Geochemical constraints on the sources of Cr(VI) contamination in waters of Messapia (Central Evia) Basin

M. Economou-Eliopoulos a,*, I. Megremi a, Ch. Vasilatos a, R. Frei b, I. Mpouroudimos c

a Department of Geology and Geoenvironment, University of Athens, Athens 15784, Greece
b Department of Geoscience and Natural Resource Management, University of Copenhagen, Denmark
c The Municipality of Messapia-Diffis, Evia, Greece

A R T I C L E   I N F O
Article history:
Received 10 May 2017
Accepted 11 May 2017
Available online 13 May 2017
Editorial Handling by Prof. M. Kersten.

Keywords:
Contamination
Cr(VI)
Water
Leachates
Isotopes
Evia

A B S T R A C T
The present study aims to define geochemical constraints on contamination source(s) by Cr(VI) in Central Evia, through a compilation of new and literature data on an integrated set of approaches, including mineralogy and (isotope) geochemistry; leach experiments on rocks, soils and Ni-laterites; and comparison with literature data on groundwater.

The concentrations of Cr(VI) in leachates from various geological materials decrease in the following order: Ni laterites from Kastoria > soils > altered ultramafic rocks > Ni laterites from Evia. A salient feature is the diversity in the Cr(VI) concentrations and δ53Cr values in (a) groundwater, ranging from <2 to 850 μg/L Cr(VI) and 0.60–1.59‰ δ53Cr, and (b) leachates from Ni-laterites, ranging from 0.6 to 2.0 μg/L and 1.01‰ in Evia samples and from 750 to 1200 μg/L and negative to slightly positive (−0.21 to 0.03‰) δ53Cr in Kastoria samples. A positive correlation (R² = 0.514) between the δ53Cr values and depth of the aquifers, potentially reflects the decrease in soluble O₂ with increasing depth. The relatively high Cr, Mn and the abundance of fine-grained Mn-(hydr)oxides in the Kastoria laterite ore, may be major controlling factors for the existence of high Cr(VI) concentrations in the water leachates. In contrast, the low Cr(VI) concentrations and positively fractionated Cr isotopes in the Ni-laterite leachates from Evia are potentially related to redox and multistage transportation/redeposition processes.

The positive correlation between Cr concentrations and Ca/Mg ratios (R² = 0.647) for rock leachates and the negative correlation (R² = −0.694) for soil leachates suggest that Cr in groundwater may be released mainly from Cr-bearing Mg-silicates in altered ultramafic rocks and soils. The plot of δ53Cr values versus Cr(VI) concentrations for the contaminated waters from Central Evia and Assopos Basin fall within both fields defined from a global database for natural waters and waters contaminated by human activities.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Chromium occurs in different oxidation states in nature, with Cr(III) and Cr(VI) being the most abundant species. Cr(III) is a required nutrient, as opposed to the highly toxic and very soluble oxidized Cr(VI), which causes serious health problems (Kabata-Pendias, 2000) when in the form of chromate oxyanions such as CrO₄²⁻, HCrO₄⁻ and Cr₂O₇²⁻ (ATSDR, 2000; Losi et al., 1994). Council Directive 98/83/EC has established a maximum permissible limit of Cr_total in drinking water, 50 μg/L or ppb. Chromium is used in many industrial processes, including iron and steel production, chrome plating, manufacture of pigments, leather tanning, and wood processing, and it may also be released by natural processes from Cr-bearing minerals hosted in rocks and ores such as ultramafic rocks and Ni-laterites. Chromium oxidation-reduction processes in natural waters and soil environments have long been an attractive topic for intense research (Salunkhe et al., 1998; Fantoni et al., 2002; Oze, 2003; Becquer et al., 2003; Ball and Izbicki, 2004; Oze et al., 2004, 2007, 2016). Recently, high concentrations (up to 120 μg/L) of Cr(VI) were determined in unconfined aquifers of the Sarigkiol Basin (Kozani area, N. Greece), effected by Ophiolitic rocks and fly ash produced from a power plant burning lignite (Kazakis et al., 2017).

Our research interest has focused on the Assopos – Thiva Basin because it is an industrial zone; the Assopos River running through the basin has been designated as a “processed industrial waste
receiver" since 1969 (Giannoulopoulos, 2008; Vasilatos et al., 2008; Tziritis, 2009; Megremi, 2009, 2010; Megremi et al., 2013; Economou-Eliopoulos et al., 2011, 2012, 2013, 2014, 2016; Frei and Polat, 2012, Frei et al., 2014a,b; Dermatas et al., 2015; Dimitrula et al., 2015; Dokou et al., 2015). The Central Euboea Basin (Messapia) has been selected for geological and environmental studies, due to the presence of widespread masses of ophiolitic rocks and Ni-laterite deposits, such as the Psachna Ni-laterite deposits in Evia, Larymna and Kastoria (Valeton et al., 1987; Skarpelis et al., 1993; Alevizos, 1997; Eliopoulos and Economou-Eliopoulos, 2000; Skarpelis, 1997; Megremi, 2009, 2010; Kalatha and Economou-Eliopoulos, 2015; Gkoutzioupa et al., 2016).

Given population growth, the need for production of more food, and the desire to avoid further losses in ecosystem biodiversity, soil and groundwater protection is of particular significance for societies and agricultural economies. The range and average Cr content in the Assopos Basin (range: 73–300 ppm, average: 200 ppm) and in the Central Evia soils (range: 540–3800 ppm, average: 1300 ppm) (Fig. 1) are often higher than the average Cr content in the earth's crust (80 ppm), although levels in the Assopos Basin do not always indicate contamination, according to metal limits (380 ppm) given for soils by the Netherlands (Kabata-Pendias, 2000). Concentrations of Cr(VI) in groundwater above the acceptable level are common in the Assopos Basin, ranging from <2 to 900 µg/L, and the Central Evia, ranging from <2 to 350 µg/L (Megremi, 2009, 2010; Economou-Eliopoulos et al., 2012, 2014, 2016).

