



Heating effect on chromium speciation and mobility in Cr-rich soils: A snapshot from New Caledonia

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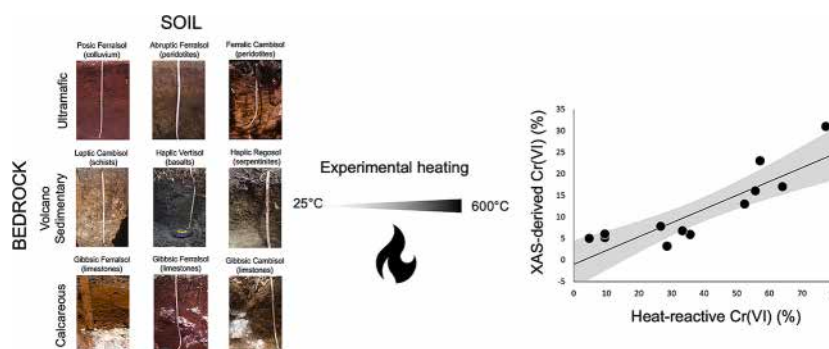
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HIGHLIGHTS

- Heating Cr-rich soils yields partial oxidation of Cr(III) to Cr(VI) from 400 °C.
- Cr(III) oxidation to Cr(VI) is driven by goethite-hematite transformation.
- Hexavalent chromium formed by soil heating is highly mobile.
- Burned Cr-rich soils can represent a significant risk towards freshwater quality.
- This risk should be further assessed at the global scale.

GRAPHICAL ABSTRACT



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ABSTRACT

In the context of global warming, wildfires are expected to increase in both frequency and intensity in the forthcoming decades. Among the environmental and ecological wildfires-induced impacts, the risk of freshwater pollution by soilborne trace metals deserves a more extensive and accurate assessment because of its potential threat to human health. This study aims to contribute to this evaluation by investigating the influence of laboratory soil heating on chromium solid speciation (including redox state) and mobility in Ferralsols, Cambisols, Vertisols and Regosols holding varying amounts of this trace metal in New Caledonia (South Pacific). A first result is that soil heating from 400 °C induces a partial Cr(III) oxidation to Cr(VI) in all the studied soils, confirming recent findings and extending them to a wider range of soil types. A second result is that the rate of heat-induced Cr(III) oxidation to Cr(VI) appears to depend on chromium speciation. This latter parameter might thus represent the primary driver of chromium reactivity in burned soils. Finally, a third result is the confirmation

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that most of the Cr(VI) formed in the heated soils is highly mobile. Heat-induced Cr(III) oxidation to Cr(VI) in burned soils thus represents a significant risk towards freshwater quality. At the local scale, this risk might concern a large range of drinking water catchments since the soils investigated in this study encompass a wide portion of the pedological diversity in New Caledonia. At a broader scale, considering the wide occurrence of Cr-bearing pedological settings worldwide, the potential threats to freshwater systems resulting from the occurrence of highly toxic Cr(VI) in burned soils should be considered as a global emerging risk towards water quality that requires further assessment.

1. Introduction

Each year, approximately 650 million ha of forest are burned and >30 % of the continental surface are concerned by wildfires (Chuvieco et al., 2018; Giglio et al., 2010). During the last decade, the world faced record-breaking giant fires as observed in Australia and California, a trend that is expected to increase in the forthcoming decades due to climate change anomalies such as drought and heat waves (Sharples et al., 2016; Sun et al., 2019; Palinkas, 2020; van Oldenborgh et al., 2021; Xiao et al., 2022). In addition to their large environmental and ecological impacts, wildfires are now regarded for their potential threat to human health (Xu et al., 2020). This relies on related air pollution due to carbon monoxide, ozone, and particulate matter release, as well as on water pollution due to enhanced erosion of burned watersheds (Biswas et al., 2007; Burke et al., 2010; Johnston et al., 2011; Kristensen et al., 2014; Burton et al., 2016; Odigie et al., 2016; Abraham et al., 2017). This latter impact is related to the high temperature generated by wildfires that usually ranges between 250 °C and 700–800 °C, but can go over 1000 °C depending on the oxygen availability and fuel biomass (DeBano et al., 1998; Bertschi et al., 2003; Ormeño et al., 2009; Saura-Mas et al., 2010). The heat generated can propagate towards several tens of centimeters in the soil, transforming or destroying organic matter, as well as Fe-Mn-Al (hydr)oxides and phyllosilicates (Ulery et al., 1996; Ketterings et al., 2000; Grogan et al., 2003; Terefe et al., 2008; Kavouras et al., 2012; Terzano et al., 2021). In addition to weakening soil physical stability, these transformation/destruction can also change the speciation of potentially toxic elements (PTEs) that are associated with these soil components, leading to enhanced mobility that could put some risk on the quality of water resources (Smith et al., 2011; Burton et al., 2016; Abraham et al., 2017; Terzano et al., 2021; Beyene et al., 2023).

In this regard, one notable PTE is chromium, which is naturally present in soils mostly as trivalent Cr(III) but can represent an environmental and/or health issue when occurring as hexavalent Cr(VI) (Cohen et al., 1993; Costa, 2003; Costa and Klein, 2008; Zhitkovich, 2011; Sun et al., 2011). A known natural pathway for Cr(VI) formation in soils is Cr(III) oxidation by Mn-oxides (Eary and Rai, 1987; Fendorf and Zasoski, 1992; Manceau and Charlet, 1992; Kim et al., 2002; Feng et al., 2006; Pan et al., 2017; Liang et al., 2021). This reaction has been proposed to explain the occurrence of Cr(VI) in Mn-rich parts of ultramafic regoliths worldwide (Oze et al., 2007; Fandeur et al., 2009a; Garnier et al., 2013; Delina et al., 2020; Botsou et al., 2022). Although oxidation by O₂ is another natural pathway for Cr(VI) formation in soils, this latter mechanism is likely not predominant at room temperature because of its slow kinetic (Eary and Rai, 1987; Saleh et al., 1989; Apte et al., 2006; Dai et al., 2010). However, the rate of Cr(III) oxidation to Cr(VI) has been shown to be kinetically favored at higher temperature (Apte et al., 2006), which raises the question of an enhanced formation of Cr(VI) in burned soils.

This issue has been first addressed in a study on veld grass *Hyperthelia dissoluta* in South Africa, which reported Cr(VI) formation in the ashes produced upon burning of the aboveground biomass during wildfires (Panichev et al., 2008). According to the authors of this study, the rate of Cr(III) oxidation to Cr(VI) in the aboveground biomass would have been favored by the alkaline characteristics of the ashes (Pereira et al., 2012; Bodi et al., 2014). Such an influence of alkaline conditions on the rate of Cr(III) oxidation to Cr(VI) has also been reported in laboratory

experiments on synthetic alkaline Ca, Na and K salts (Verbinnen et al., 2013) and on Cr-containing sludges artificially heated in presence of CaO (Mao et al., 2015). In this latter study, Cr(VI) was found to occur as CaCrO₄ and this Cr(VI) mineral species was recently reported in laboratory heated agricultural soils contaminated with Cr-rich compost made from tannery sludges in Italy (Rascio et al., 2021, 2022). In addition to Cr(III) oxidation from Cr-containing sludges, recent laboratory and field studies also demonstrated that fire-induced heating of the soil can oxidize Cr(III) from geogenic sources. Recent laboratory studies reported Cr(III) oxidation to Cr(VI) upon controlled heating of Cr(III)-doped Fe-oxyhydroxide (Burton et al., 2019a, 2019b). Besides, Cr(III) oxidation to Cr(VI) upon controlled heating was also demonstrated for different types of Ferralsols (Burton et al., 2019b; Thery et al., 2023). In these latter studies, Cr(VI) was considered to arise from chromium mainly occurring as Cr(III)-substituted goethite (Kaur et al., 2009; Dublet et al., 2012; 2015). Finally, a recent field study on burned soils at geologically different areas concerned by the large wildfires that occurred in 2019 and 2020 in California (USA) revealed the occurrence of Cr(VI) at concentration up to 6-fold those measured in the equivalent non-burned soils (Lopez et al., 2023). This study also put emphasis on the direct relationship between the amounts of reactive Cr(VI) measured in burned soils and the supposed fire severity that affected these soils.

All these previous findings suggest a significant effect of wildfires on Cr(III) oxidation to Cr(VI) in soils, with a possible influence on chromium mobility that could represent a risk for freshwater quality. This latter issue was recently addressed in a study on Cr-rich Ferralsols developed upon ultramafic rocks in New Caledonia that revealed a significant influence of soil heating on Cr(III) oxidation to Cr(VI), followed by an enhanced Cr(VI) mobility (Thery et al., 2023). This study also emphasized the possible risk of freshwater pollution due to wildfires-induced Cr(VI) release in ultramafic catchments, depending on the concentration of suspended particulate matter (SPM) issued from burned Cr-rich Ferralsols in the related waterways. Since freshwaters represent the major water resource for the inhabitants of New Caledonia, it pointed to the need for a wider evaluation of the risk of wildfires-induced Cr(VI) pollution of freshwater at other catchments covered by Cr-bearing soils.

