

## Redox reactions and the influence of natural Mn oxides on Cr oxidation in a contaminated site in northern Italy: evidence from Cr stable-isotopes and EPR spectroscopy

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**Abstract.** Hexavalent chromium-contaminated groundwaters and sediments in northern Italy have been studied using the Cr stable-isotope systematics and electron spin resonance spectroscopy (ESR), in order to explore redox changes and soil-groundwater interactions. The isotopic data indicate a possible Cr(VI) source released into the environment from an industrial plant. EPR spectra on the sediments which constitute the aquifers show a broad asymmetric absorption due to coupled Fe(III) and coupled Cr(III) ions and a well resolved hyperfine structure due to manganese ions, resulting from Mn(IV) and Mn(II). The isotopic and EPR data support the hypothesis of Cr(III) being oxidized by Mn oxides which are widespread in the aquifer, possibly related to the oscillation of the phreatic level. The obtained results highlight the usefulness of chromium stable isotopes as environmental tracers and support the observations that naturally occurring Mn oxides in soils may catalyze Cr oxidation from the stable Cr(III) form to the toxic Cr(VI) soluble form, yielding valuable information in planning remediation interventions.

**Key words:** Hexavalent chromium, Groundwaters, Chromium stable-isotopes, Chromium oxidation

### Introduction

Chromium is a transition metal mostly occurring in natural environments in two stable oxidation states: Cr(III) and Cr(VI). Cr(III) is an essential micronutrient whereas Cr(VI) is highly toxic. The hexavalent forms of chromium are very soluble and rarely found in soils. The most stable species in groundwaters are (with increasing pH and in the absence of complexing agents other than OH<sup>-</sup> and H<sub>2</sub>O) HCrO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. On the other hand, Cr(III) is sparingly soluble and mostly occurs as cations and hydrolyzed species adsorbed onto the surfaces of minerals (Kožuh et al., 2000).

Relatively high Cr concentrations usually characterize basic to ultra-basic rocks in ophiolitic sequences and related soils, where Cr primarily occurs as a member of the spinel mineral group. These lithologies represent possible natural Cr(VI) sources. However, Cr(VI) has been since long used in a number of industrial applications including electroplating, leather tanning,

production of special paints and wood preservatives, and the majority of the environmental releases of Cr(VI) is from industrial wastes. It is commonly believed that Cr(VI) contamination in groundwater remains confined to relatively limited areas, being Cr(VI) readily converted into the more stable Cr(III) form by reducing agents in soils and sediments, like bivalent iron and natural organic matter (NOM) (Kim et al., 2002a; Fendorf, 1995; Tokunaga et al., 2003). However, a number of observations demonstrate that Cr(III) may be oxidized in many naturally occurring conditions (Kim et al., 2002b), extending the potential environmental threats. Of the various known oxidizing agents for Cr(III), Mn oxides received particular attention since they represent common constituents in soils and sediments (Kim et al., 2002b; Trebien et al., 2011).

The chromium stable isotope systematics demonstrated to be an important tool in the study of the fate of chromium in the environment, since Cr(VI)/Cr(III) redox changes produce both equilibrium and kinetic

isotopic fractionation. Natural chromium has four stable isotopes at masses (approximately) 50, 52, 53 and 54. Calculations from first principles indicate that a measurable fractionation is expected in equilibrium exchange reactions between Cr(III) and Cr(VI) with the heavy species being preferentially partitioned into the oxidized forms (Schauble et al., 2004). Furthermore, kinetic isotopic fractionation has been experimentally observed, where the light species tend to be more reactive (Hoefs, 2009). During Cr(VI) reduction in groundwater, these processes yield increasingly positive  $\delta^{53}\text{Cr}$  values for Cr(VI) in the residual water, where  $\delta^{53}\text{Cr}$  represents the ‰ deviation of the  $^{53}\text{Cr}/^{52}\text{Cr}$  from a standard.

The present study is focused on the application of the chromium stable-isotope systematics and EPR spectroscopy to investigate the source and cycling of Cr(VI) contamination in groundwaters and sediments from a number of wells in the High Friuli Plain, in northern Italy.

The High Friuli Plain is characterized by fluvio-glacial sediments (coarse grained carbonatic gravels, locally cemented, and discontinuous sandy-silty lenses) interbedded with marine and coastal sediments (Martelli and Granati, 2007). This geological setting determines the hydrogeology of the area, characterized by an unconfined aquifer largely exploited for irrigation and drinking water supply, that partly outflows at a resurgence belt line southward (Cucchi et al., 2007). A site in the High Friuli Plain underwent severe Cr(VI) contamination by release from an electroplating industry into the phreatic aquifer during the mid 1990's. The hexavalent chromium concentration in groundwaters reached 4500  $\mu\text{g}/\text{L}$ . Since that time the area was monitored by the Regional Environment Protection Authority (ARPA FVG) through repeated surveys. After a decrease in the measured Cr(VI) concentration to below detection limits, the concentration increased again during the first months of 2008 to present, exceeding in some wells 1500  $\mu\text{g}/\text{L}$ , with a pattern roughly following the groundwater flowpath towards the coastline from the primary site of contamination. In order to investigate the sources of this contamination, the Cr isotopic composition was determined on groundwaters and from soil extracts. In addition, the Mn speciation in soils and sediments was investigated through EPR experiments.

