

# Geochemical modelling as a tool to investigate chromium contamination in groundwater

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## Abstract

Geochemical modelling is an essential tool to understand the water-rock interaction processes. In this work has been used the reaction path modelling to investigate the release and fate of geogenic Cr in ophiolitic Italian areas. During the water-rock interaction the geogenic trivalent Cr hosted in Cr-bearing minerals (serpentine minerals, spinels, pyroxene, etc.) of serpentinites rocks is oxidized in Cr (VI) highly toxic, resulting largely dangerous for environment and human health. This geochemical modelling was performed varying  $\text{Fe}_2\text{O}_3/(\text{FeO}+\text{Fe}_2\text{O}_3)$  weight ratios considering the trivalent Fe the main oxidant present in suitable amounts in serpentinite rock. The reaction paths reproduces the analytical concentrations of relevant solutes, including Cr(VI), in the Mg-HCO<sub>3</sub> groundwaters hosted in the ophiolitic aquifers of Italy.

**Keywords:** Geochemical modelling, hexavalent chromium, groundwater

## 1. Introduction

Reaction path modelling is a proven geochemical tool based on fundamental principles of thermodynamics and chemical kinetics to understand the water-rock interaction processes. Indeed, starting from 1960s several software packages are developed with the purpose to investigate several processes of geochemical interest which occur into near-surface environment including weathering (e.g. Helgeson et al., 1970; Reed, 1982; Wolery and Jarek, 2003; Parkhurst and Appelo, 2013). During water-rock interaction some potential harmful elements could be release due to weathering actions and geochemical condition variations. In this context, it is possible an increase of these elements concentration into water which could cause adverse effects of human health. In this work, geochemical modelling was used to understand the causes of chromium (Cr) release and its fate during weathering processes in ophiolitic areas of Italy. It is known that ophiolitic areas are peculiar environments where enriched of trace elements, mainly Cr, in soils and groundwater could occur. Indeed, Cr-bearing minerals (mainly serpentine minerals, spinels and pyroxene) host trivalent Cr which is oxidized in Cr(VI) during

weathering processes becoming largely dangerous for environment and human health (WHO-IARC, 1990). Although generally accepted hypothesis is that geogenic Cr(III) oxidation is driven by the reduction of trivalent and tetravalent Mn, this work is focused on role of trivalent iron (Fe) as responsible of oxidation processes.

## 2. Geological Setting

During the Jurassic-Cretaceous times the Piemonte-Ligurian basin was formed in response to tectonic events. The relicts representing now ophiolite fragments which occupy some areas of the western and northern Mediterranean region (Vissers et al., 2013). In Italy significative ophiolitic bodies are exposed in both Alpine and Apennine belt that host the studied aquifers. These are located in some regions of Italy as Calabria, Basilicata, Tuscany and Liguria. The high-Cr content in natural groundwaters in these areas is due to the extensive weathering process that affect the outcropping ultramafic and serpentinite rocks of Alpine domain and Apennine ones.

## 3. Methods

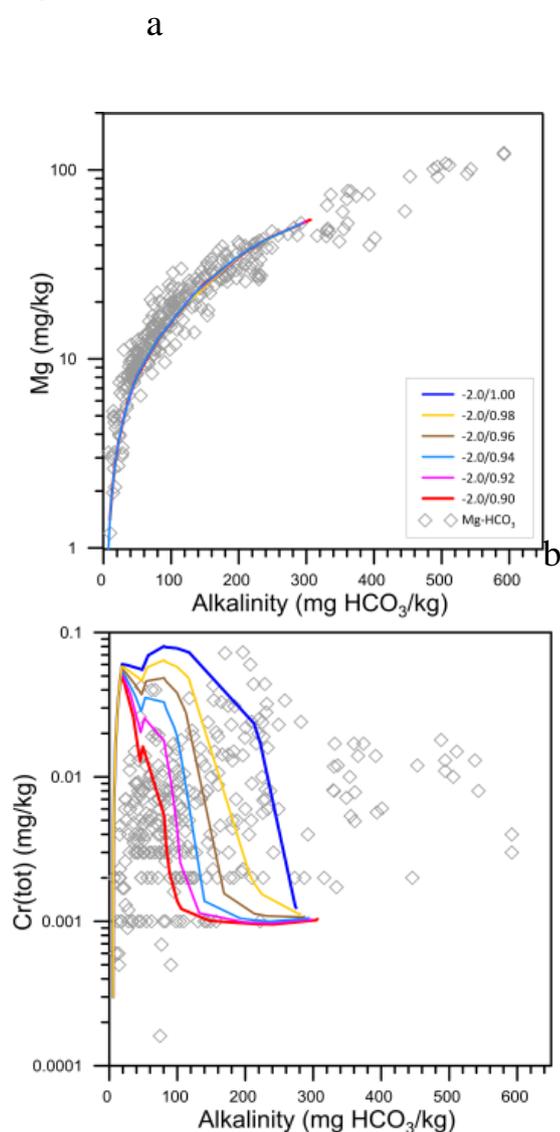
Reaction path modelling was carried out by means of the EQ3/6 software package (Wolery and Jarek, 2003) utilizing the modified thermodynamic database of Wolery and Jove-Colon (2007). The simulations were performed in kinetic (time) mode, under a closed system with secondary solid phases and an open system with CO<sub>2</sub>, adopting constant PCO<sub>2</sub> value equal to 10<sup>-2.0</sup> bar varying  $\text{Fe}_2\text{O}_3/(\text{FeO}+\text{Fe}_2\text{O}_3)$  weight ratios (1.00, 0.98, 0.96, 0.94, 0.92, 0.90). Based on literature data it was considered a serpentinite rock constituted mainly of serpentine, two types of spinel, clinopyroxene, Cr-clinochlore, magnetite, and calcite. Further information on solid reactants are present in Apollaro et al., 2019 as well as the chemical data of water samples considered.

## 4. Results and Discussion

In the Figure 1 the six theoretical paths of serpentinite dissolution for PCO<sub>2</sub> of 10<sup>-2</sup> bar and an  $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$  weight ratio of serpentinite equal to 1, 0.98, 0.96 ,

0.94, 0.92, and 0.90 were reported. The binary plot alkalinity vs. Mg illustrate that theoretical paths are superimposed whereas in alkalinity vs. total Cr plot they reproduce the range of analytical Cr concentrations. These results show that the variation of  $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$  weight ratio in serpentine rocks doesn't influence dissolved Mg during the water-rock interaction whereas Cr concentration varies significantly to increase of  $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$  weight ratio. In this context it could affirm that the trivalent Fe hosted in serpentine mineral could drive the oxidation processes of Cr and its enrichment into groundwaters.

**Figure 1.** Results of reaction path modelling for (a) Mg and (b) total Cr under a  $\text{PCO}_2$  of  $10^{-2}$  bar and variable  $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$  weight ratio of serpentine (see legend)



## 5. Conclusion

Geogenic Cr(VI) contamination is a worldwide environmental issue which mainly occur in areas where ultramafic and serpentinite rocks crop out. In this paper geochemical modelling was performed varying  $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$  weight ratios to investigated the role of trivalent Fe on the oxidation processes of Cr(III) to Cr(VI). Despite Mn oxides are considered in this process the only oxidant by scientific literature, the obtain results show that the oxidation processes could be drive by trivalent Fe. Indeed the theoretical paths computed reproduce the all range of Cr concentration in Mg- $\text{HCO}_3$  water type of Italian ophiolitic acquifers.

These results are the global interest to expand the knowledges on environment issue linked to Cr-contamination that can cause several negative effect of human health.

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