The present review study is a compilation of new and literature data from a variety of topical studies, including mineralogy, (isotope) geochemistry, and leaching experiments on rocks, soils and Fe-Ni-laterites from Central Evia (Messapia). This database is compared to that of other contaminated groundwater and leachates, in an attempt to define mineralogical and geochemical constraints on the source(s) of contamination.

2. Geological and hydrogeologic outline

The regional aquifer is a complex heterogeneous system in the area of central Euboea, composed mainly of alluvial Neogene sediments and ultramafic rocks. The shallow portion of the regional aquifer is predominantly under phreatic (unconfined) conditions, has limited thickness (less than 100 m), and is commonly used for agricultural activities. Ophiolitic outcrops, consisting mainly of serpentinitized peridotites (harzburgites and lherzolites) with some minor mafic rocks, are common. The area is characterized by strong geomorphological contrast and consists mainly of Pleistocene to Holocene sediments, which host the most productive aquifers in this area (Fig. 1; Katsikatsos et al., 1980). Central Evia, aside from the Quaternary alluvial formations and ophiolites covering lowland areas, is characterized by widespread Ni-laterite deposits. The Ni-laterite deposits in Central Evia, in the proximity of the studied area, as well as those in Larymna, Central Greece, are well-known due to a production level corresponding to approximately 2–3% of the world’s total nickel output (Megremi, 2010; Eliopoulos et al., 2012). Ni-laterite ores have been transported and deposited either onto peridotites or onto karstified Jurassic limestone and overlain by Lower Cretaceous limestone. The multistage transportation and redeposition of the latter deposits is well-documented by the
presence of a conglomerate, composed mostly of rounded-elongated saprolite and silicified saprolite blocks (of varying size) within a matrix of pisolith laterite and calcite, at the contact between the laterite body and the carbonate basement (Alevizos, 1997; Skarpelis, 1997; Eliopoulos and Economou-Eliopoulos, 2000; Kalatha and Economou-Eliopoulos, 2015; Valeton et al., 1987).

Thus, two different types of aquifers can be found: (a) Neogene aquifers in conglomerates, sandstones and marly limestone, and/or in highly fractured zones of ultramafic rocks (harzburgites and herzolites), reaching depths between 11 and 180 m, which are tapped by many shallow wells for agricultural activities, and (b) a deeper karst-type aquifer associated with Jurassic-Cretaceous limestones. The deep portion of the regional aquifer is predominantly under confined conditions, and it appears that the hydraulic connection between the phreatic zone and deeper parts of the aquifer is poor (Katsikatsos et al., 1980; Megremi, 2010).

3. Methods of investigation

More than 60 soil samples were collected from cultivated and non-cultivated sites of Central Evia, covering an area of approximately 200 km² (19 km × 12 km). Soil samples, along with 25 rock and ore samples, collected between 2007 and 2012, have been analysed by inductively coupled plasma mass spectroscopy (ICP/MS), the soils after hot aqua regia digestion, and rock/ores after multi-acid digestion (HNO₃, HClO₄, HF, HCl), at ACME Analytical Laboratories in Canada. Detection limits and the results for the quality control samples, the precision of the analyses of the minor and trace elements is in good agreement with international standards (Table 1 in the Annex after Megremi, 2009, 2010; Economou-Eliopoulos et al., 2014, 2016).

Polished sections prepared from rock, soil and Fe-Ni-laterite ores from Evia and Kastoria (Greece) were carbon coated and examined by reflected light microscopy and scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS). SEM-EDS analyses were carried out at the University of Athens Department of Geology and Geoenvironment using a JEOL JSM 5600 scanning electron microscope, equipped with automated energy-dispersive analysis system ISIS 300 OXFORD, with the following operating conditions: accelerating voltage 20 kV, beam current 0.5 nA, time of measurement 50 s and beam diameter 1–2 μm (Tables 2 and 3).

Groundwater samples collected from over 40 domestic and...
irrigation wells covering the area studied (2007–2013) have been analysed by ICP/MS at ACME Analytical Laboratories in Canada (Table 4 in the Annex; Economou-Eliopoulos et al., 2014, 2016).

A series of natural water leaching experiments were carried out to understand the impact of environmental conditions on the leaching of Cr(VI) at varying time, and selected samples were subjected to leaching tests, following those used currently (ATSDR, 2014) for leaching of Cr(VI) at varying time, and selected samples with a to understand the impact of environmental conditions on the deposit.

Table 2

<table>
<thead>
<tr>
<th>Central Evia</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite (Fig. 2e)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>wt%</td>
<td>Light grey</td>
<td>Dark grey</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>6.2</td>
<td>5.8</td>
<td>2.9</td>
<td>5.7</td>
<td>12.9</td>
<td>7.1</td>
<td>7.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.9</td>
<td>4.9</td>
<td>3.3</td>
<td>5.1</td>
<td>4.6</td>
<td>7.2</td>
<td>8.3</td>
<td>19.6</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.6</td>
<td>0.5</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>74.1</td>
<td>72.5</td>
<td>77.7</td>
<td>72.8</td>
<td>66.2</td>
<td>69.8</td>
<td>67.6</td>
<td>64.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>n.d.</td>
<td>1.4</td>
<td>1.9</td>
<td>1.3</td>
<td>n.d.</td>
<td>1.6</td>
<td>1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>MgO</td>
<td>1.2</td>
<td>n.d.</td>
<td>0.3</td>
<td>n.d.</td>
<td>0.3</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>CaO</td>
<td>0.4</td>
<td>0.3</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>MnO</td>
<td>0.4</td>
<td>0.4</td>
<td>0.6</td>
<td>0.4</td>
<td>n.d.</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>NiO</td>
<td>0.9</td>
<td>0.4</td>
<td>n.d.</td>
<td>0.4</td>
<td>0.7</td>
<td>0.4</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Total</td>
<td>85.5</td>
<td>86.2</td>
<td>86.7</td>
<td>86.3</td>
<td>85.9</td>
<td>86.9</td>
<td>86.4</td>
<td>87.4</td>
</tr>
</tbody>
</table>

