

Fire-induced oxidation of Cr(III) in serpentine soils

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Abstract Ophiolite rocks and their weathering products are the major hosts of Cr(III)-bearing phases in the Earth's crust. Trivalent Cr is rather benign, but risks arise because of its potential for oxidation to the toxic and carcinogenic hexavalent form. Manganese oxides are the most effective natural oxidants, whereas oxidation by atmospheric oxygen is, luckily, very slow. However, oxidation reactions under the highly oxidizing environment of wildfires is largely unexplored. Under this context, we examined the genesis of Cr(VI) by fire-induced heating of ultramafic rocks and serpentine soils. Total Cr(VI) contents of unheated soils ranged from 1.3 to 24 mg kg⁻¹, while the water soluble fraction accounted for less than 2% of total Cr(VI). After heating the soil samples at 600°C for 1 h, total Cr(VI) contents increased by factors 2–41. The water soluble fraction accounted for 33–52% of total Cr(VI). Our results suggest that in fire-impacted areas, there is an increased risk of geogenic Cr(VI) contamination. Even though soil temperatures could exceed 700 °C, our preliminary results showed that Cr(VI) contents in a fire-impacted site did not change as dramatically as under laboratory conditions.

Keywords: ophiolites, serpentinites, geogenic Cr, oxidation, wildfire

1. Introduction

Redox reactions occurring in nature and involving Cr(III)/Cr(VI) species are of great scientific interest and concern, because the two forms have different chemical and toxicological profiles. Trivalent Cr has low mobility in natural waters, as it forms low solubility hydroxide precipitates and binds strongly on mineral surfaces (Fendorf 1995). Hexavalent Cr, present as chromate or dichromate anions, binds less extensively on soil and sediment minerals, and thus, has both greater dissolved concentrations and propensity for transport within aquatic systems (Hausladen and Fendorf, 2017). In terms of toxicity, Cr(III) is considered a nutritional supplement, whereas Cr(VI), mimicking sulphate and phosphate anions, can be transported into human body cells with toxic and carcinogenic effects (Costa and Klein, 2008).

Ultramafic rocks, such as peridotite, their alteration products (serpentinites) and deriving soils, generally called serpentine soils, are the major hosts of Cr(III)-bearing minerals with typical concentrations hundred times more than average contents of the Earth's upper crust (Chrysochoou et al., 2016). In Cr-bearing minerals, Cr occurs in the trivalent form, however, it may be released and oxidized to Cr(VI), jeopardizing water quality. In fact, as reviewed by Chrysochoou et al. (2016), numerous cases of geogenic Cr(VI) contamination have been reported in groundwater worldwide, occasionally exceeding the 50 µg L⁻¹ WHO limit for drinking water.

The most effective, native oxidizing agents of Cr(III) are Mn(III)/Mn(IV) oxides. Oxidation by atmospheric oxygen, although thermodynamically feasible, is luckily, very slow (Eary and Rai, 1987). Nevertheless, the oxidation reaction is accelerated under high-temperature, oxidizing conditions, as for example the industrial production of chromate salts from chromite, coal and cement production, and Cr-enriched waste incineration (Apte et al., 2006; Panichev et al., 2008). Although largely unexplored, some studies have shown that similarly favorable conditions could be created under wildfires (Burton et al., 2019; Panichev et al., 2008). On average, about 65,000 fires occur in Europe every year and over 85% of the burnt area is in the European Mediterranean region (San-Miguel-Ayanz et al., 2012), while the length and severity of the fire season, the area at risk, and the probability of large fires are expected to increase due to climate change (EEA, 2017).

Previous studies on the effects of fire on Cr speciation were conducted either by using synthetic Cr(III)-compounds, or in non-contaminated soil of relatively low Cr content (<220 mg kg⁻¹) (Apte et al., 2006; Burton et al., 2019). Given the widespread occurrence of ultramafic rocks in Greece, as well as other high-risk wildfire areas around the globe (e.g. Eastern USA coast, southern Europe, Africa), this study aims at further exploring the potential of Cr(III) fire-induced oxidation of native, Cr(III)-bearing rocks and soils. In this context, we collected ultramafic rock and serpentine soil samples and analysed them for their water-soluble and total Cr(VI) before and after subjecting them to laboratory heating, as well as after a wildfire event.

2. Material and Methods

2.1. The study areas and fieldwork

Rock and soil sampling took place in two ultra mafic-rock related settings of Greece (Fig. 1). The first study area was parts of the Venzia Basin in Grevena region, Northern Greece, and samples included serpentine soils (n=6) developed on serpentinite. The second study area was in Messapia municipality, in Central Evia, and took place in September 2019, less than a month after a devastating wildfire that burnt 23,500 ha of forest and agricultural land. Rock and soil samples were obtained from both burnt (n=2) and unburnt sites (n=3) and included in total five rock (pyroxenite), and five soil samples. Rock samples were crushed and subsequently ground in a mechanical mill until passing a 2 mm nylon sieve. Soil samples were homogenized and sieved through a 2 mm nylon sieve.



