Immobilisation of chromium in magnesium carbonate minerals

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Abstract

Hexavalent chromium (Cr${}^{6+}$) is a toxic carcinogenic pollutant that might be released by the mining and processing of ultramafic rocks and nickel laterites and which requires permanent removal from the contaminated biosphere. Ultramafic material can also serve as a feedstock for the sequestration of CO$_2$ resulting from the growth of new minerals, raising the intriguing proposition of integrated sequestration of both pollutants, CO$_2$ and chromium, into magnesium carbonates. Such a synergistic process downstream of ore recovery and mineral processing could be an elegant proposition for more sustainable utilisation and management of the Earth’s resources. We have therefore carried out an experimental and microanalytical study to investigate potentially suitable carbonate minerals. Uptake of chromium in carbonate phases was determined, followed by identification of the crystalline phases and characterisation of the local structural environment around the incorporated chromium centres. The results suggest that neither nesquehonite nor hydromagnesite have the structural capacity to incorporate Cr${}^{6+}$ or Cr${}^{3+}$ significantly at room temperature. We therefore propose that further research into this technology should focus on laboratory assessments of other phases, such as layered double hydroxides, that have a natural structural capacity to uptake both chromium and CO$_2$.

Keywords: hexavalent chromium; hydromagnesite; nesquehonite; ultramafics; laterites; environment; ore processing; carbon capture

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Introduction

Decarbonising the world economy relies on a secure and sustainable supply of critical metals and minerals that underpin low-carbon technologies. The development of wind, hydro- and geothermal energy technologies, as well as energy storage systems and transport solutions with less environmental impact will continue to rely on primary mining for the foreseeable future, as more sustainable options, e.g. the recovery of metals from e-waste, cannot satisfy the demand for critical resources. However, although mining can bring numerous benefits to society and global economic development, almost all mining operations are associated with negative effects on the environment, including ecosystem loss and the heavy-metal pollution of water, soil, or dust. Mining is currently responsible for up to 7% of greenhouse-gas emissions globally (Delevingne et al., 2020), of which emissions incurred directly through mining operations and power consumption make up ~1%. An additional 28% of global emissions are indirect and include coal-based power or gas combustion to process metals, and emissions generated upstream to produce mining equipment (Delevingne et al., 2020).

The mitigation of greenhouse-gas emissions from mining operations can thus make a substantial contribution to climate change mitigation. This will require integration of clean energy technologies and carbon capture and storage (CCS) at different stages of the mining operation, from ore recovery to mineral processing. CCS can theoretically be achieved by either the injection of CO$_2$ in situ into suitable geological formations, where it can be immobilised by several mechanisms (Matter and Kelemen, 2009; Kelemen et al., 2011; De Silva et al., 2015) or by the reaction of CO$_2$ with feedstock materials to produce carbonate minerals. The latter is typically referred to as ex situ Carbon Capture and Storage by Mineralisation (CCSM). Recent advances in CCSM propose utilising carbonation as a metal recovery process (Wang et al., 2021; Wang and Dreisinger, 2022, 2023). Some of the best feedstock materials for CCSM are magnesium (Mg)-rich ultramafic rocks, serpentinites and their weathering products (laterites). The last twenty years have seen significant progress in the understanding of mineralogical and geochemical factors controlling efficient carbonation (Zevenhoven et al., 2003; Maroto-Valer et al., 2005; Fagerlund et al., 2009; Hanchen et al., 2008; Fagerlund and Zevenhoven, 2011; Kelemen et al., 2011; Werner et al., 2013; Harrison et al., 2013; Oskierski et al., 2013; Power et al., 2013; Lacinska et al., 2016; Lacinska et al., 2017; Power et al., 2021), or the economic assessment of the technology (Strunje et al., 2022) and CCSM is now advancing to pilot projects and medium-scale industrial...
There are several naturally occurring minerals that contain Notable amounts of Cr\(_6^+\) found in natural systems have a direct oxidation state. Trivalent Cr occupies the octahedral site of travertines (Olsson et al., 2014) and hydrometallurgical processing of ultramafic rocks and Ni laterites (PT Vale Indonesia Tbk., 2017).