Table 3

| Kastoria |  |  |  |  |  |  |  |  |
| Goethite (Fig. 3) |  |  |  |  |  |  |  |  |
| wt% | Light grey | Dark grey | White | White | Veinlets |  |  |  |
| SiO₂ | 4.4 | 1.5 | 1.5 | 1.8 | 1.6 | 1.5 | 5.7 | 1.9 | 2.1 | 3.9 |
| Al₂O₃ | 1.4 | 2.1 | 2.1 | 2.1 | 2.9 | 2.9 | 0.8 | n.d. | n.d. | 1.3 |
| Cr₂O₃ | 0.6 | 2.1 | 2.1 | 3.4 | 1.6 | 4.2 | 0.5 | n.d. | n.d. | n.d. |
| Fe₂O₃ | 73.3 | 76.1 | 76.2 | 75.1 | 76.9 | 74.3 | 70.8 | 93.3 | 92.9 | 35.3 |
| MgO | 0.9 | 0.6 | 0.6 | 0.7 | 0.6 | 0.7 | 0.7 | 0.8 | 0.7 | 4.1 |
| CaO | 0.4 | 0.3 | 0.3 | 0.2 | n.d. | 0.4 | n.d. | 0.4 | n.d. | 0.4 |
| MnO | 3.2 | 1.8 | 1.6 | 0.7 | 1.6 | 1.5 | 4.6 | 2.4 | 2.8 | 33.1 |
| NiO | 2.3 | 0.7 | 0.7 | 1.3 | 0.7 | 0.7 | 2.6 | 1.5 | 0.8 | 7.1 |
| Total | 86.5 | 85.2 | 85.3 | 85.1 | 85.1 | 86.1 | 99.8 | 99.4 | 85.2 | 85.2 |

Table 4

<table>
<thead>
<tr>
<th>Trace element concentrations in groundwater from central Evia.</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>µg/L</td>
<td>mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

High-precision stable chromium isotopes (expressed as ⁵³Cr values) have been measured in groundwater and in water leachates of ultramafic rocks, soils and Fe-Ni-laterite ores (Economou-Eliopoulos et al., 2014, 2016) on a multi-collector inductively coupled plasma source mass spectrometry (MC–ICP–MS) (Schoenberg et al., 2008; Schiller et al., 2014). The final isotopic composition of a sample (Table 6) was determined as the average of the repeated analyses and reported relative to the certified SRM 979 standard as ⁵³Cr (‰) = ([(⁵³Cr / ⁵²Cr)sample / (⁵³Cr / ⁵²Cr)SRM979] – 1) × 100.

4. Results and selected characteristics of rocks, soils and ores

The occurrence of highly serpentinized and tectonized rocks and the multistage transportation and re-deposition of the Fe-Ni-laterite deposits is in Central Evia and Lokris are well documented by the presence of a conglomerate, composed mostly of rounded-elongated saprolite and silicified saprolite blocks (of varying size) within a matrix of pisolithic laterite and calcrete, at the contact between the laterite body and the carbonate basement (Fig. 2a–d). Soil, rock and Fe-Ni-laterite samples from Central Evia
are characterized by significant Cr values (Table 1 in the Annex; Megremi, 2010; Economou-Eliopoulos et al., 2014, 2016) as compared to the Cr content (90–110 ppm) in the earth crust (Rudnick and Fountain, 1995). Soils from the cultivated region are mostly composed of quartz, calcite, serpentine, chromite, Fe-chromite, goethite, magnetite, kaolinite, montmorillonite, illite, illmenite, rutile, zircon and rare earth element minerals. Fine pyrite, which is commonly frambooidal is also present (Fig. 2f). Chromium in soils is contained in chromite grains or fragments, Cr-bearing goethite and silicates transported as residual components inherited from both ophiolitic parent rocks and Fe-Ni-laterite deposits, as suggested by highly positive correlations of Cr with Ni, Co, Mn, V and Ti (Economou-Eliopoulos et al., 2012).

In the Kastoria laterite ore Mn-Fe hydroxides mixed with silicates (commonly Fe-serpentinite) (Fig. 3), chromite grains, quartz, carbonates (calcite, siderite), Mn (hydr)oxides (pyrolusite, lithiophorite and asbolane) are dominant components, zircon and apatite are minor minerals, and organic matter is higher (5.4–10.2 wt%) than that in Central Evia laterites (1–2.0 wt%) (Megremi, 2010).

Furthermore, investigation of Fe-Ni-laterites by SEM-EDS indicated that goethite, occurring as rounded fragments from a previous stage, as well as in the matrix, is a dominant component in both laterites from Central Evia and Kastoria. However, there are significant differences in their mineral chemistry: Goethite in the Kastoria laterites showed higher Cr and Mn contents and negligible Ti content compared to that in laterite ores from Central Evia and Kastoria. However, there are significant differences in their mineral chemistry: Goethite in the Kastoria laterites showed higher Cr and Mn contents and negligible Ti content compared to that in laterite ores from Central Evia (Table 2). Also, several stages in goethite formation can be distinguished in the Kastoria ore, such as (a) high-Fe/light grey goethite of a previous stage occurring as rounded fragments in the matrix (Fig. 3d, e), (b) goethite in the matrix, with varying grey colour, fine aggregates of hematite, and dark-grey fine aligned elongate hematite field of high-Cr type and there is an abundance of quartz in the Kastoria ores, whilst there is a wide range from high-Cr to high-Al type in the Evia laterites (Fig. 4).

