text{Cr}_2\text{O}_3$  for garnets, and 19 % for epidotes). However, their low abundance renders them secondary hosts in terms of the overall mass retained in the rock. Other less

**Fig. 2** Overview of the most important minerals found within ultramafic rocks, serpentinites, and the derived serpentine soils



important Cr hosts in rocks are amphiboles, such as actinolite and tremolite [6, 52, 54], micas [2, 6], talc [5], and olivines [4, 6, 32]. Silicates overall have been found to account for less than 10 % of the total Cr mass in soil [51].

Fe(III)-oxides and (oxy)hydroxides such as goethite, hematite, and maghemite, either well-crystallized or amorphous, are generally considered as important hosts for Cr in serpentine soils [2, 37, 52, 54]. These can provide surface sites (via sorption) or structural sites (via isomorphic substitution) for Cr(III) sequestration. Goethite and hematite were found to be the main Cr scavengers in soils derived from ultrabasic rocks in New Caledonia, with 40 % of the total available Cr included in goethite from Ferralsols [5] and between 67 and 75 % of the total Cr in goethite and hematite from Oxisols [37]. In both cases, while the  $\text{Cr}_2\text{O}_3$  content was relatively low ( $\sim 2$  %), these highly weathered soils had high contents of Fe oxides. To a lesser extent, Cr-bearing goethite was found to accommodate Cr ( $\sim 1.70$  wt.%  $\text{Cr}_2\text{O}_3$ ) in sediments and soils influenced from ultramafic parent rocks (i.e., peridotite) in Greece [55]. Soils developed from serpentinites and/or partially serpentinized peridotites from Poland had Cr in a mixture phase consisting of oxyhydroxides and clay minerals (0.14 wt.%  $\text{Cr}_2\text{O}_3$ ) [13]. Finally, Cr-bearing ferrihydrite was identified in California soils [49].

Secondary phyllosilicates and in particular clays (such as smectite and vermiculite) can trap Cr(III) either via isomorphic substitution into their crystal lattices or via sorption onto their surfaces [2]. These are typically found in soils in temperate climates, as they are the weathering products of primary silicates, and specifically chlorite and serpentine [45, 56], while in tropical climates complete leaching of Mg leads to direct formation of metal oxides [6]. A sequence between different secondary clay minerals and oxides along soil profiles developed from serpentinites from the bottom (lower profile/horizon) toward the top (surface profile/horizon) under temperate climate can be expressed as Mg-clays  $\rightarrow$  Fe-clays  $\rightarrow$  Al-clays  $\rightarrow$  Fe and Al (oxy-hydr)oxides [56]. Kierczak et al. [6] and Caillaud et al. [56] associated drainage conditions and thickness of serpentine soils with clay mineralogy. Well-drained soils are shallow soils with very thin (mm thick) developed C horizon (saprock), containing stable vermiculite, whereas poorly drained soils are thicker soils with well-

developed (meter thick) saprock and saprolite containing smectites. Smectite is the ultimate weathering product under impeded, poorly drained landscape positions in temperate [57, 58] or humid tropical climates [59]. From the above analysis, it follows that the significance of clays in hosting Cr on a mass basis depends on the weathering stage of the soil or sediment. For example, Caillaud et al. [45] reported that vermiculite was the most significant Cr host in the uppermost weathered B horizon in French soil, while spinels and chlorite persisted and contained most Cr in the lower C horizon and in the bedrock.

In Taiwan, soils in more advanced development stage at the footslope of a toposequence had more Cr bound in clays, especially vermiculite, and this was also associated with higher availability for leaching [60].

More exotic species that can accumulate Cr(III) include sulfides and alkaline oxides and sulfates. In particular, sulfides from ultramafic rocks from Mexico were found to contain less than 1 wt.% of Cr [32]. Also, at a rock complex at the Nabi Musa locality (Judean Desert, Israel), where processes like high and ultrahigh temperature combustion of metamorphic rocks and low-temperature hydrothermalism have resulted in a hyperalkaline environment ( $\text{pH} > 11$ ), Cr(III) was found in bentorite, a Cr(III)-rich variety of ettringite [ $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26(\text{H}_2\text{O})$ ], and in uncommon oxides such as brownmillerite [ $\text{Ca}_2(\text{Al}, \text{Fe}^{3+})_2\text{O}_5$ ] and perovskite ( $\text{CaTiO}_3$ ) [61].

