

# Natural presence of hexavalent chromium in spring waters of South-West Mountain Vermion, Greece

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## Abstract

Hexavalent chromium in water occurs as oxoanions that are toxic for plants and animals. Furthermore, they are soluble and extremely mobile under environmental conditions. Chromium in its other common oxidative state ( $\text{Cr}^{+3}$ ) is less toxic and in general immobile. Chromium is found in nature mainly in the  $\text{Cr}^{+3}$  form. However, human activities and natural occurring Mn oxides that can oxidize  $\text{Cr}^{+3}$  to  $\text{Cr}^{+6}$ , increase the concentration of the toxic form of  $\text{Cr}^{+6}$  in nature. The extended worldwide problem of  $\text{Cr}^{+6}$  pollution makes essential the understanding of the oxidation mechanism of  $\text{Cr}^{+3}$  from Mn oxides, for assessing the danger of  $\text{Cr}^{+3}$  oxidation as well as for developing processes to reduce its formation and presence. In this study, the natural occurrence of  $\text{Cr}^{+6}$  was examined in ground and surface waters of the South-West part of mountain Vermion (Kozani, Greece), an area where human activity is absent. The aim is to identify a natural background for  $\text{Cr}^{+6}$  concentration which can assist in legislation limit definition. Results show that in cases of waters exiting ophiolite or water permeable limestone having underlying layers of ophiolitic rocks,  $\text{Cr}^{+6}$  is detected. On the contrary when a thin layer of water impermeable schistolith interposes between limestone and ophiolite, then  $\text{Cr}^{+6}$  is not detected.

**Keywords:** hexavalent chromium, natural occurrence, ophiolite

## 1. Introduction

Hexavalent chromium in water occurs as chromate anions,  $\text{CrO}_4^{2-}$  and dichromate anions,  $\text{Cr}_2\text{O}_7^{2-}$  both toxic for plants and animals. Furthermore, they are soluble and extremely mobile under environmental conditions. Chromium in its other common oxidative state ( $\text{Cr}^{+3}$ ) is less toxic and in general immobile. Chromium is found in nature mainly in the  $\text{Cr}^{+3}$  form. However, human activities and Mn oxides, existing in ophiolitic ultramafic rocks, can oxidize  $\text{Cr}^{+3}$  to  $\text{Cr}^{+6}$ , increasing the concentration of the toxic  $\text{Cr}^{+6}$  in nature (Fendorf, 1995; Ndung'u et al., 2010; Zhong et al., 2015). According to many studies, the oxidation of  $\text{Cr}^{+3}$  to  $\text{Cr}^{+6}$  by  $\text{Mn}^{+4}$  and  $\text{Mn}^{+3}$  oxides takes place at the oxide/water interface of ultramafic rocks. The main ultramafic

minerals that can oxidize  $\text{Cr}^{+3}$ , in varying degrees, are birnessite, hausmannite, romanechite, cryptomelane, manganite, pyrolusite and lithiophorite (Manceau and Charlet, 1992; Weaver and Hochella, 2003; Kim et al., 2002, Eary and Rai, 1987). Oxidation is also depending on the springs' operating mechanism (Soulis, 1985).

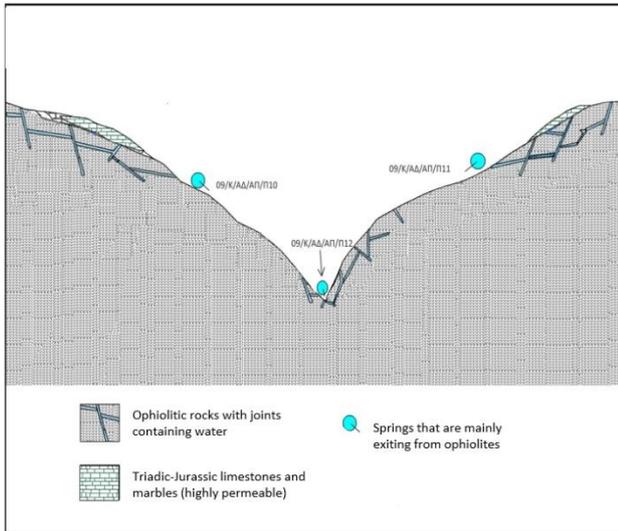
## 2. Study Area- Methodology

The study area, Western Mount Vermion, Greece, belongs geotectonically to the Pelagonian zone and the research is focused on the so-called schistokeratolitic structures with their associated chromium-rich ophiolitic formations of the Jurassic period. In this area, elevated concentrations of hexavalent chromium have been detected in spring waters and geological, hydrogeological and hydrochemical researches were investigated in order to interpret the origin of hexavalent chromium.