### Table 5

<table>
<thead>
<tr>
<th>µg/L</th>
<th>Cr(III)</th>
<th>As</th>
<th>B</th>
<th>Br</th>
<th>Li</th>
<th>Mn</th>
<th>Ni</th>
<th>P</th>
<th>Zn</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>Si</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>14</td>
<td>12</td>
<td>0.5</td>
<td>268</td>
<td>7</td>
<td>1.4</td>
<td>0.2</td>
<td>7</td>
<td>&lt;10</td>
<td>9.1</td>
<td>17</td>
<td>2.1</td>
<td>3.2</td>
<td>13</td>
</tr>
<tr>
<td>R2</td>
<td>18</td>
<td>16</td>
<td>1.6</td>
<td>154</td>
<td>13</td>
<td>2.7</td>
<td>0.1</td>
<td>4.2</td>
<td>11</td>
<td>4</td>
<td>26</td>
<td>1.9</td>
<td>4.2</td>
<td>12</td>
</tr>
<tr>
<td>R2a</td>
<td>35</td>
<td>35</td>
<td>1.7</td>
<td>124</td>
<td>&lt;5</td>
<td>3.2</td>
<td>0.2</td>
<td>2.3</td>
<td>&lt;10</td>
<td>5.5</td>
<td>26</td>
<td>1.9</td>
<td>3.4</td>
<td>12</td>
</tr>
<tr>
<td>R3</td>
<td>30</td>
<td>29</td>
<td>0.8</td>
<td>78</td>
<td>&lt;5</td>
<td>14.8</td>
<td>0.5</td>
<td>0.7</td>
<td>&lt;10</td>
<td>6.1</td>
<td>25</td>
<td>2.9</td>
<td>2.4</td>
<td>13</td>
</tr>
<tr>
<td>R4</td>
<td>3</td>
<td>&lt;4</td>
<td>0.6</td>
<td>46</td>
<td>&lt;5</td>
<td>3.4</td>
<td>0.1</td>
<td>0.7</td>
<td>&lt;10</td>
<td>6.9</td>
<td>18</td>
<td>4.7</td>
<td>2.1</td>
<td>15</td>
</tr>
<tr>
<td>R5</td>
<td>3.2</td>
<td>&lt;4</td>
<td>0.5</td>
<td>23</td>
<td>&lt;5</td>
<td>1.6</td>
<td>0.7</td>
<td>1.1</td>
<td>&lt;10</td>
<td>6</td>
<td>18</td>
<td>6.8</td>
<td>1.9</td>
<td>17</td>
</tr>
<tr>
<td>R6</td>
<td>2</td>
<td>&lt;4</td>
<td>0.5</td>
<td>103</td>
<td>12</td>
<td>1</td>
<td>0.1</td>
<td>0.7</td>
<td>&lt;10</td>
<td>3.5</td>
<td>12</td>
<td>11.4</td>
<td>3.3</td>
<td>18</td>
</tr>
<tr>
<td>R7</td>
<td>2.3</td>
<td>&lt;4</td>
<td>0.6</td>
<td>204</td>
<td>&lt;5</td>
<td>1.4</td>
<td>&lt;0.05</td>
<td>0.9</td>
<td>&lt;10</td>
<td>3.7</td>
<td>13</td>
<td>11.8</td>
<td>1.9</td>
<td>23</td>
</tr>
<tr>
<td>R8</td>
<td>2.2</td>
<td>&lt;4</td>
<td>0.7</td>
<td>106</td>
<td>&lt;5</td>
<td>0.8</td>
<td>0.2</td>
<td>0.8</td>
<td>&lt;10</td>
<td>8.2</td>
<td>13</td>
<td>8.6</td>
<td>1.8</td>
<td>20</td>
</tr>
<tr>
<td>R10</td>
<td>3.1</td>
<td>&lt;4</td>
<td>0.7</td>
<td>272</td>
<td>5</td>
<td>0.5</td>
<td>0.2</td>
<td>0.2</td>
<td>&lt;10</td>
<td>4.7</td>
<td>15</td>
<td>11.6</td>
<td>1.7</td>
<td>26</td>
</tr>
<tr>
<td>R11</td>
<td>4.5</td>
<td>&lt;4</td>
<td>0.5</td>
<td>46</td>
<td>11</td>
<td>0.5</td>
<td>0.5</td>
<td>0.4</td>
<td>&lt;10</td>
<td>29</td>
<td>25</td>
<td>8.1</td>
<td>1.5</td>
<td>33</td>
</tr>
<tr>
<td>R13</td>
<td>3.4</td>
<td>&lt;4</td>
<td>0.5</td>
<td>148</td>
<td>&lt;5</td>
<td>0.4</td>
<td>&lt;0.05</td>
<td>0.2</td>
<td>&lt;10</td>
<td>&lt;0.5</td>
<td>12</td>
<td>13.8</td>
<td>1.6</td>
<td>23</td>
</tr>
<tr>
<td>R15</td>
<td>6.4</td>
<td>5</td>
<td>0.5</td>
<td>143</td>
<td>13</td>
<td>0.6</td>
<td>&lt;0.05</td>
<td>0.7</td>
<td>&lt;10</td>
<td>1.8</td>
<td>16</td>
<td>11.3</td>
<td>2.3</td>
<td>22</td>
</tr>
<tr>
<td>R16</td>
<td>5.5</td>
<td>4</td>
<td>0.5</td>
<td>58</td>
<td>18</td>
<td>0.9</td>
<td>&lt;0.05</td>
<td>&lt;0.02</td>
<td>&lt;10</td>
<td>0.5</td>
<td>20</td>
<td>13.2</td>
<td>2.1</td>
<td>19</td>
</tr>
<tr>
<td>R17</td>
<td>3.6</td>
<td>&lt;4</td>
<td>0.5</td>
<td>229</td>
<td>&lt;5</td>
<td>1.6</td>
<td>&lt;0.05</td>
<td>0.6</td>
<td>&lt;10</td>
<td>1.9</td>
<td>18</td>
<td>6.3</td>
<td>2.1</td>
<td>17</td>
</tr>
<tr>
<td>R18</td>
<td>8.8</td>
<td>7</td>
<td>0.5</td>
<td>48</td>
<td>5</td>
<td>0.5</td>
<td>&lt;0.05</td>
<td>0.4</td>
<td>&lt;10</td>
<td>1.6</td>
<td>21</td>
<td>8.1</td>
<td>1.7</td>
<td>17</td>
</tr>
<tr>
<td>R19</td>
<td>15</td>
<td>&lt;3</td>
<td>0.5</td>
<td>292</td>
<td>27</td>
<td>0.9</td>
<td>0.1</td>
<td>0.7</td>
<td>&lt;10</td>
<td>5.8</td>
<td>20</td>
<td>6.8</td>
<td>4</td>
<td>20</td>
</tr>
</tbody>
</table>