#### Chromium (VI) Speciation

Chromate minerals are extremely rare in nature and their occurrence has not, thus far, been linked to areas with geogenic Cr exhibiting elevated Cr(VI) concentrations in the aqueous phase. The average Cr–O distance in chromate ( $\approx 1.65$  Å) is within the range of S–O distance in sulfate (1.46 Å), P–O distance in phosphate ( $\approx 1.52$  Å), and As–O distance in arsenate ( $\approx 1.68$  Å), so that solid solutions are found between these oxyanions in secondary minerals [62]. For example, crocoite ( $\text{PbCrO}_4$ ) is extremely rare in serpentinites and the occurrence of this mineral is mainly limited to specific localities such as in Australia, Tasmania, and the Urals [2] and references therein]. Chromatite ( $\text{CaCrO}_4$ ) has been identified in Jordan as lemon-

yellow precipitates within fractures of Upper Cretaceous limestones and marls, co-occurring with gypsum [63] and at the Nabi Musa locality (Judean Desert, Israel) where hashemite ( $\text{BaCrO}_4$ ) occurred in solid solution with barite ( $\text{BaSO}_4$ ) [61]. In general, Cr(VI) occurrence and mobility in serpentine environments is mostly affected by redox reactions and sorption, instead of precipitation, and these will be considered next.

### Transformation and Release Processes

Cr may be transported in the subsurface either through physical weathering and transport of the rock and soil constituents [64] or through chemical weathering and transport in the aqueous phase. As previously discussed, almost all minerals (e.g., spinels such as chromite and Cr-magnetite, Fe-oxides, pyroxenes, chlorites, clays, serpentines, and various silicates) may contain variable amounts of Cr(III), while Cr(VI) is hardly ever present in the solid phase. Conversely, transport of Cr in the aqueous phase occurs almost exclusively in the hexavalent form, given the low mobility of Cr(III). Thus, mobility of Cr in ultramafic systems depends primarily on two subsequent reactions: release of Cr(III) into solution due to mineral weathering and oxidation of Cr(III) to Cr(VI). Following these reactions, Cr(VI) may also react with the solid phase either via sorption or via re-reduction by naturally occurring reductants (mostly ferrous iron and sulfide). These processes are illustrated in Fig. 3, assuming that chromite is the primary Cr(III)-bearing phase in the soil or sediment and which is typically the most important Cr(III) host on a mass basis. However, all Cr-bearing minerals are subject to chemical weathering and release of Cr(III) into solution. Even minerals with lower Cr concentrations compared to chromite, e.g., chlorite, pyroxenes, and clay minerals, may be substantial sources of Cr to soil solution given their relative susceptibility to weathering and dissolution [51].

The relative stability of minerals encountered in ultramafic and serpentine soil may be summarized in the following sequence (with increasing resistance to weathering): olivine < pyroxenes < serpentine < chlorite < talc < Fe-oxides (hematite, goethite) + spinels (chromite, magnetite) [2, 52, 55, 56]. From this weathering sequence, it can be concluded that Cr-spinels (chromite and Cr-magnetite) are the most recalcitrant minerals and indeed, the bioavailability of Cr is typically very low, in the order of 1 % of the total concentration [2].

Weathering of primary and secondary minerals is influenced by several factors, such as pH, presence of organic acids, and microbial activity [47, 65]. Kierczak et al. [66] observed that the relationship of these parameters and Cr mobility was more pronounced in soils exhibiting advanced serpentinization. The effect of soil organic acids such as oxalic and citric acid to metal (Cr, Mg, Fe, Ni, and Co) leaching and enhancing of the dissolution of the Cr-bearing phases is pronounced. Oxalic acid produced from a lichen may also