The extent of water–rock interactions during the weathering of ultramafic rocks and serpentinites affects the concentration of Cr in the surrounding waters and soils, with the oxidation state dependent on the degree of redox reaction with other electron donors and acceptors present (McClain and Maher, 2016). For example, the occurrence of Cr\(_6^+\) (3–8% of the total chromium) in the lateritic regolith developed on ultramafic rocks in New Caledonia has been associated strongly with the presence of Mn\(_{2+}\) or Mn\(_{3+}\) (Fandeur et al., 2009; Santos et al., 2022). Notable amounts of Cr\(_6^+\) found in natural systems have a direct anthropogenic origin, related to the sediment drainage from open pit mining (Gunkel-Grillon et al., 2014) or pyro- and hydrometallurgical processing of ultramafic rocks and Ni laterites (PT Vale Indonesia Tbk., 2017).

Current Cr\(_6^+\) remediation mechanisms include physical, chemical and/or biochemical processing of the waste materials. However, a recent review suggests that notwithstanding the significant capability of the various mechanisms, the associated cost, sustainability of the methods, sludge generation and huge amount of chemicals necessitate new innovative, environment-friendly propositions (Kumar and Dwivedi, 2021). An alternative process for Cr\(_6^+\) remediation is to remove it through precipitation. This occurs naturally through reduction to Cr\(_3^+\) and precipitation of insoluble Cr\(_3^+\) oxides and hydroxides (Palmer, 1991). In naturally forming carbonates, the scavenging of potentially toxic elements (PTE), e.g. Cr, has been reported previously from travertines (Olsson et al., 2014) and hydromagnesite (Boschi et al., 2020). The pathway in which Cr can be incorporated crystallographically in minerals is determined primarily by its oxidation state. Trivalent Cr occupies the octahedral site of many minerals by substituting for Fe\(_3^+\), Al\(_3^+\), or Ti\(_4^+\). In contrast, Cr\(_6^+\), which is typically in the form of the chromate anion (CrO\(_4^{2-}\)), assumes tetrahedral coordination (Liu et al., 2017). There are several naturally occurring minerals that contain both Cr\(_3^+\) and carbonate ions in their crystal structures, including stichtite Mg\(_6\)Cr\(_2\)CO\(_3\)(OH)\(_{16}\)⋅4H\(_2\)O and grguricite CaCr\(_2\)(CO\(_3\))(OH)\(_3\)⋅4H\(_2\)O, however there are currently no known minerals with concurrent chromate and carbonate anions listed in the International Mineralogical Association database (Pasero, 2023). Such a combination is theoretically possible, albeit in actuality not yet reported, in layered double hydroxide or the ettringite-group minerals (Juroszek et al., 2020). Hexavalent chromium has been reported from experimentally produced Ca carbonates, where chromate substitutes for the carbonate groups in calcite (Tang et al., 2005; Hua et al., 2007; Tang et al., 2007; Sanchez-Pastor et al., 2011). The incorporation mechanism requires overcoming a geometric incompatibility between the tetrahedral sites hosting Cr with the planar triangular carbonate groups causing local strain of the crystal structure (Tang et al., 2007; Sanchez-Pastor et al., 2011). Nevertheless, successful partitioning of Cr\(_6^+\) into calcite has been observed, especially in strongly contaminated media, suggesting that the fate of this pollutant in natural environments can be influenced significantly by co-precipitation processes with carbonates (Sanchez-Pastor et al., 2011).

Co-precipitation of chromium with magnesium carbonates has been less well studied, though nesquehonite (Mg\(_2\)CO\(_3\)⋅3H\(_2\)O) has been shown to incorporate Cr\(_3^+\) through substitution with Mg\(_2^+\) (Hamilton et al., 2016; Hamilton et al., 2018). Understanding the potential of Mg carbonates to trap chromium is of significant importance to mining and processing of ores hosted by ultramafic rocks. Here, we present an outlook on that potential based on experimental and microanalytical investigations.

**Methodology**

A series of co-precipitation experiments were conducted using aqueous solutions of MgCl\(_2\)·6H\(_2\)O (1.8 mol L\(^{-1}\)), K\(_2\)Cr\(_2\)O\(_7\) (0.18 mol L\(^{-1}\)) and Na\(_2\)CO\(_3\) (1.8 mol L\(^{-1}\)). Upon mixing at room temperature (20°C), the material became turbid immediately and a yellow gel formed. To monitor the speciation of chromate and its localisation in the resulting phases, a portion of the material was monitored continuously for eight hours by X-ray absorption near-edge structure (XANES) measurements during carbonate mineral crystallisation (Supplementary Fig. S1). A different portion of the same starting material was placed in an oven at 60°C for 6 hours, and XANES spectra were obtained subsequently. Additionally, an attempt to precipitate stichtite was made (Supplementary Figs S2 and S3), which resulted in poorly crystalline, albeit Cr-bearing, nano-scale particulates that are also the subject of investigation.