Figure 1. The study areas of the present study marked on map showing the main ophiolite rock occurrences in Greece (green areas).

2.2. Laboratory work

Water-soluble Cr(VI) was determined after extracting the solid samples with deionized water (MilliQ) in a 1:10 solid: solution ratio for 24 h at room temperature. After centrifugation and filtration through a 0.22 μm syringe filter, Cr(VI) was measured by the 1,5 diphenylcarbazide (DPC) method (James et al., 1995) with a Varian Cary 1E UV-vis spectrophotometer. Total Cr(VI) contents were determined as above after a strongly alkaline (pH 12) digestion under heat (90–95 °C) (James et al., 1995). Mineralogical analysis was conducted on selected soil samples before and after the heating process. X-ray diffraction (XRD) analysis was conducted by using a Siemens D5005 X-ray diffractometer applying Cu K α radiation at 40 kV and 40 nA, and mineral identifications were made with the Diffrac Plus software. Carbon-coated grains of pulverized rock samples were studied by scanning electron microscope (SEM, Jeol JSM-5660

instrument) equipped with an energy dispersive X-ray spectrometer for analysis (EDS, Oxford Link ISIS 300). The soil pH and EC were potentiometrically determined in a 1:10 solid: deionized water, using a Thermo Orion 3 Star meter equipped with a Senorex Polymer body sealed pH & ORP electrode. For the laboratory simulation of fire, a portion of rock and soil samples were placed in crucibles and heated in a high temperature muffle furnace (CARBOLITE CWF 1200).

3. Results and Discussion

3.1. Initial characterization of samples

Grevena serpentine soil was slightly acidic to neutral (pH range: 6.2–7.4; median: 6.9). Total Cr(VI) contents, consisting of soluble, precipitated, exchangeable and non-exchangeable forms, ranged from 3.36 to 24.35 mg kg^{-1} (median: 8.43 mg kg^{-1}).

Total Cr(VI) contents comprised only a small fraction of total Cr (hexavalent and trivalent) present in the samples, accounting for 0.05–0.29% of total Cr. This is in line with other studies reporting that only a small fraction of Cr(III) is oxidized to the toxic hexavalent form (Mills et al., 2011). Water soluble Cr(VI) contents ranged from below detection limit ($5 \cdot 10^{-3} \text{ mg kg}^{-1}$) to 0.11 mg kg^{-1} , which are comparable to those found in surface soil of California by McClain et al. (2019) (<0.18 mg kg^{-1}), but much lower than those found in acidic soils in Niquelandia, Brazil (64–1014 mg kg^{-1}) (Garnier et al., 2009), where the low pH values (~ 5) promote the dissolution of Cr(III) from the mineral phases. Water soluble contents of Grevena soil accounted for only 0.2% of total Cr(VI).

3.2. Cr(VI) formation after heating

Surface soils temperatures during fires are in the range 100–700 °C, while temperatures up to 850 °C could occur for brief periods (Burton et al., 2019). Based on our preliminary tests on the duration of heating and bibliographic data on temperature, heating experiments were conducted at 600 °C for one hour.

Heating of the Grevena soil samples resulted in substantially increase of pH (Fig. 2a). Total Cr(VI) contents ranged from 14.0–77.6 mg kg^{-1} (Fig. 2b), corresponding to an increase by factors 2–10 of native Cr(VI).

These results clearly evidence that fire-induced oxidation of Cr(III), previously reported for synthetic Cr(III) phases (Apte et al., 2006; Burton et al., 2019), also takes place in native Cr-bearing mineral assemblages (i.e. serpentine soil), at temperatures that could occur in surface soils during fires.

An even higher increase was found for the water-soluble fraction (Fig. 2c) that was 33 to 52 times higher than the initial values. This could be explained by the fact that at the alkaline pH (7.4–9.4) of the heated soil samples, adsorption of Cr(VI) is expected to be minimal (Eary and Rai, 1987; Hausladen and Fendorf, 2017), thus, more Cr(VI) resides in soluble forms.