## Materials and Methods

Water samples were filtered at 0.45  $\mu\text{m}$  in the field. Cr from soils was extracted following the EPA 3060 (UNI EN 15192) procedures for alkaline digestion. Samples were double-spiked before elution by anion exchange chromatography to separate Cr from isobars. The Cr isotopic composition was determined by thermal-ionization mass spectrometry (TIMS) after sample loading on a Re filament and using silica gel and boric acid.

EPR spectra on sediments were recorded at X-band and room temperature on a EPR Varian E 112 instrument equipped with an Oxford EPR 900 cryostat for

temperature control, a Bruker ER035M NMR Gaussmeter and a XL Microwave 3120 frequency counter for a precise g-value determination.

## Results and Discussion

The  $\delta^{53}\text{Cr}$  values measured on groundwaters range between +1.20‰ to -3.00‰. The  $\delta^{53}\text{Cr}$  in soil extracts reaches -2.99‰. Negative  $\delta^{53}\text{Cr}$  values in groundwaters are unusual, since positive  $\delta^{53}\text{Cr}$  values for Cr(VI) are generally measured in response to fractionation during the progressive reduction to Cr(III).

A possible explanation for these isotopically light compositions involves the role of Cr(III) which forms during Cr(VI) reduction. These species become enriched in the heavy isotopes and are characterized by negative  $\delta^{53}\text{Cr}$ . During oxidation, little Cr isotopic fractionation occurs and the Cr(VI) which forms may have negative  $\delta^{53}\text{Cr}$  values. A possible scenario is summarized as follows:

- a widespread groundwater contamination by hexavalent chromium from anthropogenic sources occurred in the area during the 1990's;
- part of the Cr(VI) was naturally reduced to Cr(III), which was adsorbed onto the sediments of the aquifer;
- the newly formed Cr(III) species preferentially incorporated the heavy Cr isotopes. This isotopic record distinguishes the anthropogenic-originated Cr from natural sources;
- the oxidation of the isotopically heavy Cr(III) yielded the negative  $\delta^{53}\text{Cr}$  values measured for Cr(VI) in some of the groundwaters;
- the further reduction of this Cr(VI) is testified by the positive  $\delta^{53}\text{Cr}$  observed in some of the samples.

In this hypothesis, the  $\delta^{53}\text{Cr}$  of groundwaters has been modeled in terms of a Rayleigh-type fractionation process, assuming a constant fractionation factor ( $\alpha$ ). The hypothesis of Cr(III) oxidation was investigated by EPR, considering that Mn, which in the studied soils ranges between 49 mg/Kg and 1200 mg/Kg, was the most likely oxidant agent. EPR is known to be a valuable source of information with respect to the local environment of some transition elements, including Mn. The EPR spectra obtained for 3 samples of the sediments which constitute the aquifer are shown in Figure 1 a and b. Figure 1a consists of a weak resonance at  $g=4.32$  (\*1), which denotes a strong rhombic distortion of Fe(III) ions. A broad asymmetric absorption is observed at  $g=2.25$  (\*2), due to coupled Fe(III) and coupled Cr(III) ions that may occur in pairs, in groups of several ions or even in clusters. The large absorptions centered at  $g=2.01$  (\*3) and 1.99 (\*4) are consistent with the presence of hexacoordinated Mn(IV and II) and Cr(III) centers, respectively, having the central metal atom in an octahedral field. Figure 1b shows a well resolved hyperfine structure of six lines due to manganese ions, resulting from absorptions ascribable to Mn(IV) and Mn(II) ions. These results suggest a close correspondence between iron and manganese species and the redox cycle of chromium.