In the present study, we propose a first contribution to such an evaluation by investigating the influence of soil heating on chromium mobility in Cambisols, Vertisols and Regosols holding variable amounts of this PTE in New Caledonia (Becquer et al., 2003, 2006; Fandeur et al., 2009a, 2009b; Isnard et al., 2016; Houles et al., 2018; Vincent et al., 2018). In addition, in order to gain further insights on the actual mechanisms likely driving the rate of Cr(III) oxidation to Cr(VI) upon soil heating, we have also followed the changes in chromium speciation (including redox state) induced by laboratory-controlled heating of these soils, as well as of the Ferralsols previously studied by Thery et al. (2023). In addition to providing further insights on the actual mechanisms that drive chromium reactivity and mobility in burned soils, the results obtained help to evaluate the relative sensitivity of Ferralsols, Cambisols, Vertisols and Regosols from New Caledonia towards Cr(III) oxidation to Cr(VI) upon heating during a wildfire. Considering the local extent of the studied soils, they provide a useful basis for evaluating the risk of wildfires-induced freshwater Cr(VI) pollution at the whole territory scale. Beyond the single case of New Caledonia, regarding the wide occurrence of Cr-bearing pedological settings worldwide

(Vithanage et al., 2019; Gwenzi, 2020; Kierczak et al., 2021) and considering the toxicity of Cr(VI) (Cohen et al., 1993; Costa, 2003; Costa and Klein, 2008; Zhitkovich, 2011; Sun et al., 2011), such an evaluation of the risk of wildfire-induced freshwater Cr(VI) pollution would deserve to be performed at the global scale.

2. Materials and methods

2.1. Study site and samples

New Caledonia is an Oceanian archipelago located about 3200 km east of Australia and 2400 km north of New Zealand. This French overseas territory is representative of tropical ecosystems especially threatened by wildfires, since they occur every year during the dried season (September–November) with an estimated burned area of 30,000 ha (i.e. 2 % of the whole territory surface; Dumas et al., 2013). These wildfires are mainly caused by human activities, such as slash-and-burn practice, but they are also triggered by the El Nino Southern Oscillation (ENSO) that is known to reinforce the effects of drought (Barbero et al., 2011; Toussaint, 2020). The New Caledonia archipelago is made up of a main island (“Grande Terre”), four islands along the East coast called the “Loyalty Islands”, one island in the south called “Isle of Pines”, and several small islands in the North called “Belep archipelago” (Fig. 1). Due to its geological history, New Caledonia displays a wide diversity of soils including Ferrasols, Acrisols, Cambisols, Vertisols, Leptosols and Regosols (Fig. 1; Fritsch, 2012). In this study, nine topsoils (0–15 cm depth) spread across the archipelago were sampled (Figs. 1, SM-1 and SM-2) with the aim to capture the diversity of these soils in terms of chemistry and mineralogy (Houles et al., 2018; Vincent et al., 2018). The selected soils can be divided into three categories: Cambisols, Regosols and Vertisols developed on volcano-sedimentary rocks (hereafter called volcano-sedimentary soils or VS soils), Ferrasols and Cambisols developed on ultramafic rocks (hereafter called ultramafic soils or UM soils), and Al-rich Ferrasols developed on coral reef formation (hereafter called calcareous soils or CA soils) (Figs. 1, SM-1 and SM-2;

Table SM-1).

Among these soils, Ferrasols are the most enriched in chromium (up to 30,000 mg/kg) and other PTE such as nickel, cobalt and manganese, especially when they have developed on ultramafic rocks (i.e. peridotites; Houles et al., 2018; Vincent et al., 2018). Soils developed on volcano-sedimentary settings such as basalts, diorites, micaschists, cherts and flyschs are less enriched in chromium and other PTE, although they can still show significant concentration (up to 1500 mg/kg). Finally, soils developed on coral reef formations are usually less enriched in chromium (up to 600 mg/kg) and other PTE. According to the data clustered by the Environmental Observatory of New Caledonia (<https://geoportail.oeil.nc/AlerteIncendies/>), the sampling sites have not been affected by wildfires during the 5 years that preceded sampling in 2013.

2.2. Soil preparation and thermal treatment

Each of the studied soil samples was sieved to 2 mm, mechanically ground in an agate mortar and thoroughly homogenized. By increasing the specific surface area of the studied soil samples, grinding is expected to provide an estimate of the maximum effect of heating on Cr(III) oxidation to Cr(VI) and enhanced chromium mobility. This effect was simulated in the laboratory by heating a sub-sample of the ground and homogenized soil samples at 200 °C, 400 °C, and 600 °C. Such a range of temperature is the one expected during wildfires at the sampled sites where the major type of vegetation was scrubland with limited biomass fuel (Gomez et al., 2015). For each temperature, depending on the need for replicates, between 3 g and 6 g of soil were loaded in ceramic crucibles that were introduced in a pre-heated muffle furnace for 2 h. After that heating time, the crucibles were removed from the furnace and air cooled in a sand bed.

2.3. Chemical and mineralogical analyses

Total concentrations of selected major and trace elements (Si, Mg,

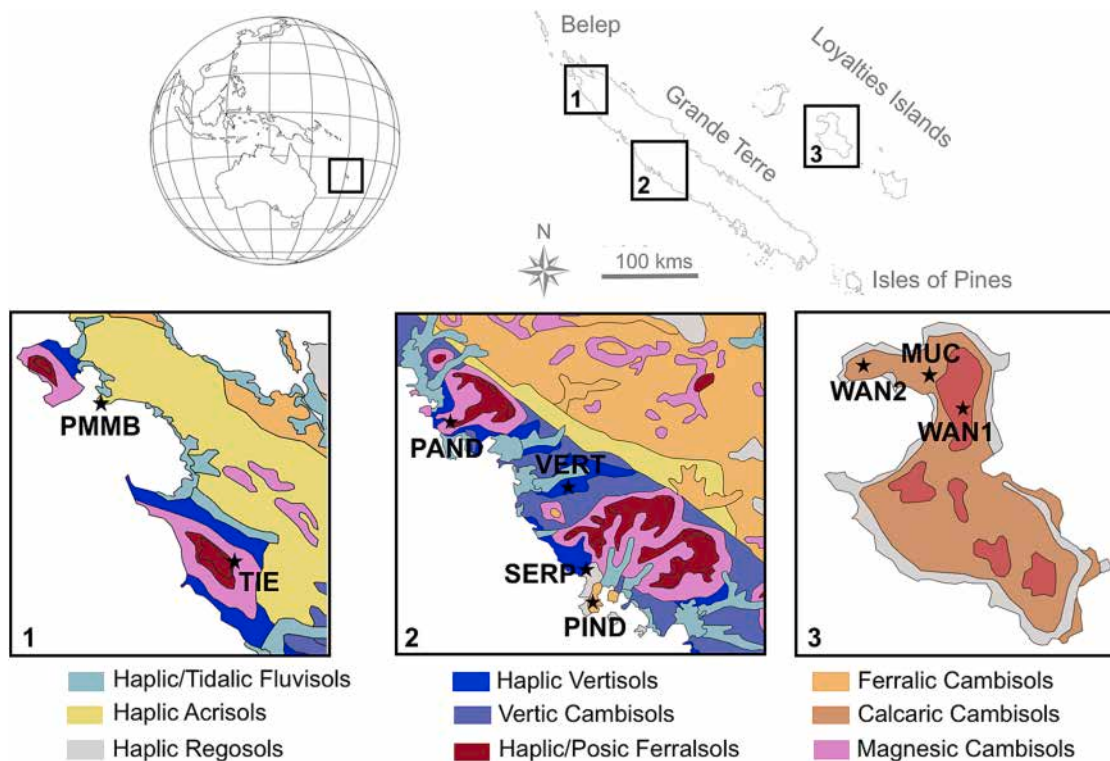


Fig. 1. Composite maps showing the location of New Caledonia at the world scale and the location of the nine studied soils in selected zones of the pedological map of New Caledonia (after Fritsch et al., 2012)

Ca, P, Fe, Al, Mn, Ni, Cr, Co, Zn) were quantified in a sub-sample of each non-heated and heated ground and homogenized sample. Quantification was performed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) after alkaline fusion according to the normalized EN ISO 14869-2 procedure. Analyses were done with a Varian 730-ES (PerkinElmer®) at the Laboratoire des Moyens Analytiques (LAMA-IMAGO) of the Institut de Recherche pour le Développement (IRD) in Noumea (New Caledonia). This ISO 9001 certified laboratory is member of the Global Soil Laboratory Network (GLOSOLAN; <http://www.fao.org/global-soil-partnership/glosolan/en/>) labelled by the Food and Agriculture Organization of the United Nations (UN-FAO). Quality control on the chemical analyses was performed with the WEPAL 986 Sandy Soil Certified Reference Material (Table SM-2). Uncertainties on total concentration were below 7 % except for Co (17 %) (Table SM-2). The organic carbon content (C_{org}) in the studied samples was determined with the potassium dichromate oxidation method (standard ISO 14235). Their mineralogical composition, before and after heating, was assessed by X-ray diffraction (XRD). Non-heated soil samples were analyzed at Institut de Mineralogy, de Physique des Matériaux et de Cosmochimie (IMPMC, Paris, France) with an X'PERT PRO (Malvern Panalytical®) diffractometer configured in Bragg-Brentano geometry and equipped with a Co anti-cathode and an X'celerator® detector. Each sample was analyzed for 60 min in continuous mode at a voltage of 40 kV and intensity of 35 mA, using a sample spinner. Heated soil samples were analyzed at Institut des Sciences Exactes et Appliquées (ISEA) of the University of New Caledonia (Noumea, New Caledonia) with an AERIS (Malvern Panalytical®) diffractometer configured in the Bragg-Brentano geometry and equipped with a Co anti-cathode and a PIXcel3D detector. Each sample was analyzed for 25 min in continuous mode at a voltage of 40 kV and intensity of 15 mA, using a sample spinner. For each sample, phase identification was performed with the X'Pert HighScore Plus software and the relative proportion of the identified mineral species was estimated on the basis of the intensity of their major XRD peaks.