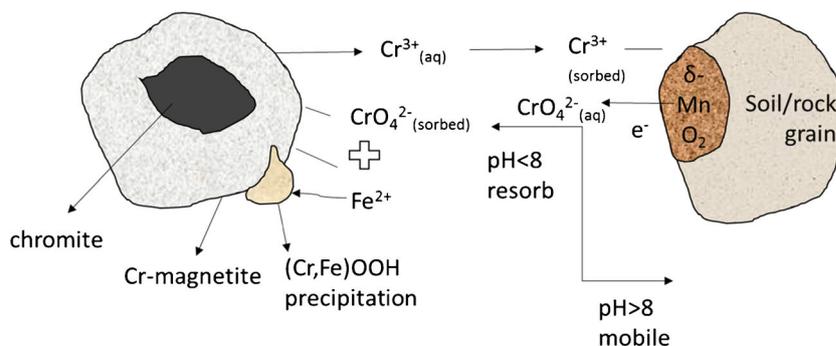
accelerate mineral weathering. The growth of *Lecanora atra* (lichen) on chrysotile in a serpentinic rock formed a crust, where accelerated decomposition of chrysotile was observed, presumably with oxalic acid as the active agent [67].

Another influencing factor is agricultural activity and specifically the use of ammonium fertilizers. Mills et al. [29, 68] observed higher Cr(VI) concentrations in surficial soil compared to deeper layers and attributed this phenomenon to the addition of ammonium fertilizers to the soil. Nitrification (oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ ) results in production of  $\text{H}^+$  and soil acidification, which favors the increased dissolution of Cr(III), which is the limiting step for oxidation and production of Cr(VI) [29]. Becquer et al. [5] also observed increased aqueous Cr(VI) concentrations in the presence of phosphate fertilizers, in which case the mechanism was most likely related to increased chromate desorption and not enhanced Cr(III) release. However, the relative contribution of these mechanisms have been insufficiently studied and additional research is required to understand the rates of geogenic Cr release.

The release of Cr(III) in solution results in almost immediate immobilization due to its low solubility. If the conditions are conducive, it may be included in secondary phases, such as clays and Fe oxyhydroxides. A simple geochemical model using Visual Minteq [69] indicates that the solubility of Cr(III) with respect to  $\text{Cr}(\text{OH})_3$  is approximately 5  $\mu\text{g/L}$  in the pH range 7–10.5 and increases rapidly to 40  $\mu\text{g/L}$  at pH 6 and 100  $\mu\text{g/L}$  (the initial assumed concentration) at pH 5.5. Observed concentrations of Cr(III) in weakly alkaline natural waters have typically been well below solubility, in the range <0.01 to 0.1  $\mu\text{g/L}$  and one occurrence at 70  $\mu\text{g/L}$ , indicating that its concentration is likely controlled by lower solubility minerals in these ultramafic environments [70].

There are very few oxidants for Cr at room temperature and Mn-oxides have been considered the primary oxidants in soil and rock environments [71]. Particularly, mixed-high-valence Mn(IV/III)-oxides, such as birnessite [72], pyrolusite, and cryptomelane [73] as well as hausmannite ( $\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$ ) and manganite ( $\text{Mn}^{3+}\text{OOH}$ ) [74], are all potential Cr oxidants and typically present as coatings on soil/rock grains (Fig. 3). Manceau and Charlet [75] showed that Cr(III) oxidation occurs through electron transfer in the solid phase, once Cr(III) has been adsorbed to the Mn oxide surface. Oze et al. [76] studied the interaction between chromite and birnessite and provided a pH-dependent expression for Cr(VI) production, with decreasing pH resulting in increased Cr(VI) production. Incubation experiments with natural soils yielded Cr(VI) production of 1.3 nM/h at pH 5. Rajapaksha et al. [77] recently studied the interaction between Cr(III)-muscovite and birnessite and found that up to 380 nM/h (or 48 nmol/g\*h) of Cr(VI) could be produced by a 8 g/L fuchsite (Cr-bearing muscovite) suspension at pH 3; this rate decreased by one order of magnitude as the pH increased to 5 and two orders of magnitude at pH 8. At pH 5, the observed rate was 23 nM/h,