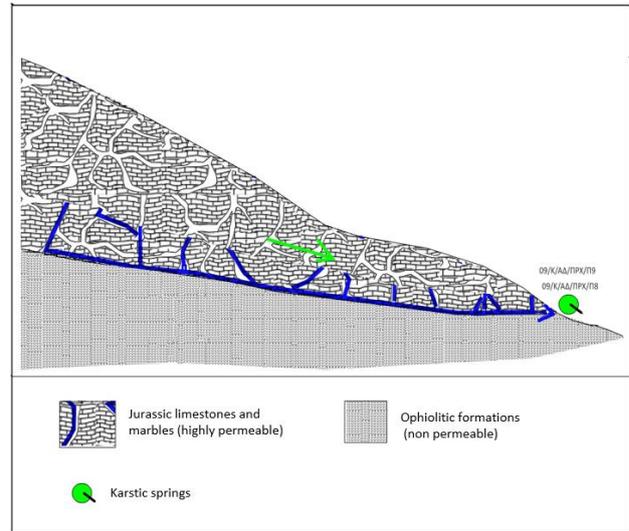
## 3. Results

At eleven springs, the operating mechanism, the feed zone and its relation to the chromium ophiolites were investigated. Four main springs' operating mechanisms are recorded: **a)** Ophiolitic springs in which the groundwater supply zone is the fractured and fragmented ophiolite (saturated with groundwater), with increased concentrations of hexavalent chromium, between 24-50  $\mu\text{g/L}$  (Fig. 1); **b)** Contact springs between the overlying limestones and the underlying impermeable ophiolites, in which the feed zone is the supernatant limestones (karstic springs). In these springs, the precipitation water infiltrates the water-permeable limestone, then follows the surface of the underlying non-permeable rocks and exits between the two rocks as spring with increased concentrations of hexavalent chromium, between 23-32  $\mu\text{g/L}$  (Fig. 2); **c)** Contact springs between the overlying limestones (karstic springs) and the underlying ophiolites with interference between them of an impermeable schistolith layer, preventing the contact of water with the ophiolite, without hexavalent chromium appearance, < 3  $\mu\text{g/L}$  (Fig. 3); **d)** Fracture zone -related small springs on the schistolith surface, preventing the contact of water with the ophiolites, without hexavalent chromium, < 4  $\mu\text{g/L}$  (Fig. 4).

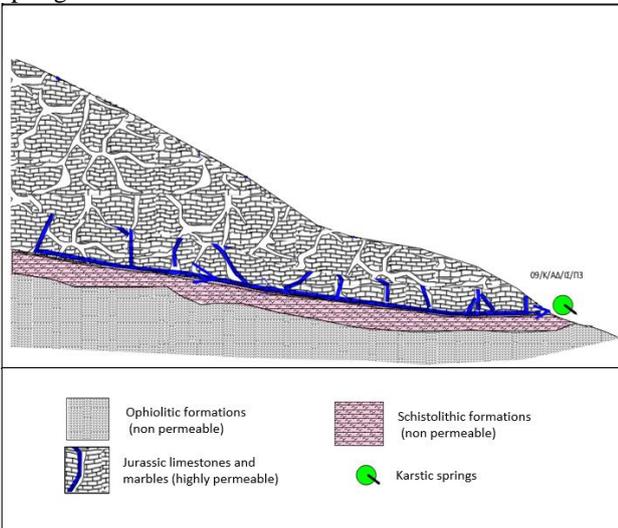




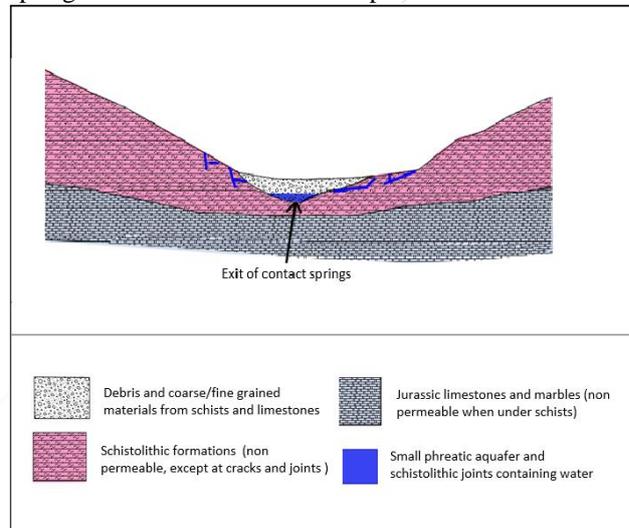
**Figure 1.** Schematic hydrogeological section of ophiolitic springs



**Figure 2.** Schematic hydrogeological section of Karstic springs between limestones and ophiolites



**Figure 3.** Schematic hydrogeological section of Karstic springs between limestones and ophiolites with interference of schists



**Figure 4.** Schematic hydrogeological section of contact springs on the schistolithic surface

#### 4. Conclusions

In all karstic contact springs between the overlying water - permeable limestones and the underlying impermeable ophiolites as well as in all springs with the

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feed zone lied in the ophiolitic formations, elevated concentrations of naturally occurring hexavalent chromium have been detected (23-50  $\mu\text{g/L}$ ).

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