A multi-scale, multi-technique analytical programme was applied to elucidate the mineralogy and composition of the resulting materials, including overall material morphology by scanning electron microscopy (SEM), determination of crystalline phase composition by X-ray diffraction (XRD), element depth profiling by energy-dispersive (EDX) X-ray analysis by SEM and laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) mapping. Determination of the chromium oxidation state and its local coordination environment in the crystal structure was achieved by XANES.

Scanning electron microscopy analyses were performed using a Zeiss Sigma 300 VP-HEG with Bruker Quantax XFlash 6|30 EDX detectors system at the British Geological Survey. Samples were analysed in the form of carbon sputter coated (≈25 nm thick) polished blocks and as rough materials distributed on an aluminium stub with carbon tab. The SEM was operated under conditions of high vacuum (1.2 × 10\(^{-6}\) Torr) at accelerating voltages ranging from 3–15 kV, with 8.5 mm optimal analytical working distance and an X-ray detector take-off angle of 35°. Qualitative compositional analyses of the mineral phases were performed using Bruker systems SDD EDS. Quantitative analysis was not undertaken due to analytical challenges associated with the fine grain size and beam sensitive nature of the experimental materials. High-resolution imagery was performed at low kV (3–5 kV) and using an in-lens secondary electron detector.
X-ray diffraction was performed using a Malvern PANalytical X’Pert Pro series X-ray diffractometer at the British Geological Survey, equipped with an X’Celerator detector, cobalt-target tube and generator operated at 45 kV and 40 mA, in Bragg-Brentano geometry. Samples for XRD were ground in an agate pestle and mortar and <10 mg sub-samples mounted on silicon crystal ‘zero background’ substrates using a single drop of acetone. Diffraction data were analysed using Malvern PANalytical X’Pert HighScore Plus version 5.1 software coupled to the 2022 version of the International Centre for Diffraction Data (ICDD) PDF4+ database (https://www.icdd.com/).

X-ray absorption near-edge structure (XANES) data were collected at the B18 beamline at the Diamond Light Source in Harwell, United Kingdom. The measurement conditions for reference data and the sample were the same. The Cr K XANES were recorded in fluorescence-yield mode with a 36-element solid-state Ge detector. A Si(111) double crystal monochromator was used, which provides an energy range from 4 to 11 keV (Dent et al., 2009). The spectra were acquired in continuous scanning (‘quick EXAFS’, QEXAFS) mode from 5790 eV to 6630 eV with a step size of 0.25 eV. X-ray absorption spectroscopy (XAS) data analysis was performed using the Demeter software package (Ravel and Newville, 2005). Data were extracted using WebPlotDigitizer (Rohatgi, 2015).

Laser ablation inductively couple plasma mass spectrometry (LA-ICP-MS) analyses were done on polished blocks using Elemental Scientific Lasers imageGEO193 (British Geological Survey). For mapping these samples, the 193 nm excimer laser spot was a 10 × 10 μm square and the laser set to 20Hz repetition rate and a fluence of 4.4 J/cm²; the beam was then rastered as a series of lines at 25 μm/s across the target area, all being controlled by the proprietary ‘AV2’ software. The ICP-MS was an Agilent 8900 series instrument controlled by MassHunter software, data were collected in a time resolved fashion for isotopes 23Na, 24Mg, 39K, 42Ca and 52Cr with a dwell time of 14 ms except Cr with 35 ms. As well as the samples, standards SRM610 (NIST, USA) and GSD-1G (USGS, USA) were analysed as calibrants. All calibration calculations and mapping were performed using the Elemental Scientific Lasers Iolite4 software taking the both the Iolite4 software and the proprietary ‘AV2’ software. The ICP-MS was an Agilent 8900 series instrument controlled by MassHunter software, data were collected in a time resolved fashion for isotopes 23Na, 24Mg, 39K, 42Ca and 52Cr with a dwell time of 14 ms except Cr with 35 ms. As well as the samples, standards SRM610 (NIST, USA) and GSD-1G (USGS, USA) were analysed as calibrants. All calibration calculations and mapping were performed using the Elemental Scientific Lasers Iolite4 software taking the both the time resolved counts/s data from an Agilent file and the laser log file; for concentration calculation Mg was used as an internal standard with an assumed stoichiometric concentration of 288,000 mg/kg.