**Fig. 3** Schematic of primary Cr reactions in an ultramafic system considering chromite as the primary mineral host



i.e., ten times faster compared to the natural soil by Oze et al. [76]. This is expected, as the concentration of active Mn-oxides and the dissolution of Cr(III) are expected to be lower in a natural soil compared to a controlled system, as well as to the lower expected solubility (due to higher weathering recalcitrance) of chromite compared to a phyllosilicate mineral such as muscovite; still, the values are relatively comparable. Saputro et al. [70] studied the release of Cr(VI) from natural serpentinite and reported 11.5 nmol/gh at pH 4–6 and 60 nmol/gh at pH 8–10. Thus, while the values are relatively comparable to Rajapaksha et al. [77], the pH trend was opposite. This was attributed to the presence of natural reductants such as humic acids, as well as Cr(III) complexation by organic matter [70]. Similarly, Rajapaksha et al. [77] reported that the presence of humic matter resulted in inhibition of the oxidation reaction due to the formation of soluble Cr(III) organic complexes that presumably inhibits sorption and electron transfer from the Mn oxide surface. However, Cr(III) complexation with organic matter increases with pH [78], so that the pH trend observed by Saputro [70] cannot be explained by this phenomenon alone.

There is only one study that has recently reported on the heterogeneous reaction between solid  $\text{Cr}(\text{OH})_3(\text{s})$  and Mn oxides. Specifically, Namgung et al. [79•] reported that the oxidation of dissolved Mn(II) by oxygen was catalyzed on the surface of  $\text{Cr}(\text{OH})_3$ , which was in turn oxidized by the produced high-valence Mn oxide, a birnessite-like product. The production of Cr(VI) was highest at pH 9 and reached 8  $\mu\text{M}$  or 400  $\mu\text{g/L}$  within 20 days of reaction. The fact that Cr(VI) production increased as the pH increased from 7 to 9 indicates that oxidation likely occurred through a solid-solid reaction, given that Cr(III) solubility with respect to  $\text{Cr}(\text{OH})_3$  decreases between pH 7 and 9 and starts increasing again above pH 9.5–10. Thus, this mechanism may be important for geogenic soils with Mn(II) present in solution and also explain the pH trends observed by Saputro [70].

Other potential oxidants for Cr(III) in natural waters include dissolved oxygen (DO) and peroxide ( $\text{H}_2\text{O}_2$ ). Rai et al. [80] found that DO oxidizes Cr(III) into Cr(VI), but the rate of oxidation at room temperature is very slow and enables Cr(III) to be involved in faster concurrent reactions

(sorption or precipitation). Therefore, the oxidation of Cr(III) by DO is unlikely in soils. In another study, Eary and Rai [73] reported no oxidation in  $10^{-4.72}$  M Cr(III) solutions that were saturated with DO at 27 °C after as long as 24 days. Fendorf and Zazoski [72] found that small amounts of Cr are oxidized by DO at pH values greater than 9, but these conditions are uncommon in soil or water environments. Overall, it appears that the rate of this reaction is sufficiently slow in natural waters that it is not responsible for the higher levels of Cr(VI) observed in groundwater. Most recently, Oze et al. [81••] reported that  $\text{H}_2\text{O}_2$  is a viable oxidant for Cr(III) in ultramafic environments, even in the absence of oxygen, utilizing both laboratory tests and field observations. This study alters the currently accepted paradigm of Mn-induced oxidation and the relative contribution of each mechanism should be further explored.

The fate of Cr(VI) produced by oxidation is determined by sorption and reduction processes. Sorption is regulated by the presence of iron oxyhydroxides, which are the most common sorbents for Cr(VI) [82], and by groundwater pH. Izbicki et al. [11] observed Cr(VI) concentrations above 5  $\mu\text{g/L}$  only when the pH increased above 7.5 in the mafic environment of the Mojave Desert, and this was attributed to desorption from the solid when the pH is increased above 8. In general, oxic and alkaline conditions are necessary for enhanced mobility of Cr(VI), as these are unfavorable for sorption and reduction reactions that result in Cr immobilization.

If naturally occurring reductants are present, then Cr(VI) will be reduced and reprecipitate as Cr(III). If reduction occurs away from the original source of Cr(VI), it is possible to evaluate whether reduction has occurred through the evaluation of Cr isotopes [83, 84]. Specifically, the  $^{53}\text{Cr}/^{52}\text{Cr}$  ratio increases with increased reduction, as the lighter isotope is preferentially reduced by reductants such as magnetite [83]. Fractionation is measured using the parameter  $\delta^{53}$ , where the ratio  $^{53}\text{Cr}/^{52}\text{Cr}$  of the NIST standard 979 (a chromium nitrate salt) is  $0.11339 \pm 0.00015\%$ . Reduction of Cr(VI) has been observed to cause an increase in the  $\delta^{53}$  value from 0 ‰, which is considered the average of the Earth's crust, to values between 1.1 and 5.8 ‰ observed in groundwater plumes [11, 84]. Conversely, studies by Zink et al. [85] indicated that oxidation

of Cr(III) to Cr(VI) did not result in substantial isotopic fractionation. Sorption of Cr(VI) on mineral surfaces does not produce substantial fractionation either [86].