2.4. Chemical extractions

Chromium mobility upon soil heating was assessed with a 0.01 M $CaCl_2$ solution, which is expected to mimic the soil solution (Houba et al., 2000). This extraction was performed in 15 mL Falcon® tubes in a batch mode at a 1 g/10 mL solid/liquid ratio and with constant stirring for 2 h. After each extraction, the tubes were centrifuged for 10 min at 3500 rpm and the supernatant was filtered through a 0.45 µm cellulose acetate membrane. Filtered solutions were then stored at 4 °C to prevent any evaporation before chemical analysis. Both total chromium and Cr (VI) concentrations were quantified in the filtered $CaCl_2$ extracts within a period of time that did not exceed 76 h (3 days) after extraction. Total chromium concentration was quantified by ICP-OES at LAMA (Nouméa, New Caledonia), while Cr(VI) concentration was quantified according to the diphenyl carbazide (DPC) colorimetric method (Bartlett, 1991) using a Lambda750 (PerkinElmer®) spectrophotometer at the Laboratoire de Spectroscopie de Noumea (IRD, Noumea, New Caledonia).

2.5. Statistical analyses

Since the mean mobile chromium concentration in non-heated and heated soils were not distributed normally according to the Shapiro-Wilk test, we used the two-sided non-parametric Wilcoxon-Mann-Whitney *U* test to compare these concentrations as a function of the heating temperature among each soil type (i.e., UM, VS and CA). For these statistical comparisons, the non-heated soils were used as the reference group and results are expressed as *p*-value (a *p*-value < 0.05 indicating statistically different mean values at the 95 % confidence level). These statistical analyses were performed with the “ggpubr” package from R software that is available at <http://CRAN.R-project.org/package=ggpubr>.

2.6. X-ray Absorption Near Edge Structure (XANES) Spectroscopy

Chromium speciation was characterized by XANES spectroscopy on a subset of six soil samples (i.e., TIE, PIND, PMMB, VERT, WAN1 and WAN2), either non-heated or heated at 200, 400 and 600 °C. Cr K-edge bulk XANES data were collected at the SAMBA beamline (SOLEIL synchrotron, France) at 25 K using a liquid He cryostat. Samples were prepared as pressed pellets of powders resulting from finely hand-ground and homogenized pure samples or samples slightly diluted in cellulose. The quickscan continuous mode counting 3 min and 2 min over the 5900–6200 eV and 5985–6000 eV energy ranges was respectively used for the XANES and pre-edge regions. Data were collected in fluorescence detection mode using a Vortex Si-drift detector. The energy of the incoming X-ray beam was selected using a Si-220 double-crystal monochromator with sagittal focusing of the second crystal. Energy was calibrated in double transmission mode by measuring the XANES spectrum of a Cr metal foil and setting the position of the first maximum of its first derivative to 5989 eV. Depending on the chromium concentration, between 6 and 40 scans were collected for each sample to obtain an acceptable signal/noise ratio. XANES data were merged using the ATHENA software and further smoothed when necessary, before derivation. Quantitative analysis of Cr K-edge XANES spectra was done through a Linear Combination-Least Squares Fitting (LC-LSF) procedure performed with the ATHENA software on the first derivative of experimental data. Application of this procedure to quantify the $Cr^{VI}O_3/Cr^{III}O_3$ ratio in synthetic mixtures already described in Fandeur et al. (2009a) allowed to estimate its accuracy to ±5 % (Fig. SM-3; Table SM-3). This accuracy is similar to that reported by Gaur et al. (2013) for a study on synthetic mixtures of Cu(I) and Cu(II) chlorides. In addition to this LC-LSF fitting procedure, the $Cr(VI) / [Cr(VI) + Cr(III)]$ ratio in the studied soils was also quantified on the basis of the relative intensities of the pre-edge peaks at 5990 eV and 5994 eV that are respectively related to Cr(III) and Cr(VI) (Huggins et al., 1999; Gaudry et al., 2007; Juhin et al., 2009; Fandeur et al., 2009a). According to Huggins et al. (1999), the accuracy of this approach can be estimated to ±5 %.

3. Results and discussion

3.1. Chemical and mineralogical characteristics of the studied soils

Chromium concentration in the studied soils decreased from an average value close to 18,000 mg/kg in UM soils (i.e., Ferralsols developed on ultramafic rocks) to an average value around 600–700 mg/kg in VS soils (i.e., Cambisols and Vertisols developed on volcano-sedimentary rocks) and CA soils (i.e., Al-rich Ferralsols developed on calcareous rocks; Table 1). One of the VS soils (i.e., PMMB) showed a significant higher chromium concentration close to 1500 mg/kg. Despite much lower values, this concentration pattern was similar for nickel and cobalt. By contrast, it was slightly different for manganese and iron whose average concentration in CA soils (i.e., close to 4700 mg/kg and 14 wt%, respectively) were higher than in VS soils (i.e., close to 1000 mg/kg and 7.5 wt%, respectively). However, the highest average manganese and iron concentration were still found in UM soils (i.e., close to 10,000 mg/kg and 37 wt%, respectively). Concerning major elements, silicon concentration was the highest in VS soils (i.e., close to 25 wt%) compared to UM and CA soils (i.e., close to 6 wt% and below 2 wt%, respectively) and a similar pattern was found for magnesium. In contrast, calcium and phosphorous concentrations were higher in CA soils (i.e., close to 3.5 wt% and 9000 mg/kg, respectively) compared to VS soils (i.e., below 2 wt% and around 160 mg/kg, respectively) and UM soils (i.e., below 0.5 wt% and around 150 mg/kg, respectively). Aluminum concentration was the highest in CA soils (i.e., close to 19 wt%) compared to VS and UM soils (i.e., close to 6.5 wt% and 4.5 wt%, respectively). Finally, organic carbon content was the highest in CA soils (i.e., close to 10 g/kg) compared to VS and UM soils (i.e., close to 6 g/kg and 3 g/kg, respectively).

Table 1

Chemical composition of the 0–10 cm horizons of the 9 studied soils. Concentration for Fe, Al, Si, Ca and Mg are given in wt%, while those for Cr, Mn, Ni, Co, Zn, P are given in mg/kg and those for Corg are given in g/kg.

Type	Soil	Fe	Al	Si	Ca	Mg	Cr	Mn	Ni	Co	Zn	P	C _{org}
		(wt%)					(mg/kg)						(g/kg)
UM	TIE	50.5	4.40	1.73	0.02	0.22	16,082	17,210	2622	713.8	248.4	133.2	1.6
	PIND	25.0	5.03	14.4	0.57	1.05	20,641	4823	5107	408.1	93.3	158.1	6.8
	PAND	40.8	1.67	6.05	0.01	0.97	40,246	7054	4658	1201	318.7	107.3	0.9
VS	PMMB	5.91	5.42	28.5	0.11	3.94	1669	935.9	1669	112.5	65.6	122.5	3.5
	VERT	8.84	7.56	22.6	0.64	0.77	347.1	1084	46.9	50.3	187.8	195.7	6.9
	SERP	6.11	7.80	20.1	2.07	2.94	432.4	1292	188.1	55.1	121.2	287.9	8.4
CA	WAN1	13.6	19.9	0.75	5.25	2.24	645.8	3739	51.8	61.4	16.8	8969	7.9
	WAN2	14.9	18.9	3.13	1.45	0.28	539.5	5720	35.7	61.1	59.2	9789	13.3
	MUC	15.2	17.8	1.17	1.18	0.34	787.7	3376	58.2	53.9	64.8	6818	7.2

