



Upper soil horizons control the rare earth element patterns in shallow groundwater



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ABSTRACT

Several studies dedicated to the aquatic geochemistry of rare earth elements (REEs) have displayed a wide topography-related spatial variability in the REE signatures of shallow groundwater. The aim of this study was to understand the processes leading to this specific REE signature, notably with regard to the size of the Ce anomaly. Soils were sampled in order to encompass the expected topographic variability in the organic carbon (OC)/Fe(Mn) ratio. Leaching experiments were performed with the uppermost horizons of the soil. The REE patterns that developed in the soil leaching solution were similar to the REE patterns for the shallow groundwater collected in this catchment. The negative Ce anomaly evolves in a similar manner according to the topography. This spatial variation is strongly correlated with the soil OC/Fe ratio. For a low OC/Fe ratio, the negative Ce anomaly amplitude in the soil solution is large, whereas a high OC/Fe ratio generates a small or insignificant Ce anomaly. Reductive dissolution experiments using soil with low OC/Fe ratios demonstrated that the REE pattern for soil Fe oxyhydroxides exhibited a positive Ce anomaly and HREE enrichment, indicating a preferential association of these elements with Fe-oxyhydroxides. The rare earth element signature observed in the shallow groundwater is affected by Fe oxyhydroxides present in the upper soil horizons. In contrast, in soil with a high OC/Fe ratio, the REE pattern obtained under reducing conditions did not exhibit any Ce anomaly, suggesting that in the bottomland, the REE signature is affected by the OC content in the uppermost soil. This study highlights the impact of organic matter on the Fe pedofeatures, which control the development of a negative Ce anomaly in shallow groundwater.

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1. Introduction

Numerous studies have been dedicated to understanding the geochemistry of rare earth elements (REEs) in groundwater over the last three decades (Smedley, 1991; Viers et al., 1997; Johannesson et al., 1997, 1999; Johannesson and Hendry, 2000; Braun et al., 1998; Dia et al., 2000; Duncan and Shaw, 2003; Tang and Johannesson, 2005; Pourret et al., 2010). Rare earth elements have coherent physical and chemical properties which make them sensitive tracers of water–rock interactions and groundwater mixing. Nowadays, several important aspects of the REE geochemistry in groundwater are fairly well understood, including the role of pH with regard to the REE concentrations, the role of organic ligands in REE speciation and REE transfer, and the processes involved in the development of negative Ce anomalies (Smedley, 1991; Braun et al., 1998; Dia et al., 2000; Pourret et al., 2010). Many groundwater areas exhibit a negative Ce anomaly which has been demonstrated to be a consequence of Ce removal in response to the oxidation of Ce(III) into Ce(IV). One of the processes by which Ce(III) is oxidized into Ce(IV) and removed from the groundwater is the so-called “oxidative scavenging” by Fe and Mn oxides (e.g.

Koepfenkastro and De Carlo, 1992; De Carlo et al., 1998; Bau, 1999; Ohta and Kawabe, 2001; Davranche et al., 2005). The oxidative scavenging mechanism may be regarded as a three-stage process consisting of (i) an initial sorption of REE, including Ce(III), onto Mn and Fe oxyhydroxides, (ii) an oxidation of part of the adsorbed Ce(III) into Ce(IV), and finally (iii) a preferential desorption of the remaining Ce(III) and all other REE(III) as compared to Ce(IV) (Bau, 1999). Cerium oxidation can occur abiotically through the oxidative scavenging of dissolved Ce(III), as well as biotically, where the bacteria directly oxidize Ce(III) into Ce(IV), or catalyze the oxidation of Mn(II) into Mn(IV), which itself abiotically oxidizes Ce(III) (Moffett, 1990; Ohnuki et al., 2008; Tanaka et al., 2010).

However, one essential feature of the REE geochemistry in groundwater that remains partly unexplained is the origin and significance of the systematic, topography-related variation in the Ce anomaly that occurs worldwide in many shallow groundwater areas (e.g. Braun et al., 1998; Gruau et al., 2004; Pourret et al., 2010). In these shallow groundwater areas, the same progressive disappearance of the negative Ce anomaly is observed from the top to the bottom of the catchment. The lack of a Ce anomaly in bottomland groundwater is likely to be an effect of the input of soil-derived groundwater in which REE are bound to organic colloids that do not display a Ce anomaly (Viers et al., 1997; Dia et al., 2000; Pourret et al., 2007). The amount of organic colloids in