Fe-Ni laterites

<table>
<thead>
<tr>
<th>µg/L</th>
<th>Cr(III)</th>
<th>As</th>
<th>B</th>
<th>Br</th>
<th>Li</th>
<th>Mn</th>
<th>Ni</th>
<th>P</th>
<th>Zn</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>Si</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>La8</td>
<td>1.8</td>
<td>2</td>
<td>1.4</td>
<td>11,400</td>
<td>170</td>
<td>55.5</td>
<td>170</td>
<td>12</td>
<td>57</td>
<td>1.3</td>
<td>26</td>
<td>24</td>
<td>19</td>
<td>9.5</td>
</tr>
<tr>
<td>La12</td>
<td>1.3</td>
<td>&lt;4</td>
<td>0.5</td>
<td>1960</td>
<td>21</td>
<td>6.4</td>
<td>1.1</td>
<td>5.6</td>
<td>&lt;10</td>
<td>4</td>
<td>31</td>
<td>8.9</td>
<td>8.9</td>
<td>7.4</td>
</tr>
<tr>
<td>La15</td>
<td>0.57</td>
<td>0.6</td>
<td>1.8</td>
<td>1620</td>
<td>20</td>
<td>11.4</td>
<td>0.6</td>
<td>3.6</td>
<td>&lt;10</td>
<td>4.6</td>
<td>26</td>
<td>1</td>
<td>9.7</td>
<td>7.4</td>
</tr>
<tr>
<td>La1</td>
<td>0.74</td>
<td>0.8</td>
<td>0.9</td>
<td>600</td>
<td>17</td>
<td>4.9</td>
<td>1.5</td>
<td>2.8</td>
<td>&lt;10</td>
<td>8.3</td>
<td>46</td>
<td>18</td>
<td>15</td>
<td>7.6</td>
</tr>
<tr>
<td>Kast4</td>
<td>1200</td>
<td>1300</td>
<td>&lt;0.5</td>
<td>21,700</td>
<td>70</td>
<td>7.2</td>
<td>0.22</td>
<td>9.4</td>
<td>&lt;10</td>
<td>0.4</td>
<td>29</td>
<td>4.3</td>
<td>24</td>
<td>31.5</td>
</tr>
<tr>
<td>Kast7</td>
<td>750</td>
<td>740</td>
<td>&lt;0.5</td>
<td>8900</td>
<td>82</td>
<td>3.7</td>
<td>0.6</td>
<td>3.6</td>
<td>&lt;10</td>
<td>0.5</td>
<td>43</td>
<td>1.4</td>
<td>16</td>
<td>7.5</td>
</tr>
</tbody>
</table>

D. Limit

<table>
<thead>
<tr>
<th>µg/L</th>
<th>Cr(III)</th>
<th>As</th>
<th>B</th>
<th>Br</th>
<th>Li</th>
<th>Mn</th>
<th>Ni</th>
<th>P</th>
<th>Zn</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>Si</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>5</td>
<td>5</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>10</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>40</td>
<td>1</td>
</tr>
<tr>
<td>STD</td>
<td>404.2</td>
<td>419</td>
<td>17</td>
<td>28</td>
<td>22.6</td>
<td>327</td>
<td>330</td>
<td>&lt;10</td>
<td>497.3</td>
<td>22.4</td>
<td>5.78</td>
<td>8.8</td>
<td>428</td>
<td>7</td>
</tr>
</tbody>
</table>
concentrations over the maximum acceptable level for \( \text{Cr}_{\text{total}} \) in drinking water (50 µg/L). Chromate oxanions such as \( \text{CrO}_4^{2-} \), \( \text{HCrO}_4^- \) and \( \text{Cr}_2\text{O}_7^{2-} \) cause serious health problems (ATSDR, 2000). A wide variation in Cr concentrations is found in central Evia, ranging from <2 to 360 µg/L (Table 3, Annex), in contrast to the Cr (VI) concentrations in deep (>200 m) karst-type wells in Central Evia, which are negligible (Megremi et al., 2013). An investigation of the (Cr(VI)) variation in groundwater wells during the dry and wet seasons recorded relatively small differences (Megremi, 2010). The high values of salinization, as exemplified by seawater elements (B, Na, Mg, Li, Se), suggest a major contribution from seawater into the groundwater aquifer in Central Evia (Table 5, Annex), which is comparable with that in the Assopos Basin (Giannouloupolis, 2008). There is a negative trend between the Cr concentrations in water wells and the depth of the wells in Evia (Fig. 5). More specifically, the irrigation wells, hosted mostly in deeper ultramafic rocks (peridotites), exhibit lower Cr concentrations compared to those located at shallower depths within alluvial (unconfined) sediments. Groundwater from karst-type wells is characterized by negligible Cr concentrations (lower than 2 µg/L).