These chemical characteristics of the studied soils were consistent with their mineralogical composition. In non-heated UM soils, the main Fe-oxyhydroxides identified was hematite α -Fe₂O₃ in TIE and goethite α -FeOOH in PIND and PAND (Table 2; Fig. SM-5). This mineralogical composition is typical of Ferralsols developed on ultramafic rocks (Becquer et al., 2006; Becquer et al., 2003; Fandeur et al., 2009a, 2009b). These soils also contained minor amounts of magnetite Fe₃O₄. Moreover, quartz SiO₂ and phyllosilicates such as talc Mg₃Si₄O₁₀(OH)₂, serpentine Mg₃Si₂O₅(OH)₄ and smectite/vermiculite (Na,Ca)(Mg,Fe,Al)₃(Si,Al,Mg)₄O₁₀(OH)₄.nH₂O were also detected in low amounts in PAND and PIND. In non-heated CA soils, the most abundant mineral species was boehmite γ -AlOOH, together with ankerite Ca(Fe,Mg)(CO₃)₂ in WAN1 (Table 2; Fig. SM-5). Other Al-bearing mineral species such as kaolinite Al₂Si₂O₅(OH)₄ and gibbsite α -Al(OH)₃ were also detected, but in lower amounts. Non-heated CA soils also contained minor amounts of goethite, hematite and maghemite γ -Fe₂O₃. Finally, non-heated VS soils mainly contained silicates, with quartz SiO₂ and plagioclases (albite NaAlSi₃O₈ / anorthite CaAl₂Si₂O₈) as the primary mineral species in PMMB and VERT, and pyroxenes (enstatite Mg₂Si₂O₆ / ferrosillite Fe₂Si₂O₆) as the primary mineral species in SERP (Table 2; Fig. SM-5). These soils also contained significant amounts of phyllosilicates, with smectite/vermiculite in VERT and SERP, and talc and chlorite (Mg,Fe)₅Al(Si₃Al)O₁₀(OH)₈ in PMMB.

3.2. Mineralogical transformation upon heating

Upon heating from 200 to 600 °C, XRD powder patterns of the soils

Table 2

Mineralogical composition of the samples before and after heating at 200, 400 and 600 °C. Ak = ankerite, Bh = boehmite, Ch = chlorite, Gt = goethite, Gi = gibbsite, Hm = hematite, Kl = kaolinite, Ma = magnetite, Mh = maghemite, Pg = plagioclases (albite/anorthite), Px = pyroxenes (enstatite/ferrosillite), Sm = smectite, Sm-d = dehydrated smectite, Sr = serpentine, Sp = spinel, Ta = talc. For each sample, mineral species are qualitatively ranked with respect to the intensity of their main Bragg peak, bold characters representing primary phases.

Type	Soil	25 °C	200 °C	400 °C	600 °C
UM	TIE	Gt, Hm, Ma	Gt, Hm, Ma	Hm, Ma	Hm, Ma
	PIND	Qz, Gt, Ta, Sr	Qz, Gt, Ta, Sr	Qz, Hm, Ta, Sr	Qz, Hm, Ta, Sr
	PAND	Gt, Hm, Qz, Sm, Ta, Px	Gt, Hm, Qz, Sm, Ta, Px	Hm, Qz, Sm-d, Ta, Px	Hm, Qz, Sm-d, Ta, Px
VS	PMMB	Qz, Ch, Ta, Kl	Qz, Ch, Ta, Kl	Qz, Ch, Ta, Kl	Qz, Ch, Ta, Kl
	VERT	Qz, Sm, Pg	Qz, Sm, Pg	Qz, Sm-d, Pg	Qz, Sm-d, Pg
	SERP	Qz, Sm, Pg, Sr	Qz, Sm, Pg, Sr	Qz, Sm-d, Pg, Sr	Qz, Sm-d, Pg, Sr
CA	WAN1	Bh, Ak, Gt, Gi, Hm	Bh, Ak, Gt, Gi, Hm	Ak, Mh, Hm, Hm, Mh, Qz	Ak, Mh, Hm, Hm, Mh, Qz
	WAN2	Bh, Gi, Hm, Gt, Qz, Kl	Bh, Gi, Hm, Gt, Qz, Kl	Hm, Mh	Hm, Mh
	MUC	Bh, Gi, Gt, Hm	Bh, Gi, Gt, Hm		

that initially contained goethite (i.e., TIE, PIND, PAND, WAN1, WAN2 and MUC) showed a progressive decrease of the Bragg peaks related to this mineral species and a concomitant increase of those related to hematite (Table 2; Fig. SM-5). This evolution is due to the well-known thermal transformation of goethite to hematite above 250 °C, which may result in a defective and hydrated hematite phase at such temperature, whereas well crystalline hematite is obtained above 600 °C (Pomies et al., 1998; Cornell and Schwertmann, 2003; Quintana et al., 2007). The XRD peaks related to goethite completely disappeared after heating at 400 °C (Table 2; Fig. SM-5). In the presence of organic matter, goethite has also been shown to partially or fully transform into maghemite (Fe₃O₄) rather than hematite (Ketterings et al., 2000; Grogan et al., 2003; Perrier et al., 2006; Eggleton and Taylor, 2008; Terefe et al., 2008). The low amounts of maghemite detected at 400 °C and above in some of the CA soils (Table 2; Fig. SM-5) suggested that such transformation could have occurred in these soils where the total organic carbon concentration was significant (Table 1). By contrast, no maghemite could be detected in the other heated soils that globally showed a lower total organic carbon concentration (Table 1). Finally, the XRD peaks related to boehmite and gibbsite in CA soils disappeared at 400 °C, while broad diffraction peaks corresponding to a poorly crystalline phase appeared (Table 2; Fig. SM-5). This evolution was in agreement with the known transformation of boehmite to alumina (γ -Al₂O₃), which is expected to be fully achieved only around 800 °C and is characterized by the formation of a poorly crystallized intermediate Al₂O₃ spinel phase around 400 °C (De Souza Santos et al., 1996; Wang et al., 2006).

The XRD patterns of the soils that initially contained phyllosilicates (i.e., PIND, PAND, PMMB, VERT and WAN2) also showed some changes with heating. The XRD peaks related to serpentine decreased above 400 °C (Table 2; Fig. SM-5). This thermal evolution is in agreement with previous studies that reported a first dehydroxylation step around 450 °C and full transformation to forsterite (Mg₂SiO₄) and enstatite (MgSiO₃) around 800 °C (Cattaneo et al., 2003; Perrillat et al., 2005; Viti and Hirose, 2009; Gualtieri et al., 2012; Trittschack et al., 2012). Although soil heating did not reach such temperature in the present study, the first destabilization step of serpentine could explain the evolution of the XRD peaks related to this mineral species. A similar evolution was observed for the XRD peaks related to kaolinite in WAN2 (Table 2; Fig. SM-5), in agreement with the known dehydration and transformation of this mineral species into meta-kaolinite around 400 °C (Ptacek et al., 2010, 2011). The broad XRD peak observed at low angle in some of the UM soils (PIND and PAND) and VS soils (VERT and SERP) and related to smectite disappeared at 400 °C (Table 2; Fig. SM-5). Actually, this peak shifted towards higher angle upon heating, a well-known behavior for this mineral species whose dehydration caused by heating reduces the characteristic (001) interlayer distance from 14 Å to 10 Å (Brindley and Ali, 1950; Greene-Kelly, 1953). By contrast, talc that could be detected in non-heated PAND (UM soil) and PMMB (VS soil) showed a good thermal stability during heating, in agreement with studies that reported a stability up to 800 °C (Ketterings et al., 2000).

Our XRD data did not evidence talc formation during heating, as reported in other studies (MacKenzie and Meinhold, 1994). Finally, silicates (i.e., quartz, pyroxenes and plagioclases) did not evolve upon soil heating, in agreement with the P-T stability diagrams of these mineral species (Swamy et al., 1994; Stalder et al., 2001; Ulmer and Stalder, 2001; Gasparik, 2014).

3.3. Heat-induced changes of chromium speciation

Linear combination least-square fitting (LC-LSF) analysis of the first-derivative of Cr K-edge XANES data collected on a subset of six soils before heating (i.e., TIE, PIND, PMMB, VERT, WAN1 and WAN2) indicated that chromite, goethite and clay minerals were the primary Cr-bearing mineral species (Figs. 2 and SM-6; Table SM-3). The relative contribution of these mineral species to chromium speciation varied from one soil type to another. The contribution of chromite to chromium speciation was the highest around 50 % in UM soils, while it was close to 35 % in one of the VS soils (PMMB) and around 5 % in the other (VERT)

and in CA soils. The contribution of goethite to chromium speciation was the highest between 70 and 80 % in CA soils, while it ranged between 20 and 30 % in the other soils. Finally, the contribution of clay minerals to chromium speciation was the highest around 70 % in one of the VS soils (VERT), whereas it was close to 35 % in the other (PMMB), around 20–25 % in UM soils and in one of the CA soils (WAN2) and 15 % in the other (WAN1). The results obtained on UM and CA soils were in agreement with those from previous studies that reported chromite and goethite as the primary Cr-bearing mineral species in Ferralsols from New Caledonia, Brazil, Sri Lanka, China or Greece (Oze et al., 2004; Becquer et al., 2006; Garnier et al., 2006, 2009; Fandeur et al., 2009a, 2009b; Vithanage et al., 2014, 2019; Botsou et al., 2022; Sun et al., 2022). In the same way, the results obtained on VS soils were in agreement with those from previous studies that emphasized the significant contribution of silicates to chromium speciation in Cambisols and Leptosols from USA, France, Poland and Italy (Kaupenjohann and Wilcke, 1995; Soubrand-Colin et al., 2007; Caillaud et al., 2009; McClain et al., 2017; Rascio et al., 2021, 2022).