Results

The room-temperature (20°C) experiments with stirring resulted in the formation of prismatic crystals (<1 mm) of nesquehonite (MgCO₃⋅3H₂O) and lesser amounts of hydromagnesite [Mg₆(CO₃)₄(OH)₂⋅4H₂O] as spherules. Combined microbeam analyses on the nesquehonite crystals provided evidence that neither Cr⁶⁺ nor Cr³⁺ were incorporated into the structure of this mineral (Fig. 1a,e), however element-distribution maps did not show Cr⁶⁺ in the solution to Cr³⁺, driven by reactions involving the chloride ion and the reduction of chromium to Cr⁵⁺ in the solution. The processes are complex and proceed via several intermediates, however they could lead to the formation of chlorine gas (and temperature driven evaporation) and/or chloride (ClO₃⁻) catalysed by the presence of chromate (CrO₄²⁻) (Busch et al., 2022). As no redox reaction occurred during the 20°C experiment, we can exclude radiolytic reduction by the X-ray beam. The increase of temperature to 60°C appears to be the trigger of the reactions. Indeed, previous in situ XANES of Cr (OH)₃ revealed strongly temperature-dependent interconversions between Cr⁵⁺ and Cr⁷⁺ (Schroeder et al., 1997). This dependence of speciation on the process conditions may be potentially important in the long-term design of industrial crystalllographic trapping of Cr in the carbonate structure and deserves further investigation.

However, if chloride–chromate redox reactions have occurred, then we speculate the following set of events resulted in the lower concentration and a more even distribution of chromium as Cr³⁺ in the carbonate structure and deserves further investigation.

The higher concentration of chromium in the outer zones of the spherulites (Fig. 1g) might have resulted from a combination of: (1) diffusion of core zone chromium towards the margin and reduction upon contact with solution; and (2) reduction of chromium upon contact with the surface of both hydration and diffusion. The width of the chromium-rich rim representing the depth of chloride-bearing solution penetration into the solid. Regardless, it is apparent that the diffused and in situ chromium has been mostly expelled from the solid upon the crystallisation of AMC into hydromagnesite/dypingite. Further trace-element investigations are needed to establish if any chromium was...
Figure 1. Secondary electron images of (a) prismatic crystals of nesquehonite locally covered by nano-sized Cr-bearing material, shown in detail in (b); (c) spherulites of hydromagnesite formed at 20°C and (d) hydromagnesite/dypingite formed at 60°C; (e) back-scattered electron and LA-ICP-MS maps showing the distribution of Mg and Cr nesquehonite prismatic crystals; (f) back-scattered electron and LA-ICP-MS maps showing the distribution of Mg and Cr in the hydromagnesite, 20°C; (g) LA-ICP-MS maps showing the distribution of Mg and Cr in the 60°C precipitates. Note: Mg is shown in cps as it was used as an internal standard.
captured crystallographically, and if so, what the effect of such structural substitution is on the stability of the carbonate mineral.

Discussion and outlook

On the basis of the rapid precipitation of carbonate (seconds) in the static experiment and the spherical morphology and texture of hydromagnesite and dypingite, we infer that the initial material formed was amorphous and attained crystalline structure over time. Nesquehonite was the predominant phase identified in the stirred experiments. Such dynamic systems are known to promote the transformation of amorphous magnesium carbonate in aqueous solution to long-range ordered minerals, such as nesquehonite (Yamamoto et al., 2021).

Our current understanding of the striking, albeit inconsistent association of Cr\(^{6+}\) with the cores of hydromagnesite spherulites does not support a structural incorporation mechanism, instead it suggests a physical trapping of Cr-bearing material in the intercrystalline microporosity of the aggregates (Fig. 3). The coexistence of and, the notably more even distribution of Cr\(^{3+}\) within hydromagnesite–dypingite spherical aggregates formed at 60°C, in addition to the similarity of our XANES data with that of Cr\((\text{OH})_3\), are intriguing (Fig. 2) and suggest the potential incorporation of hydroxide. Trivalent chromium might be incorporated into carbonate as shown by previous investigations (Hamilton et al., 2016; Boschi et al., 2020) although not necessarily by a direct Cr\(^{3+}\) to Mg\(^{2+}\) substitution. In calcium carbonate, Cr\(^{3+}\) cannot substitute directly for Ca\(^{2+}\), however as hydroxide, it may be adsorbed to crystal surfaces or occupy interstitial voids in the crystals (Fang et al., 2022). A similar phenomenon might be true for magnesium carbonates (Fig. 3), and in such cases, chromium would have been expelled from the carbonate structure during the crystallisation of AMC. The crystallisation of AMC and the degree to which incompatible elements are incorporated structurally or physically, and/or expelled from the crystalline material might depend on the mechanism of crystallisation, i.e. dissolution–reprecipitation versus solid-state crystallisation. In the latter, a cascade of fast exchanges of hydrogen between the AMC and H\(_2\)O molecules from the hydration shell and the surrounding solution, enhances mobility of ions/molecules that compose the AMC (Von Euw et al., 2020). This allows for the rearrangement of AMC into crystalline domains via solid-state transformation (idem), possibly promoting the expulsion of incompatible elements and their physical entrapment in the local microporosity, as observed in the spherulites formed in this investigation. Although the spherulite morphology of hydromagnesite–dypingite precipitates is consistent with solid-state crystallisation, the dissolution–reprecipitation mechanism or a combination of both crystallisation pathways can not be ignored. Dissolution–reprecipitation would probably remove incompatible elements from the carbonate structure.