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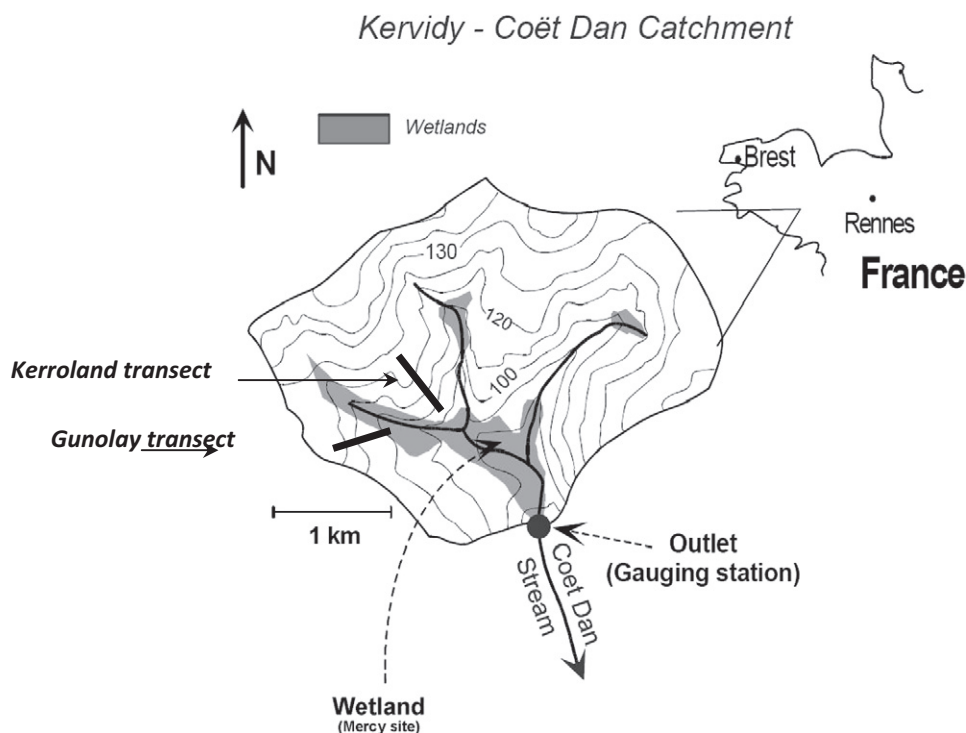


Fig. 1. Sketch showing the topography, channel network geometry, location of the Kervidy/Coët-Dan catchment.

shallow groundwater increases downhill due to the decrease in the distance between the water table and the uppermost organic-rich soil horizons (Pourret et al., 2010). The binding of REE by the organic colloids in the soil solution suppresses the oxidative-scavenging of Ce by Fe and Mn oxyhydroxides (Davranche et al., 2004, 2005, 2008). The distance between the soil organic-rich horizons and the water table downhill and the increased flux of organic colloids entering into the groundwater are therefore the major controls of the insignificant amount or the lack of a negative Ce anomaly (Pourret et al., 2010). A question then arises: do all of the topographic gradients observed in the Ce anomaly development have a shallow origin? More specifically, is the origin of the negative Ce anomaly found in uphill groundwater coming from the upper soil horizons? These questions are worth examining to the extent that the composition of the soils evolves with the topography. Soils in bottomland domains are expected to be Fe- and Mn-depleted but enriched in organic matter (OM) as compared to their uphill equivalents (Walter and Curmi, 1998). This results from differences in moisture and the redox conditions in bottomland soils, as compared to the well-drained and permanently oxidized uphill soils (Riou, 1999). Therefore, the organic carbon (OC)/Fe(Mn) ratio in soils decreases from uphill to the bottomland. Thus, the major source of dissolved REE in the uphill soil solution is probably mineral surfaces, leading to the possible development of Ce oxidative scavenging. Should this be the case, soil water in uphill domains may exhibit a negative Ce anomaly, the amplitude of which may be closely linked to the soil OC/Fe(Mn) ratio. If so, the topography-related variation of Ce anomaly observed in shallow groundwater could have a surficial origin.

In this study, we explored the possibility of a Ce anomaly variability with a fully surficial origin by conducting percolation experiments and reductive dissolution experiments on soils relative to a toposequence (Kervidy/Coët-Dan catchment, France). This catchment provides a typical example of shallow groundwater that exhibits the characteristic Ce anomaly topographic variations. Soils were sampled in order to encompass the expected topographic variability in the OC/Fe(Mn) ratio. The aims of this study were to (i) experimentally investigate whether or not the variations in the upper soil horizon composition along the toposequence, and notably in the OC/Fe(Mn) ratio, are likely to generate

variations in the Ce anomaly development in the groundwater recharge waters, (ii) discern the key factors controlling the development of a Ce anomaly in soil solutions, and (iii) identify the source of the REE signature variability in shallow groundwater.

2. Materials and methods

2.1. Site description

Soil samples were collected in the Kervidy/Coët-Dan catchment (north-western France) from the Kerroland and Gunolay transects in January 2008 (Fig. 1). The region is marked by a humid temperate climate with a mean annual rainfall of 909 mm. The Kervidy/Coët-Dan is a part of the regional observatory (ORE) AgrHyS dedicated to the study of the effects of intensive agriculture on water quality (Molénat et al., 2008 and references therein). The bedrock is constituted of fissured and fractured upper Proterozoic schists (Dabard et al., 1996). Detailed information about soils and prevailing hydrogeochemistry can be found elsewhere (Mérot et al., 1995; Durand and Juan Torres, 1996; Curmi et al., 1998; Dia et al., 2000; Molénat et al., 2002; Pourret et al., 2010).

2.1.1. Soil samples

The soils are developed from loamy material and eolian Quaternary deposits. They are locally dominated by silt, clay or sandstone materials (Pellerin and Van Vliet-Lanoë, 1998). A large number of secondary mineral phases including illite, smectite, kaolinite, various Fe oxides and Fe oxyhydroxides and Mn oxides can be observed in the soil horizons (Pauwels et al., 1998). With regard to the topography, soils are well-drained Dystric Cambisols and Luvisols (Dystrichrepts and Alfisols respectively, USDA Soil Taxonomy) from the upland to the bottomland areas. Epistagnic Luvisols and Epistagnic Albeluvisols (Aqualfs, USDA Soil Taxonomy) are also developed in the poorly-drained domains, in which Mn and Fe-oxyhydroxides are depleted due to seasonal waterlogging by the rising groundwater.

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