LC-LSF analysis of the first-derivative of the Cr K-edge XANES data collected on the subset of six soils heated at 200, 400 and 600 °C emphasized the heat-induced changes in chromium speciation (Figs. 2 and SM-6; Table SM-3). A first result of this analysis was that chromium speciation in the soils heated at 200 °C did not change significantly from that in the non-heated soils. By contrast, heating the studied soils at 400 °C or 600 °C induced major changes in chromium speciation. Indeed, a contribution of hematite to chromium speciation was detected at the expense of that of goethite, and a small but significant fraction of Cr(VI) was identified as detailed in the two next sections. The contribution of chromite to chromium speciation remained stable or slightly increased with temperature, ranging between 40 and 60 % in UM soils and in one of the VS soils (PMMB). This chromite contribution was lower in the other VS soil (VERT) and in the CA soil 10 and 25 % but also increased above 400 °C in the two latter soils. The contribution of clay minerals to chromium speciation that remained rather stable upon heating was the highest between 40 and 55 % in one of the VS soils (VERT), while it ranged between 20 and 35 % in the other soils.

These results thus indicated a shift of chromium speciation from Cr-bearing goethite to Cr-bearing hematite as the major heat-induced change in the studied soils (Fig. 2; Table SM-3). Such a shift is not surprising regarding the known capacity of Cr(III) to substitute for Fe(III) in the hematite structure (Sileo et al., 2007). In addition to this shift of chromium speciation, LC-LSF analysis of the first-derivative of Cr K-edge XANES data also suggested a slight increase in the contribution of chromite to chromium speciation above 400 °C in CA soils. This latter point could indicate a possible partial transformation of Cr-bearing goethite to chromite upon heating of these soils that contain organic matter, in agreement with the recently proposed formation of chromite upon heating at 500 °C in a Cr-impacted agricultural soil from Italy (Rascio et al., 2021, 2022).

3.4. Heat-induced Cr(III) oxidation to Cr(VI)

The above-mentioned results indicate that LC-LSF analysis of the first-derivative of Cr K-edge XANES data did not reveal any occurrence of Cr(VI) neither in the non-heated soils nor in those heated at 200 °C (Fig. 2; Table SM-3). By contrast, Cr(VI) could be quantified in variable amounts in all the soils heated at 400 or 600 °C (Fig. 2; Table SM-3). After heating at 400 °C, the highest fraction of Cr(VI) ranged between 15 and 25 % in CA soils (WAN1 and WAN2), while it ranged between 5 and 10 % in UM (TIE and PIND) and VS soils (PMMB and VERT). After heating at 600 °C, the highest fraction of Cr(VI) was close to 30 % in one of the CA soils (WAN1), while it was close to 15 % in the other (WAN2) and in one of the VS soils (PMMB) and close to 5 % in the other VS soil (VERT) and in UM soils (TIE and PIND).

These fractions of Cr(VI) were further confirmed by detailed analysis of the relative intensity of the peaks related to Cr(VI) (i.e., 5994 eV) and

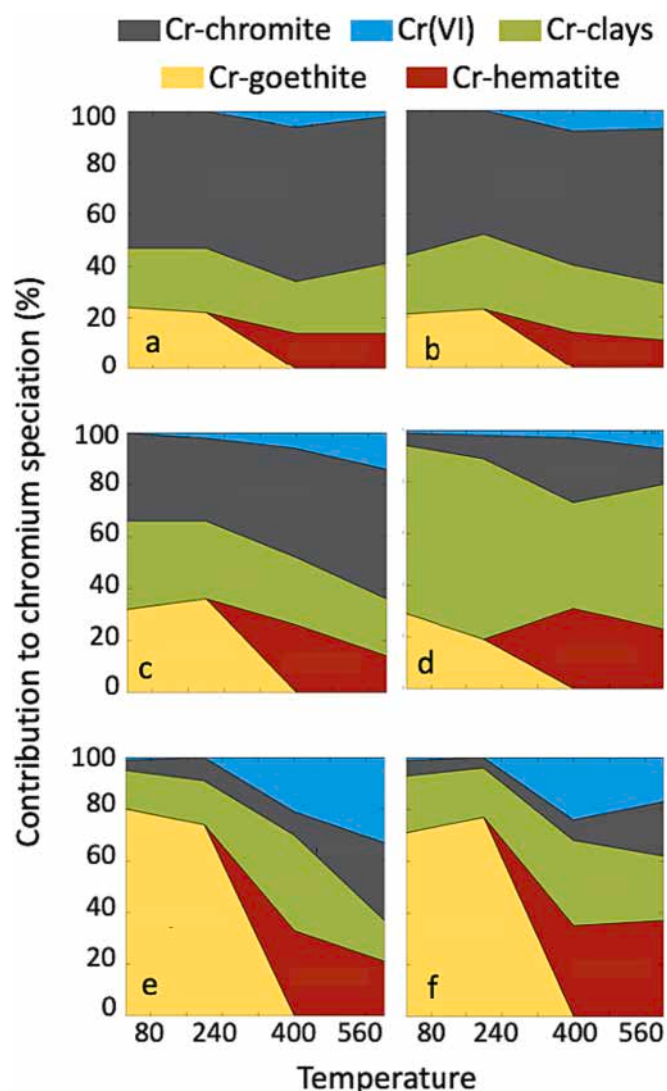


Fig. 2. Temperature-dependence speciation of chromium retrieved from the LC-LSF analysis of the first derivative of Cr K-edge XANES spectra collected on the subset of six soils before (25 °C) and after heating at 200, 400 and 600 °C. a: Posic Ferralsol (TIE – UB soil), b: Ferralic Cambisol (PIND – UB soil), c: Leptic Cambisol (PMMB – VS soil), d: Haplic Vertisol (VERT – VS soil), e: Gibbsic Ferralsol (WAN1 – CA soil), f: Gibbsic Ferralsol (WAN2 – CS soil). The uncertainty on reported values is estimated to ± 5 %.

Cr(III) (i.e., 5990 eV) in the pre-edge region of normalized Cr K-edge XANES spectra (Fig. 3). Comparison with pre-edge peaks for synthetic mixtures of Cr_2O_3 and $\text{Cr}^{\text{VI}}\text{O}_3$ from our database (Fandeur et al., 2009a) indicated a fraction of Cr(VI) below 2 % in all the non-heated soils and below 5 % in all the soils heated at 200 °C (Fig. 3; Table SM-5). By contrast, this fraction ranged from 5 % to 10 % in the UM soils (TIE and PIND) heated at 400 °C and 600 °C, from 5 % to 15 % in the VS soils (PMMB and VERT) heated at 400 and 600 °C and from 10 to 25 % in the CA soils (WAN1 and WAN2) heated at 400 and 600 °C. Comparison of these fractions with those quantified by LC-LSF analysis of the first-derivative of Cr K-edge XANES data yielded a good correlation (i.e., $R^2 = 0.89$; $p\text{-value} = 2.8 \cdot 10^{-15}$; Fig. SM-7; Tables SM-3 and SM-4).

These results thus indicated a Cr(III) oxidation to Cr(VI) upon heating in all the studied soils, with a marked effect from 400 °C. This trend confirmed the findings of our previous study, which already emphasized Cr(III) oxidation to Cr(VI) in Ferralsols developed on ultramafic settings

in New Caledonia (Thery et al., 2023). Such a temperature-induced Cr(III) oxidation to Cr(VI) was also previously highlighted in a soil from Italy impacted by compost derived from tannery sludge that was artificially heated from 300 °C to 600 °C (Rascio et al., 2021, 2022) and in a Ferrisol-type soil from Australia that was artificially heated from 200 °C to 800 °C (Burton et al., 2019a). In this latter study, the highest fraction of Cr(VI) was close to 30 %, a value similar to that measured in one of our Ferralsols (WAN1) heated at 600 °C. In addition to confirming the heat-induced Cr(III) oxidation to Cr(VI) in Ferralsols from New Caledonia, the present study also emphasizes the potential importance of this reaction by showing that it can also concern Cambisols, Vertisols and Regosols. Interestingly, all these results on laboratory heated soils have been recently field-validated by the findings of a recent study that detected significant amounts of Cr(VI) in different soils burned by large wildfires in California (USA; Lopez et al., 2023).