Figure 2. (a) Cr K-edge XANES spectra, with the 5984.5 eV Cr\(^{3+}\) pre-edge peak, collected from isolated spherulites of hydromagnesite formed at 20°C (in red – this study), K\(_2\)Cr\(_2\)O\(_7\), CaCr\(_2\)O\(_4\) (Tang et al., 2007) and Cr-doped calcite (c25-1hr from Tang et al., 2007). (b) XANES of hydromagnesite/dypingite spherulites formed at 60°C (in red – this study), compared to Cr\(^{3+}\)-bearing reference materials, including Cr in nesquehonite (Nes) (Hamilton et al., 2016) and K\(_2\)Cr\(_2\)O\(_7\), i.e. the initial host of chromium.
elements from the vicinity of the crystallising solid into the solution, decreasing the degree of entrapment and ultimately leading to the release of these elements. The phase-transformation mechanisms, including both the AMC to crystalline and subsequent changes to crystal structure within the hydrated–anhydrous magnesium carbonate system, are highly relevant to the cycling of potential contaminants such as chromium (Harison et al., 2019). Further experimental and nanoscale investigations are required to appraise the incorporation mechanism in detail. One potential avenue to explore is pressure-induced crystallisation that has been shown as an efficient pathway to dope incompatible elements into crystals of calcium carbonates (Matsunuma et al., 2014).

In our opinion, experimental efforts should also focus on such Cr³⁺-bearing materials that have a natural long-term capacity to retain chromium, rather than forcing structure-modifying
incompatible chromate ions into an otherwise stable structure of magnesium carbonates. Accordingly, we recognise that minerals belonging to the layered double hydroxides (LDHs), specifically the CO2-bearing hydrotalcite supergroup with pyroaurite–hydrotalcite–stichtite end-members might present a viable matrix for chromium. These minerals comprise positively charged brucite-like layers \((A_{x-}\cdot B_{x+})(OH)_2\)
, where A is a divalent cation (e.g. Mg or Fe) and B is a trivalent cation (e.g. Al, Fe or Cr). Interlayer regions typically contain a monovalent or divalent anion X, such as \(\text{CO}_3^{2-}\), \(\text{SO}_4^{2-}\), \(\text{Cl}^-\) and \(\text{OH}^-\). The well-defined structural site for trivalent elements and the wide range of possible cation–anion substitutions suggest that hydrotalcites represent a potentially suitable matrix for chromium or other PTE and CO2 (Aschenbrenner et al., 2011). Although the incorporation of trivalent chromium in hydrotalcite is relatively straightforward, albeit requiring metal reduction, the substitution of chromate for carbonate is challenging because of structural affinity of the \(\text{CO}_3^{2-}\) ion to the local symmetry of the interlayer site in hydrotalcite and the strong hydrogen bonding between the hydroxyl ions of the layer with the carbonate ions (Prassana and Kamath, 2008). This makes the CO2-bearing hydrotalcite very stable and thus it has a wide range of applications, including the cement industry (Bernard et al., 2022). The hydrotalcite supergroup with pyroaurite–hydrotalcite–stichtite end-members represents a potential stable host for chromium and the CO2 formed through integrated CCSM.

We, thus hypothesise that a disruptive innovation in the design of Ni laterite ore processing to include CO2 and chromium sequestration through the precipitation of hydrotalcite will lead to more sustainable utilisation and management of the Earth’s resources. Such process integration necessitates knowledge cross-fertilisation and a shared vision between industry and academia to timely assess its potential and drive the theory of change in the ore processing industry.

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Competing interests. The authors declare none.

References


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