### 6. Chromium and other trace element concentrations in leachates

In general, the Cr concentrations in leachates from peridotites are much lower than those in soils, while the highest concentrations of Cr in rock leachates were measured in highly serpentinitized samples with abundant calcite (Fig. 2; Table 5, Annex).

The correlation between Cr concentrations and Ca/Mg ratios is positive (\( R^2 = 0.647 \)) for rock leachates whereas this correlation is negative (\( R^2 = -0.694 \)) for soil leachates (Fig. 6a,c). In contrast, the correlation between Cr concentrations and Mg/Si ratios is negative (\( R^2 = -0.467 \)) for rock leachates, while this ratio does not exhibit any clear (\( R^2 = 0.017 \)) correlation vs Cr concentrations for soil leachates and groundwater (Fig. 6d and e).

Also, there is a positive correlation (\( R^2 = 0.39 \)) between Mn and Fe versus Cr concentrations in rock and soil leachates (Fig. 7a and b), while Cr concentrations exhibit a negative correlation (\( R^2 = -0.513 \)) with Ca in soil leachates and a positive correlation (\( R^2 = 0.39 \)) in rock leachates (Fig. 7c). Chromium concentrations in rock leachates show a positive correlation (\( R^2 = 0.39 \)) with Ca content (Fig. 7d) and a negative correlation (\( R^2 = -0.54 \)) with Mg content (Fig. 7f). Finally, Ca concentrations in and soil leachates are positively (\( R^2 = 0.69 \)) correlated with the Ca content in soil samples (Fig. 7e).

### 7. A compilation of chromium stable isotopes in natural waters and water leachates

Variations in \( \delta^{53} \text{Cr} \) values, ranging from 0.84 to 1.98‰ in groundwater samples from Evia, from 0.98 to 1.16‰ in samples from the Assopos Basin and from 0.6 to 1.99‰ in samples from the Thiva Basin, have been recorded (Economou-Eliopoulos et al., 2014, 2016; Frei et al., 2014a,b). The water samples with the highest Cr(VI) concentrations (230 µg/L) from shallow wells in Central Evia Basin and (900 µg/L) in the Assopos Basin correspond to \( \delta^{53} \text{Cr} \) values of 0.98‰ and 1.16‰, respectively (Table 6).

The \( \delta^{53} \text{Cr} \) values measured in natural water leachates of Fe-Ni-laterites from Kastoria range between +0.03 ± 0.06‰ and -0.21 ± 0.08‰, which are much lower than the positively fractionated value (+1.01 ± 0.05‰) for the laterite leachates from Central Evia (Table 6; Fig. 8). However, many of the Evia leachates contained very low Cr concentrations, and \( \delta^{53} \text{Cr} \) values could not adequately be measured (Economou-Eliopoulos et al., 2016). Chromium stable isotope values in leachates from highly serpentinitized peridotites have shown a relatively small range of \( \delta^{53} \text{Cr} \) values (+0.56 to +0.96‰), as have those for the soil leachates (+0.51 to +0.59‰) (Economou-Eliopoulos et al., 2014, Fig. 8).

In general, there is a positive correlation (\( R^2 = 0.514 \)) between the \( \delta^{53} \text{Cr} \) values and the depth of wells (Fig. 9).

The \( \delta^{53} \text{Cr} \) measurements (+1.13 and +0.55‰) of surface seawater from the Mediterranean Sea (Evioic Gulf), selected from a location far away from the heavily Cr(VI)-contaminated point source of the Assopos River estuary, are comparable to those for surface seawater sampled at the Assopos River estuary (+0.79 ± 0.14‰) (Table 6). These \( \delta^{53} \text{Cr} \) values fall within the range published for global oceans, as exemplified by waters from Southampton and the Argentine Ocean (Scheiderich et al., 2015) and elsewhere (Campbell and Yeats, 1981; Cranston, 1983; Jeandel and Minster, 1987; Mugo, 1997; Sirinawin et al., 2000).

There is a negative correlation between the \( \delta^{53} \text{Cr} \) values and Cr(VI) concentrations in seawaters (\( R^2 = -0.625 \)), in natural waters (\( R^2 = -0.384 \)), in contaminated waters from Central Europe (\( R^2 = -0.565 \)), and California (\( R^2 = -0.636 \)) (Table 6; Fig. 10). The plot of \( \delta^{53} \text{Cr} \) values and Cr(VI) concentrations for contaminated waters from Messapia (Central Evia) and Assopos Basin showed that they fall within fields defined by global data on contaminated water, due to natural processes and industrial activities (Fig. 10).

### 8. Discussion

The assessment of the sources of Cr(VI) in groundwater is a complicated subject. The present study focuses on geochemical constraints concerning the contamination source(s) by Cr(VI) in Central Evia, through an integrated set of approaches and comparison with literature data on groundwater. It is noticeable that...
certain groundwater samples showing Cr(VI) concentrations lower than 5 µg/L contain low (5 mg/L) NO₃⁻ and high (4.1–7.5 mg/L) TOC (total organic carbon), in contrast to highly contaminated irrigation wells (>50 µg/L Cr(VI)) showing <1 mg/L TOC (Giannoulopoulos, 2008). In addition, the reduction of Cr(VI) by organic matter is supported by field (Qin and Wang, 2017) and laboratory experimental work applying the commercial material EDC-M (Electron Donor Compound-Metals) for testing of contaminated water treatment demonstrated the ability of the organic matter to directly reduce Cr(VI) (Moraki, 2010).