The observed Cr(III) oxidation to Cr(VI) upon soil heating could be caused by electron transfer to Mn-oxides that are well-known natural oxidants of Cr(III) (Eary and Rai, 1987; Fendorf and Zasoski, 1992; Manceau and Charlet, 1992; Kim et al., 2002; Feng et al., 2006; Pan et al., 2017; Liang et al., 2021). However, thermodynamic calculations indicate phase transition from MnO_2 to Mn_2O_3 around 400 °C, and to Mn_3O_4 around 800 °C (Cheragi et al., 2019). This means that the redox state of Mn decreases from Mn(IV) to Mn(III) around 400 °C, and then to Mn(II,II) around 800 °C. The electron transfer capacity of Mn-oxides towards Cr(III) is thus expected to decrease with increasing temperature, which suggests that this mineral species might not play a major role on the rate of Cr(III) oxidation to Cr(VI) observed in the soils heated from 400 °C. Another possible electron transfer mechanism that could explain this observed Cr(III) oxidation to Cr(VI) in heated soils is photochemical oxidation by free radicals (Liang et al., 2021). However, this pathway seems quite unlikely in laboratory heated soils because the experiments were performed in a light-free oven environment. Moreover, the free radicals involved in this pathway towards Cr(VI) are expected to react with $\text{Fe}(\text{OH})_2$ and/or $\text{Cr}(\text{OH})_3$ species that have not been detected in the studied soils. Finally, the enhanced rate of Cr(III) oxidation to Cr(VI) observed upon heating the studied soils from 400 °C might thus be mainly driven by enhanced direct electron transfer to O_2 . Although this latter redox reaction is known to be very slow at room temperature (Schroeder and Lee, 1975; Eary and Rai, 1987; Richard and Bourg, 1991), it has to be considered at higher temperature regarding its enhanced kinetics (Apte et al., 2006).

3.5. Goethite/hematite thermal transformation as the primary driver of Cr(III) oxidation to Cr(VI) in heated soils

Whatever the electron acceptors and the mechanisms involved, the rate of Cr(III) oxidation to Cr(VI) in heated soils is expected to depend on the actual speciation of chromium. In this regard, the common contribution of Cr(III)-bearing Fe-(hydr)oxides to chromium speciation in soils is thought to play a major role (Oze et al., 2004; Soubrand-Colin et al., 2007; Becquer et al., 2006; Garnier et al., 2006, 2009; Fandeur et al., 2009a; Vithanage et al., 2014, 2019; McClain et al., 2017; Botsou et al., 2022; Rascio et al., 2021, 2022; Sun et al., 2022). This assumption is notably supported by previous studies that reported up to 65 % and 95 % Cr(VI) in Cr(III)-substituted amorphous Fe-oxyhydroxides/ferrihydrite, goethite, or hematite heated at 400 °C and 600 °C, respectively (Burton et al., 2019a, 2019b). In our study, the highest fraction of Cr(VI) was found in CA soils heated at 400 and 600 °C, where it ranged from 20 to 30 % (Tables SM-3 and SM-4). Moreover, Cr K-edge XANES data also indicated that these CA soils contained the largest fraction of Cr(III) hosted by goethite (i.e., between 70 and 80 % of total Cr) before heating. Interestingly, they also showed the largest difference between the fraction of Cr(III) hosted by goethite before heating and that of Cr(III) hosted by hematite after heating at 400 or 600 °C (Fig. 2), in proportions that appear to be comparable with the formation of Cr(VI) upon heating (Fig. 3). This latter comparison suggested that the goethite/hematite

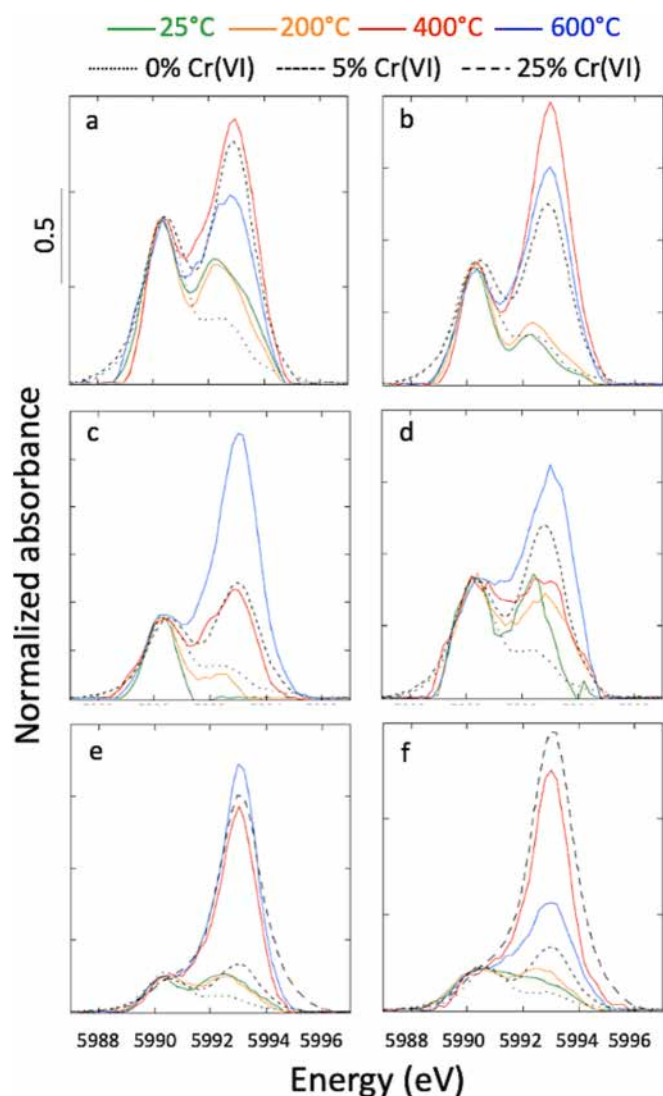


Fig. 3. Pre-edge peaks at 5990 eV and 5994 eV on the Cr K-edge XANES spectra collected on the subset of six soils before (25 °C) and after heating at 200, 400 and 600 °C. a: Posic Ferralsol (TIE – UB soil), b: Ferralic Cambisol (PIND – UB soil), c: Leptic Cambisol (PMMB – VS soil), d: Haplic Vertisol (VERT – VS soil), e: Gibbsic Ferralsol (WAN1 – CA soil), f: Gibbsic Ferralsol (WAN2 – CA soil). Pre-edge peaks on the Cr K-edge XANES spectra collected on synthetic mixtures of Cr_2O_3 and $\text{Cr}^{\text{VI}}\text{O}_3$ containing 0, 5 and 25 % Cr(VI) are also shown for comparison (see Fandeur et al., 2009a for detailed information on these model compounds).

thermal transformation could have been the primary driver of Cr(III) oxidation to Cr(VI) in heated soils. In order to test this hypothesis, the fraction of heat-reactive Cr(III) in goethite was estimated by subtracting the fraction of Cr(III) hosted by hematite in the heated soils to that hosted by goethite in the non-heated soils (Eq. (1)).

$$\text{Heat-reactive Cr(III)} = \left[\left(\text{Cr(III)}_{\text{goethite}}^{\text{non-heated}} - \text{Cr(III)}_{\text{hematite}}^{400^\circ\text{C or } 600^\circ\text{C}} \right) / \left(\text{Cr(III)}_{\text{goethite}}^{\text{non-heated}} \right) \right] \times 100 \quad (1)$$

Further comparison of this fraction of heat-reactive Cr(III) in goethite with the XAS-derived fraction of Cr(VI) in the heated soils yielded a good correlation (i.e., $R^2 = 0.74$; $p\text{-value} = 2.1 \cdot 10^{-4}$; Fig. 4), which confirmed that the fraction of Cr(VI) formed in the soils heated at 400 and 600 °C initially corresponded to Cr(III) hosted by goethite.

The results of our study thus suggest that the rate of Cr(III) oxidation to Cr(VI) in heated soils might be primarily driven by the fraction of heat-reactive Cr(III), which corresponds to the fraction of Cr(III) initially hosted in goethite in the non-heated soils that did not incorporate into hematite following the thermal conversion of goethite to hematite upon soil heating. This hypothesis is in agreement with our Cr K-edge XAS data, which indicated goethite as the primary Cr(III)-hosting Fe-oxide in the studied soils. It is also supported by the results of previous studies on synthetic Cr(III)-doped Fe-oxides, which showed that Cr(III) hosted in goethite was the most prone to oxidize to Cr(VI) upon soil heating up to 800 °C (Burton et al., 2019a, 2019b). However, these studies also reported contrasted temperature effects on the rate of Cr(III) oxidation to Cr(VI) as a function of the Cr(III)-hosting mineral species. More precisely, the amount of Cr(VI) formed from Cr-bearing goethite showed a progressive increasing trend from 25 to 800 °C, while that formed from Cr-bearing hematite increased from 25 to 200 °C before decreasing back to almost its initial value at 800 °C, and that formed from Cr-bearing ferrihydrite increased from 25 to 400 °C before decreasing back to almost its initial value at 800 °C (Burton et al., 2019a). Such a bell-shaped temperature-dependence of Cr(III) oxidation to Cr(VI) was also shown for synthetic Cr-bearing Fe-oxyhydroxides with various Cr(III)/Fe(III) ratios (Burton et al., 2019b). Although the primary Cr(III) hosting by goethite in the non-heated soils from New Caledonia means that the observed effect on Cr(III) oxidation to Cr(VI) at 600 °C might be

enhanced in case of heating these soils up to 800 °C, this assumption needs to be further evaluated for other soils (in New Caledonia and elsewhere) regarding the possible influence of chromium speciation, and notably the actual nature of the Cr(III)-holding Fe-oxides, on the rate of Cr(III) oxidation to Cr(VI).