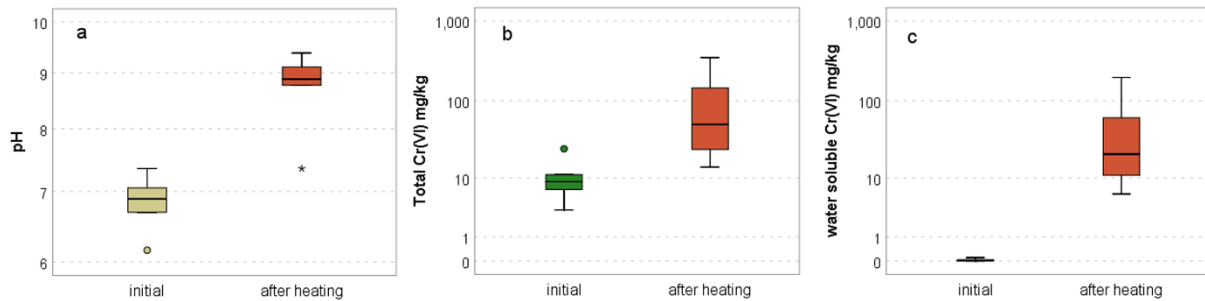


Figure 2. Variations of (a) pH, (b) total Cr(VI), and (c) water-soluble Cr(VI) contents of the initial and after laboratory heating of Grevena soil samples

A change in the mineralogical composition of the heated soil samples has been noticed with disappearance of XRD peaks of nontronite and appearance of talc and chromite. Furthermore, clastic chromite grains became visible in SEM photomicrographs in the heated samples (Fig. 3).

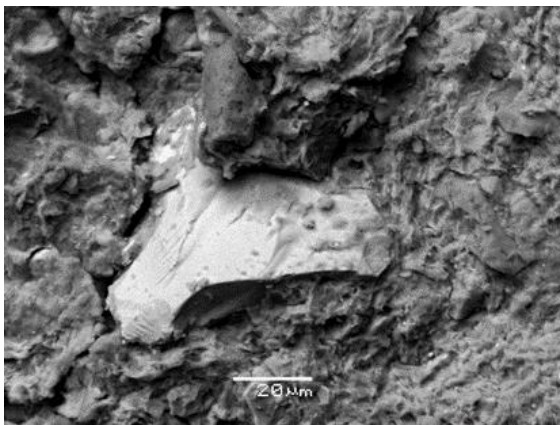


Figure 3. SEM photomicrograph showing a clastic chromite fragment (bright area) within the burned matrix of serpentine soil from Grevena heated at 600 °C in the muffle furnace.

3.3. Effects of a wildfire

The effects of a wildfire on the genesis of Cr(VI) were studied in the second study area, Messapia, Central Evia. Rock and soil samples were obtained from both burnt and unaffected by the fire sites.

Total Cr(VI) contents of unburnt rock and soil samples were 3.94 mg kg^{-1} and 9.81 mg kg^{-1} , respectively. Significantly lower levels ($0.2\text{--}1.04 \text{ mg kg}^{-1}$) were determined in soil rhizosphere zone in C. Evia by Megremi (2010), probably due to back reduction of Cr(VI) to Cr(III) by the abundant organic matter.

Water-soluble Cr(VI) contents of rock and soil samples were 0.07 and 0.02 mg kg^{-1} , respectively.

At the fire-affected sites, median total Cr(VI) contents were higher in the soil samples (8.66 mg kg^{-1}), followed by rock (4.90 mg kg^{-1}), and ash samples (2.00 mg kg^{-1}). Thus, there is no evidence that the wildfire resulted in the formation of excess Cr(VI). It seems that the temperatures developed during the fire event were not high-enough to

enhance the oxidation of Cr(III). The temperatures developed in wildfires are controlled by several factors that affect the combustion process, such as the amount, nature, and moisture of fuel, air temperature and humidity, wind speed, and topography of the site (Certini, 2005). Similarly to our results, Burton et al. (2019), observed that Cr(VI) formation after laboratory heating of a low-Cr content (220 mg kg^{-1}) Ferrosol-type soil, occurred only at temperatures higher than 400°C and peaked at 600°C . Nevertheless, the water soluble Cr(VI) contents were higher in the burnt soils (0.103 mg kg^{-1}) compared to the unburnt ones (0.021 mg kg^{-1}). Thus, after the fire in the Central Evia, more Cr(VI) could be leached to groundwater. This is of concern, as Cr(VI) groundwater concentrations in the broader area, already exceed occasionally (2020) the regulatory limit for drinking water ($50 \mu\text{g L}^{-1}$) (Pyrgaki et al., 2020).

4. Conclusions

Formation of the toxic and carcinogenic Cr(VI) readily takes place during heating of native, Cr(III)-bearing mineral assemblages found in ophiolitic rocks and serpentine soil, at temperatures that could occur after severe wildfires. Most importantly, a significant portion of the generated Cr(VI) resides in readily water-soluble forms that could be leached in groundwater bodies. Thus, in ultramafic settings, fire-induced oxidation of Cr(III) during wildfires could further enhance groundwater and soil geogenic Cr(VI) contamination.

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