Chromium in ultramafic rocks and Ni-laterites is mainly hosted in chromite, which is thermodynamically stable, within silicate minerals and Fe-hydroxides (goethite). Such minerals are more easily weathered than chromite and are potential contributors to environmental contamination by chromium (Oze, 2003; Oze et al., 2007, 2016; Megremi et al., 2013; Rajapaksha et al., 2014; Economou-Eliopoulos et al., 2014, 2016). Furthermore, fine-grained Fe (hydr)oxides, have lower surface energies than corresponding anhydrous oxides and are unstable (Navrotsky et al., 2008), since the surfaces of nano-scale Mn-oxides provide locations for hydration and redox reactions, and their reduction is thermodynamically spontaneous (negative ΔG) at low temperature (Mugo, 1997; Birkner and Navrotsky, 2012).

The mobility of chromium through rocks and soils is dependent upon its oxidation state and in turn on a complex network of synergistic and competing processes. Major factors controlling the oxidation state are the soil redox conditions, pH, and the presence of certain other metals and organic compounds (Bartlett and James, 1979; Richard and Bourg, 1991; Banerjee and Nesbitt, 1999), while the adsorption of Cr(VI), in anionic forms such as HCrO₄⁻ or CrO₄²⁻,
depends on pH (Drever, 1997). Immobilization (possibly by adsorption/co-precipitation on/with Fe-oxy-hydroxides) of Cr(III) during transport in the weathering profile (Berger and Frei, 2014) and the oxidation of Cr(III) to Cr(VI) by Mn (di)oxides (Eary and Rai, 1988a,b; Oze, 2003; Oze et al., 2007) have been well-established. Furthermore, the compilation of geological, mineralogical and geochemical data with the distribution of the δ⁵³Cr values may contribute in a better way to define the contamination source(s).

8.1. Evidence from chromium stable isotopes

8.1.1. Diversity of the δ⁵³Cr and Cr(VI) values in Ni-laterite water leachates

A diversity between Cr(VI) concentrations in the water leachates for Ni-laterites from Central Evia and Kastoria (Table 6; Fig. 10), and fractionation of the δ⁵³Cr values relative to the average bulk silicate earth δ⁵³Cr composition of about −0.1‰ (Schoenberg et al., 2008), may imply differences in the effectiveness of the dissolution of Cr from the Ni-laterite ore during serpentinization/weathering of the parent peridotites, in transport and/or in post mobilization redox processes. Relatively high δ⁵³Cr values (0.56–0.96‰) in water leachates from highly altered peridotites (Fig. 2a) and Ni-laterites (up to 1.01‰ δ⁵³Cr) from Central Evia seem to be consistent with those determined (up to +1.22‰ δ⁵³Cr) in serpentinites (Farkas et al., 2013). These authors proposed that serpentinization could shift altered peridotites to isotopically high δ⁵³Cr, and interpreted the extreme high δ⁵³Cr in serpentinites as a result of isotopic fractionation during dehydration accompanying subduction and/or addition of Cr(VI) that was fractionated on mineral surfaces prior to entering solution (Farkas et al., 2013; Wang et al., 2016).
et al., 2015; Paulukat et al., 2015) indicate higher than bulk silicate earth $\delta^{53}\text{Cr}$ values, and mass balance modelling imply that river waters should also be characterized by heavy Cr isotopes (Frei et al., 2014a,b; D’Arcy et al., 2016). Assuming, by results hitherto published on riverine waters, that partial back-reduction of mobile Cr(VI), either already in the soils and/or during riverine transport, must be responsible for the generally positive $\delta^{53}\text{Cr}$ values in these systems. The fate of Cr(VI) in the seawater has been addressed by Scheiderich et al. (2015), and confirmed by Paulukat et al. (2015), who argued for the mixing trend in $[\text{Cr}]$ vs. $\delta^{53}\text{Cr}$ values of modern seawater to arise from fractionation during the reduction of Cr(VI) in surface waters and oxygen minimum zones, scavenging of isotopically light Cr(III) to deeper water and sediment, and subsequent release of this seawater-derived Cr(III) back into seawater, either as organic complexes with Cr(III) or after oxidation to Cr(VI). The above scenarios also seem to be consistent with the general increasing trend defined between $\delta^{53}\text{Cr}$ values and the depth of the aquifer (Fig. 9), which potentially reflects the decrease in soluble O$_2$ which would be expected with increasing depth.

However, the Kastoria Fe-Ni-laterites that have experienced seawater alteration during re-deposition and significant fluid infiltration during diagenesis and post-diagenetic stages show very limited fractionation of their isotopes. The presence of pyrite and the absence any zone of ferrian chromite at the peripheral parts and along cracks of chromite fragments in samples of Ni-laterites from Central Evia (Fig. 2f) as well as the presence of siderite cross-cutting earlier stages of Fe-(hydr)oxides and the Fe-depleted zones (dark grey) of goethite (Fig. 3d,f; white arrows) in the Kastoria laterites may point to reducing conditions that prevailed during diagenetic/post-diagenetic processes in both areas. Although a variety of reductants are present that could have potentially back-reduced mobilized Cr(VI), in the Kastoria Ni-laterite ores (Fig. 3) nearly unfractonated $\delta^{53}\text{Cr}$ values measured in the Kastoria leachates may indicate the existence of oxidative materials in excess, and/or the effects of additional factors on the kinetics of redox reactions. Also, the development of the Kastoria laterite deposit atop of peridotites, in contrast to those in Evia which were tectonically emplaced over a carbonate basement (Valeton et al., 1987), may indicate a significant role of the transportation flow for the enrichment of heavy Cr isotopes, which seems to be consistent with the positive trend between the $\delta^{53}\text{Cr}$ values and the depth of groundwater (Fig. 9).