Farkaš et al. [87] observed that even though the average  $\delta^{53}$  value in chromites around the world is  $-0.079\text{‰}$ , substantial increase was observed with increased alteration and serpentinization of ultramafic rocks, reaching a maximum value of  $1.219\text{‰}$ . The authors theorized that this may be related to contact of produced Cr(VI) with magmatic Fe(II) during alteration and serpentinization. This observation is important in evaluating field data from ultramafic regions, since the base  $\delta^{53}$  value may be different than the commonly assumed  $0\text{‰}$  of the Earth's crust. Izbicki et al. [11] investigated Cr isotope ratios in a geogenic Cr plume in Mojave Desert and observed that while the  $\delta^{53}$  value was not by itself diagnostic of anthropogenic vs. geogenic origin, it was possible to evaluate the anthropogenic input by combining the isotope data with oxygen and deuterium isotope, as well as major ion data.

### Outlook and Knowledge Gaps

Natural occurrence of hexavalent chromium in natural waters and especially groundwater is a potential public health concern in several areas globally, given that the observed concentrations often exceed  $10\text{ }\mu\text{g/L}$ , the current standard in the state of California, and some cases even  $50\text{ }\mu\text{g/L}$ , the suggested maximum contaminant level by the World Health Organization for total Cr. While policy on the regulation of Cr(VI) and total Cr in drinking water remains inconsistent, the current state of knowledge clearly dictates that hazardous levels of Cr may be produced in aqueous environments with ultramafic geologic backgrounds, under favorable geochemical conditions. The surveyed literature indicates that alkaline ( $\text{pH} > 8$ ) and oxic environments are favorable for enhanced Cr(VI) mobilization, as these conditions minimize competing immobilization processes, i.e., sorption and reduction, both of which are favored by more acidic pH, and reduction is correlated with anaerobic and anoxic conditions. The genesis of Cr(VI) from the rock, sediment, or soil involves an oxidation step, given that Cr is exclusively present as Cr(III) in the various minerals comprising the solid phase. These minerals include chromite, which appears to be the most important host for Cr(III) on a mass basis, followed by chlorite, Fe–Cr oxyhydroxides and clays that are formed as a result of weathering processes. Cr(III) released by these minerals upon weathering and dissolution is available to participate in redox reactions. Oxidation has been thought to be primarily driven by high-valence Mn oxides (birnessite, pyrolusite, and others), but recent analyses indicate that metastable hydrogen peroxide may also be an important oxidant in the subsurface. The role of dissolved oxygen remains unclear, even though the available studies indicate that this mechanism is too slow to produce substantial levels of Cr(VI) in groundwater.

Dissolved oxygen may be important to drive oxidation of dissolved Mn(II) that can precipitate on Cr(III)-bearing solids as birnessite and drive solid-solid Cr oxidation.

Despite the understanding of the speciation of Cr in natural geological settings, as well as the general mechanisms of oxidation and release, there are still several unanswered questions to address. The most important of these are the following:

- To what extent are oxidation mechanisms active over time, as the surface of the participating minerals is passivated and how can the groundwater levels of Cr(VI) be predicted as a function of geochemical conditions?
- At what rate is Cr(VI) produced in productive aquifers today and what is the influence of the measured concentrations on the quality of irrigation water and the impacted crops in agricultural areas?
- What is the impact of agricultural and other anthropogenic activities on the background levels of Cr in different areas around the world?

Additional research is necessary to address the aforementioned issues, both at the fundamental level (e.g., to further investigate oxidation mechanisms) as well as at a larger scope to assess the feedback between agricultural activity and Cr levels in groundwater, soil, and crops.

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### Compliance with Ethical Standards

**Conflict of Interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

**Human and Animal Rights and Informed Consent** The article does not contain any studies with human or animal subjects performed by any of the authors.

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