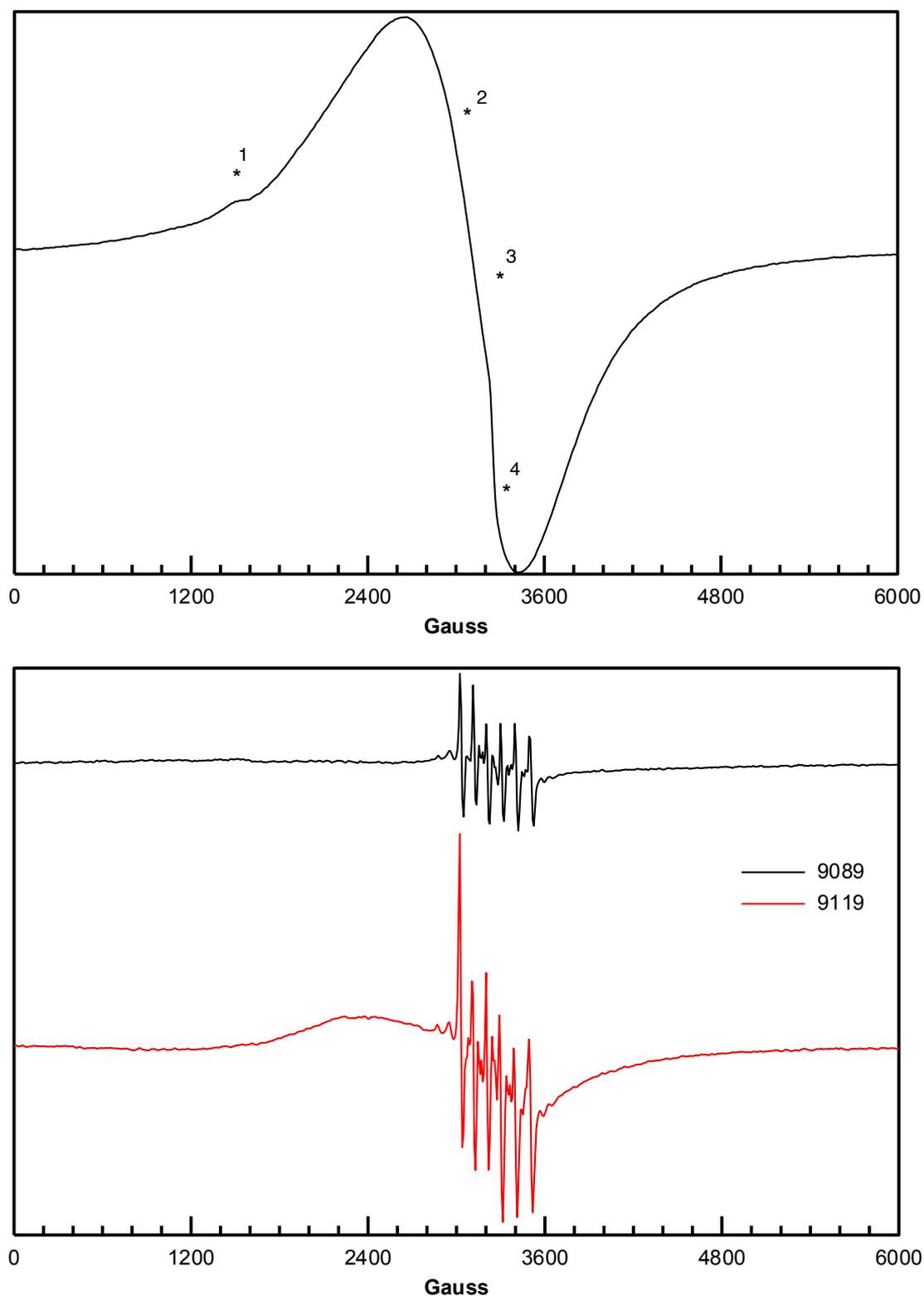


Fig. 1. The EPR Spectra of 3 samples of sediment from the studied area: a - above) the asterisks identify the absorptions described in the paragraph; b - below) two spectra exhibiting the hyperfine structure.

The hypothesis of an active reduction of Cr(VI) has been investigated by monthly sampling at the same station. The data show a decrease in the Cr content coupled with

the increase of  $\delta^{53}\text{Cr}$ , consistently with a Rayleigh-type fractionation. Additional processes of dilution are also highlighted.

The occurrence of oxidation and reduction processes for chromium seems to be dependent on the oscillation of the phreatic level. Nevertheless, this hypothesis deserves further investigations.

### Conclusion

In the present study the chromium stable-isotope systematics has been applied to a site which in the past underwent a strong Cr(VI) contamination by industrial outflows. Despite the industrial activity has been made environmentally protective, new spikes in the Cr(VI) concentration have been recently observed, after a period of absence of contamination. The Cr-isotope data suggest a possible Cr(VI) source from oxidation of Cr(III) which formed by reduction of the pristine Cr(VI) contamination and which was adsorbed onto sediments constituting the aquifers. Sediments contain variable amounts of Mn; electron paramagnetic resonance spectroscopy reveal the occurrence of Mn(II) species, supporting the hypothesis that manganese oxides are responsible for Cr oxidation from a stable form to the more toxic and mobile hexavalent form.

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