### 8.1.2. Variation on the $\delta^{53}\text{Cr}$ vs Cr(VI) values in groundwater

Chromium(VI) concentrations in excess of the European permeable level of 50 µg/L are common in shallow alluvial aquifers in Central Evia, where ultramafic rocks and alkaline and oxic groundwater conditions are well known (Megremi, 2010) and in the Assopos Basin (Tables 4 and 6). Positive $\delta^{53}\text{Cr}$ values of 1.2 and 2.3‰ measured in groundwater having low Cr concentrations, have been attributed to the addition of Cr(VI) that was fractionated on mineral surfaces prior to entering solution and/or to the decrease of the estimated O$_2$ concentrations caused the reduction of Cr(VI) to Cr(III) and subsequently removed from solution (Farkas et al., 2013; Wang et al., 2016). Thus the highest $\delta^{53}\text{Cr}$ values recorded in water from deep wells (Fig. 9), seems to be consistent with those in wells of long flow paths through alluvial aquifers (Izbicki et al., 2008).

Higher Cr(VI) concentrations and lower $\delta^{53}\text{Cr}$ values in aquifers may suggest that either reductive fractionation and removal of Cr(VI) from solution has not occurred, or origin of Cr from a different source and evolution of the $\delta^{53}\text{Cr}$ composition along a different geochemical pathway (Izbicki et al., 2008). The $\delta^{53}\text{Cr}$ values around zero in the water leachates of the Ni-laterites from Kastoria (Table 6) are consistent with the suggestion that only $\delta^{53}\text{Cr}$ values are not necessarily diagnostic of anthropogenic contamination by Cr (Izbicki et al., 2008). In addition, the near zero $\delta^{53}\text{Cr}$
values in the water leachates of the Kastoria Ni-laterites suggesting lack of reductive fractionation and removal of Cr(VI) from solution point to excess of oxidative reagents.

In a comparison of the variation of $\delta^{53}\text{Cr}$ values in groundwater, from Central Europe and California, indicating fractionation, and the Cr isotope compositions of worldwide seawater (Bonnand et al., 2013; Farkas et al., 2013; Economou-Eliopoulos et al., 2014, 2016; Scheiderich et al., 2015; Lelli et al., 2014; Novak et al., 2014; Izbicki et al., 2015) it appears that the groundwater samples from the Evia and Assopos basins fall within the fields of both naturally and anthropogenically contaminated waters (Fig. 10). In particular, the data conforming to those from California (Izbicki et al., 2012), as plotted in Fig. 10, may be helpful in providing clues for the source of potential contamination.

9. Conclusions

The compilation of SEM/EDS results and literature data from a variety of perspectives, including mineralogy, geochemistry, isotopes, leaching experiments on rocks, soils and Ni-laterites from Central Evia and elsewhere, leads us to the following conclusions:

1) Although near zero $\delta^{53}\text{Cr}$ values in groundwater are commonly interpreted as the result of human activities, unfractionated (near zero) $\delta^{53}\text{Cr}$ values in leachates from Ni-laterites of Kastoria suggest that such values are not necessarily diagnostic for anthropogenic sources alone.

2) Mn-(hydr)oxides in excess of potential reductants, and the fine-grained nature of these components in the Kastoria Fe-Ni-laterite ore, may be major controlling factors for the increased release of Cr(VI) into the water leachates of the ore.

3) A positive correlation ($R^2 = 0.514$) between the $\delta^{53}\text{Cr}$ values and depth of the aquifers, may reflect the decrease in soluble O$_2$ with increasing depth.

4) The development of the Kastoria laterite deposit atop parent peridotites, in contrast to those in Evia tectonically emplaced atop a carbonate basement, after a long transportation flow, may support the role of a long distance transportation to explain positively fractioned $\delta^{53}\text{Cr}$ values.

5) The $\delta^{53}\text{Cr}$ values and Cr(VI) concentrations in contaminated water from the Evia and Assopos Basins, are plotted in fields defined by global database for contaminated water by both natural processes and anthropogenic activities, reflecting probably potential contamination sources.
Fig. 7. Plots of the Mn, Fe, and Ca contents versus Cr concentrations in rock and soil leachates (Fig. 7a, b, c); Ca and Mg versus Cr (Fig. 7d, e) concentrations in rock and soil leachates (Fig. 7d, f); Ca content in rocks and soils versus Ca concentration in leachates (Fig. 7f). Data from (Tables 1 and 5).

Fig. 8. Bivariate plot of $\delta^{53}$Cr values in leachates (L) for rocks, soils and laterites from Central Evia (Data from Table 6).

Fig. 9. Bivariate plot of wells depth from central Euboea and W, Mojave (USA) versus their $\delta^{53}$Cr values in water (Data from Table 6; Izbicki et al., 2008).
6) Variation in $\delta^{53}$Cr values versus Cr(VI) concentrations in water from a global database, compiled with geological, mineralogical and geochemical data, may provide a basis for the discrimination of potential contamination sources.

Acknowledgments

The Mayor and the Municipality of Messapia-Dirfis is acknowledged for the financial support of this work (A.K. 70/3/11730). Financial support through the Danish Agency for Science, Technology and Innovation grant number 11-103378 to RF is highly appreciated. We would like to thank Toby Leeper for always maintaining the mass spectrometer in optimal running conditions, and Toni Larsen for help in separation of Cr from the samples. Many thanks are expressed to Prof. Dr. Michael Kersten, Executive Editor and the anonymous reviewers for their constructive criticism and suggestions that improved the manuscript.

References


Chromatography and Innovation grant number 11-103378 to RF is highly appreciated. We would like to thank Toby Leeper for always maintaining the mass spectrometer in optimal running conditions, and Toni Larsen for help in separation of Cr from the samples. Many thanks are expressed to Prof. Dr. Michael Kersten, Executive Editor and the anonymous reviewers for their constructive criticism and suggestions that improved the manuscript.

References


Economou-Eliopoulos, M., Megremi, I., Asatsrou, K., Megremi, I., 2014b. Application of chromium stable isotopes to the evolution of Cr(VI) contamination in soils from the Assopos to Thiva basin and C. Evia (Greece) and potential source(s): Anthropogenic versus natural processes. Geosciences 3, 140–158.