3.6. Exploring the possible additional influence of organic matter and pH on Cr(III) oxidation to Cr(VI) in heated soils

In soils, the Cr(III)/Cr(VI) ratio results from an equilibrium between oxidative and reductive reactions. A fraction of Cr(VI) formed from Cr(III) oxidation during soil heating could thus be reduced back to Cr(III) upon reductive reactions. Although Fe(II)-bearing minerals could play a major role in specific soil conditions (Fendorf, 1995; Buerge and Hug, 1997; Li et al., 2016; Joe-Wong et al., 2017; Bibi et al., 2018; Bishop et al., 2019; Lv et al., 2019), the primary driver of reductive reactions in soils is organic matter (Richard and Bourg, 1991; Fendorf, 1995; Xiao et al., 2012; Aldmour et al., 2019). This parameter could thus counter-balance Cr(III) oxidation to Cr(VI) in heated soils. Such an influence of organic matter would likely depend on the temperature since this soil component is known to thermally decompose gradually, with a first organic labile fraction that is mineralized between 200 and 300 °C, a second more stable organic fraction that is mineralized between 300 and 450 °C and a last organo-clay fraction that is mineralized between 450 and 550 °C (Plante et al., 2009; Kucerik et al., 2014). In soils heated below 200 °C, organic matter is thus expected to be mostly preserved. Although in our soils the formation of Cr(VI) might have been limited at this temperature because of a lack of goethite/hematite thermal transformation, any fraction of Cr(VI) that would have been formed could potentially have been reduced back to Cr(III). The low amounts of Cr(VI) measured in the soils heated at 200 °C could thus be partly explained by such a backward reduction of Cr(VI) by organic matter after thermal oxidation of heat-reactive Cr(III) (i.e., the fraction of Cr(III) that did not shift from goethite to hematite upon soil heating). This hypothesis has already been proposed to explain the lack of Cr(VI) detection in a Ferrosol-type soil heated at 200 °C (Burton et al., 2019a). By contrast, in the soils heated above 400 °C, organic matter is expected to have been significantly altered (Giovannini et al., 1990). The large increase in the rate of Cr(III) oxidation to Cr(VI) observed from heating our soils at this temperature and at 600 °C could thus be partly explained by a lack of backward reduction of Cr(VI) by organic matter after thermal oxidation of heat-reactive Cr(III).

Opposite to organic matter and/or pyrogenic carbon having a strong reducing capacity towards Cr(VI), Mn-oxides have been demonstrated to act as the primary driver of Cr(III) oxidation in soils. Although thermodynamic calculations suggest a decrease of their electron transfer capacity related to phase transition with increasing temperature (Cheragi et al., 2019), the redox activity of Mn-oxides towards Cr(III) has also been shown to mainly depend on pH with contrasted results. On the one hand, some laboratory studies on simplified systems reported inhibited Cr(III) oxidation by Mn-oxides at pH above 5–6 (Fendorf and Zasoski, 1992; Fendorf, 1995; Kim et al., 2002; Feng et al., 2006). By contrast, enhanced Cr(III) oxidation by Mn-oxides was found in soils incubated under close to real conditions from pH 6 to pH 4 (Feng et al., 2006; Reijonen and Hartikainen, 2016). In addition, soil pH has also been shown to influence the oxidizing capacity of Mn-oxides by driving their Mn(IV)/Mn(III) ratio (Negra et al., 2005). Finally, decreasing kinetic of Cr(VI) reduction for increasing pH has been reported from laboratory controlled incubation experiments (Yang et al., 2022).

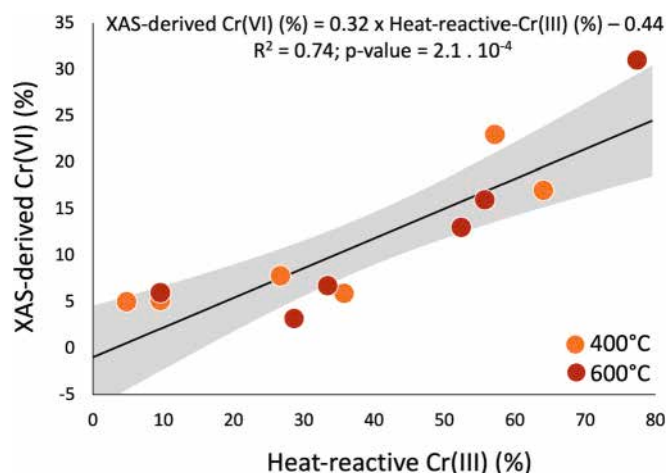


Fig. 4. Correlation between the XAS-derived fraction of Cr(VI) and the fraction of heat-reactive Cr(III) (i.e., the fraction of Cr(III) that did not shift from goethite to hematite upon soil heating, as defined by Eq. (1)) in the soils heated at 400 and 600 °C. The grey area indicates the uncertainty of the regression line at the 95 % confidence level.

Table 3

Results of various single and multiple linear regression models across the fraction of XAS-derived Cr(VI) as a function of heat-reactive Cr(III) (i.e., the fraction of Cr(III) that did not shift from goethite to hematite upon soil heating), pH and/or TOC.

Model	Intercept	R ²	p-value	Parameter	Coefficient	t-value	p-value
Single							
Heat-reactive Cr(III)	−0.439	0.737	0.00021	–	0.320	5.651	–
pH	−38.694	0.469	0.00840	–	7.656	3.272	–
TOC	2.652	0.302	0.03750	–	1.352	2.397	–
Multiple							
Heat-reactive Cr(III)	−1.536	0.709	0.00158	Heat-reactive Cr(III)	0.314	3.039	0.01400
+ pH				pH	0.199	0.066	0.94900
Heat-reactive Cr(III)	−3.123	0.795	0.00032	Heat-reactive Cr(III)	0.275	5.011	0.00073
+ TOC				TOC	0.655	1.952	0.08271
Heat-reactive Cr(III)	−5.340	0.770	0.00178	Heat-reactive Cr(III)	0.264	2.756	0.02480
+ pH				pH	0.400	0.150	0.88450
+ TOC				TOC	0.657	1.847	0.10190

The above-mentioned considerations support the possible role of organic matter and/or pH as possible additional drivers of Cr(III) oxidation to Cr(VI) in the studied heated soils. However, single as well as multiple linear regression models across the XAS-derived fraction of Cr(VI) in the soils heated at 400 and 600 °C considering TOC and/or pH as additional parameters yielded poor improvement compared to the single linear regression model that considered heat-reactive Cr(III) as the only parameter (Table 3).

This latter result suggests that the primary factor driving the rate of Cr(III) oxidation to Cr(VI) upon heating in the studied soils is heat-reactive Cr(III) (i.e., the fraction of Cr(III) that did not incorporated in goethite during the goethite/hematite thermal transformation). If any, the contribution of organic carbon and/or pH in regulating the rate of Cr(III) oxidation to Cr(VI) in our experiments would thus be minor. However, this finding does not preclude the potential of these two parameters to play a significant role on the capacity of the studied burned soils at maintaining high levels of Cr(VI) after heating. Especially, the laboratory-controlled soils heating experiments performed in this study did not allow to fully investigate the potential influence of pyrogenic carbon because this form of carbon was only sourced from thermally degraded soil organic matter, while the burned aboveground biomass can be an important additional source in case of a real wildfire (Bird et al., 2015). Yet, considering its strong reducing capacity towards Cr(VI) (Rajapaksha et al., 2018; Xu et al., 2019), pyrogenic carbon could represent an important driver of Cr(VI) mitigation in burned soils. This latter issue would deserve to be further addressed by dedicated field

studies that would help to better consider the contribution of pyrogenic carbon sourced from the aboveground biomass on the actual capacity of burned soils at maintaining high levels of Cr(VI) after a wildfire.

3.7. A marked increase of chromium mobility in the soils heated from 400 °C

Chemical extractions with a 0.01 M CaCl₂ solution allowed to assess the effect of thermal treatment on chromium mobility in the studied soils. The results obtained indicated a very low chromium mobility (i.e., below 0.1 % of total chromium) in all non-heated soils and in all soils heated at 200 °C (Fig. 5; Table SM-6). By contrast, the soils heated at 400 or 600 °C showed much larger chromium mobility. The highest fraction of mobile chromium ranged from 15 to 25 % of total chromium in CA soils heated at 600 °C, while it ranged from 10 to 15 % of total chromium in the same soils heated at 400 °C. This fraction ranged from 5 to 10 % of total chromium in VS soils heated at 400 and 600 °C and it was below 3 % of total chromium in UM soils heated at 400 and 600 °C.

These results thus indicated a marked increase of chromium mobility after heating the studied soils from 400 °C. This trend is in agreement with the results of a previous study that reported an enhanced chromium exchangeability from 400 °C in a Ferrosol-type soil (Burton et al., 2019a). Since exchangeable chromium was found to correspond to Cr(VI) in this latter study, such an occurrence of Cr(VI) was also checked in our CaCl₂-extracts. The results obtained indicated a very good correlation between the fraction of CaCl₂-extracted total chromium and that of

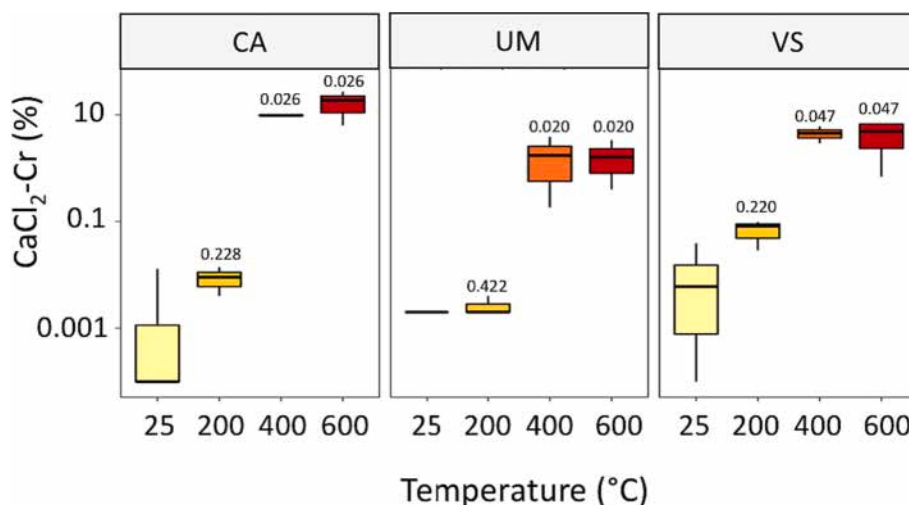


Fig. 5. Boxplots of the fraction of mobile chromium (i.e., CaCl₂-extracted) in the studied soils. Each boxplot represents the values for 3 soils. The numbers above each boxplot correspond to the *p*-value of a Wilcoxon-Mann-Whitney *U* test comparing mean values with respect to the non-heated soils (i.e., temperature = 25 °C). A *p*-value below 0.05 indicates a statistically different mean value at the 95 % confidence level.

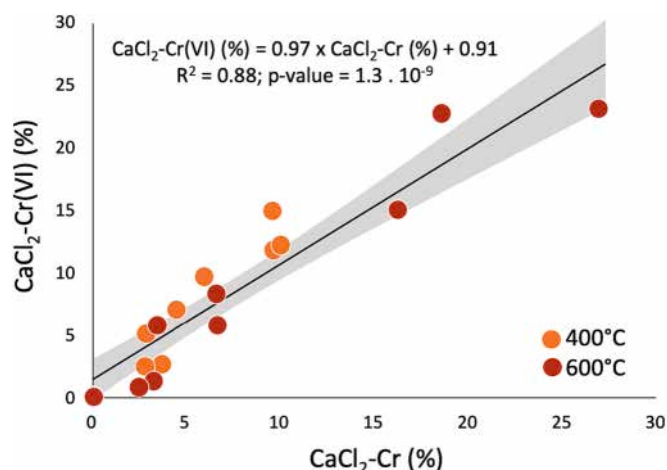


Fig. 6. Correlation between the fractions of total chromium and Cr(VI) in the CaCl_2 extracts. Standard deviations are within the dots size. The grey area indicates the uncertainty of the regression line at the 95 % confidence level.

CaCl_2 -extracted Cr(VI) (i.e., $R^2 = 0.88$; Fig. 6). Moreover, the slope of this correlation confirmed that the whole fraction of mobile chromium in heated soils from New Caledonia actually corresponded to Cr(VI).

Although less marked, quite good correlation could also be observed between these fractions of CaCl_2 -extracted Cr(VI) or CaCl_2 -extracted total chromium and that of Cr(VI) quantified in the heated soils by detailed analysis of the pre-edge region of Cr K-edge XAS data (i.e., $R^2 = 0.58$; $p\text{-value} = 2.5 \cdot 10^{-3}$; Fig. SM-8 and $R^2 = 0.73$; $p\text{-value} = 2.5 \cdot 10^{-4}$; Fig. SM-9, respectively). However, the slopes of these correlations suggested that the CaCl_2 solution actually extracted only 80 % of the fraction of Cr(VI) formed upon soil heating. This latter result is in agreement with the known sorption capacity of soil mineral components towards chromate ions that can only be fully exchanged with a dedicated phosphate ions solution (James and R.J., 1983). This latter phosphate/chromate competition for sorption onto soil mineral species could also explains the higher fraction of mobile chromium found in CA soils (Fig. 5), which hold much higher P concentration than VS and UM soils (Table 1).

3.8. Environmental implications

Considering that the studied soils are representative of the local pedological diversity, the enhanced chromium mobility observed after heating these soils from 400 °C emphasizes the high potential of Cr(VI) release upon wildfires across most of the landscapes of New Caledonia. In this regard, this study complements well our previous investigation that already highlighted the risk of wildfire-induced freshwater Cr(VI) pollution at ultramafic catchments in New Caledonia (Thery et al., 2023). It suggests that this risk might finally concern a wide range of local drinking water catchments and thus emphasizes the need for further investigating the health risk associated with the consumption of freshwater at burned catchments in New Caledonia. On a broader scale, considering the recent catastrophic wildfires around the world (i.e., USA, Canada, Greece, Chile), the potential threats to freshwater systems arising from the occurrence of Cr(VI) in burned soils might be more widespread than currently considered worldwide. Such an impact should be regarded as an emerging risk towards water quality at the global scale that requires to be further assessed in the context of climate change. In this regard, the Driver-Pressure-State-Impact-Response (DPSIR) approach that has been tentatively applied to global-scale assessment of wildfire risks towards water security (Robinne et al., 2018) might hold an interesting potential. Integrating our results to this approach, along with those from similar studies that would expand them to a wider range of pedological context, would undoubtedly strengthen

its contribution to the assessment of wildfire-induced risk towards freshwater resources at the global scale.

4. Conclusions

The results of this study indicate that Cr(VI) is formed from heat-induced Cr(III) oxidation from 400 °C in a range of Cr-rich Ferralsols, Cambisols, Vertisols and Regosols from New Caledonia showing contrasted chemical and mineralogical characteristics. They also show that chromium speciation influences the extent of this reaction. More precisely, the fraction of Cr(III) converted to Cr(VI) in the soils heated to 400 °C and 600 °C appears to be primarily driven by that initially hosted in goethite in the non-heated soils and which did not incorporate into hematite after thermal conversion of goethite to hematite (i.e., a fraction referred to as the *heat-reactive Cr(III)* in the present study). Despite the known influence of pH and/or organic matter on the regulation of redox reactions in soils, the potential contribution of these parameters to the rate of thermal oxidation of Cr(III) appears to be negligible compared to that of heat-reactive Cr(III). In the same way, the decreasing average redox state of Mn related to phase transition of Mn-oxides around 400 °C and 800 °C casts some doubt on the actual contribution of this mineral species to the rate of Cr(III) oxidation to Cr(VI) upon soil heating. Considering this, the most probable final electron acceptor in this redox reaction is likely O_2 , whose electron transfer capacity increases with temperature. From an environmental point of view, an important result of this study is the confirmation that most of the Cr(VI) formed in the heated soils is highly mobile. Since the soils investigated in this study represent a substantial portion of the pedological diversity found in New Caledonia, our results suggest that the risk of wildfire-induced freshwater Cr(VI) pollution in this French overseas territory might affect a wide range of drinking water catchments. Beyond the single case of New Caledonia, the risk of wildfires-induced freshwater Cr(VI) pollution deserves to be further assessed at the global scale regarding the wide occurrence of Cr-bearing pedological settings worldwide and considering the high toxicity of Cr(VI). In this regard, field studies encompassing the contribution of all the soil-plant-water system components would yield additional information that would usefully complement those provided by laboratory-controlled experiments on burned soils.

CRedit authorship contribution statement

Gaël Thery: Writing – original draft, Validation, Methodology, Investigation, Formal analysis. **Farid Juillot:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Damien Calmels:** Writing – review & editing, Validation. **Quentin Bollaert:** Writing – review & editing, Validation, Investigation. **Michael Meyer:** Writing – review & editing, Investigation, Formal analysis. **Thomas Quiniou:** Writing – review & editing, Investigation, Formal analysis. **Magali David:** Writing – review & editing, Methodology, Conceptualization. **Philippe Jourand:** Methodology, Funding acquisition, Conceptualization. **Marc Ducousso:** Methodology, Funding acquisition, Conceptualization. **Emmanuel Fritsch:** Methodology, Funding acquisition, Conceptualization. **Gautier Landrot:** Methodology, Investigation. **Guillaume Morin:** Writing – review & editing, Methodology, Investigation. **Cécile Quantin:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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