Chemical condition for the appearance of a negative Ce anomaly in stream waters and groundwaters

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Nine publications showing REE data in groundwaters and river water were examined to understand the general condition of terrestrial water where a negative Ce anomaly develops. It was found that the negative Ce anomaly only appeared when Fe, Mn and dissolved organic carbon (DOC) concentrations were low (Fe and Mn $< 5 \times 10^{-5}$ mol/L and DOC < 10 mg/L). Assuming that Ce^{3+} and Fe^{2+} concentrations were limited by the formation of cerianite and ferrihydrite, respective redox potential (Eh) was calculated from each of Ce^{3+} and Fe^{2+} concentrations. For data sets displaying Ce anomalies, the calculated Ehs (*cEh*s) showed a 1:1 relationship between Ce and Fe. This relationship indicates that the absolute concentration of Ce in natural water may be thermodynamically determined *in situ* by Eh and pH when concentrations of Fe, Mn and DOC are poor.

INTRODUCTION

The distribution of rare earth elements (REEs) in waters has been mostly used as an index of water/rock interaction processes or as a hydrological tracer due to the improvement of suitable analytical techniques during recent decades (Hall *et al.*, 1995). Ample evidence has been already provided to show that REEs could be significantly mobilized during weathering, alteration and diagenesis processes (Hellman and Henderson, 1977; Nesbitt, 1979; Ward, 1986; Wood, 1990) and chemical weathering reactions leads to extensive fractionation in REE composition among river waters, continental rocks and river suspended particles (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990; Sholkovitz, 1993, 1995).

Cerium often behaves differently from the neighboring REEs due to its low ionization potential of Ce^{3+}. The value of the Ce fraction relative to neighboring trivalent REEs (La and Pr) is termed the "*Ce anomaly*" and is defined as

$$\text{Ce anomaly} = \frac{(\text{Ce})_n}{\text{Ce}*} = \frac{(\text{Ce})_n}{\sqrt{(\text{La})_n (\text{Pr})_n}} \qquad (1)$$

where $(\text{Ln})_n$ is a normalized concentration of a lanthanide element, Ln.

Anomalies of Ce have been of particular interest following the anomaly's potential use as an indicator of water/rock interaction processes or as a hydrological tracer. Previous investigations have shown that fresh water, especially groundwater, exhibits REE patterns that closely resemble those of the rocks through which they have flowed (Smedley, 1991). Patino *et al.* (2003) indicated that a negative Ce anomaly could develop in corestones during spheroidal weathering of basalts due to immobilization of Ce^{4+} compared to other trivalent REEs, implying that the negative Ce anomaly may be a source related feature. However, other processes are important in constraining the appearances of Ce anomaly in fresh water. The removal of Ce may occur either as a result of CeO_2 precipitation (Braun *et al.*, 1998), or oxidative scavenging of Ce(IV) on the surface of Fe and Mn oxyhydroxides (De Carlo *et al.*, 1998; Bau, 1999; Ohta and Kawabe, 2001). Furthermore, Moffett (1990) showed that the Ce(III) oxidation in seawater might be mediated by surface catalysis and microbial activity. Therefore, the Ce anomaly may be related to weathering, inorganic aquatic processes, or biological mediation.

In this study, we compiled some REE datasets in fresh water from the nine publications listed in Table 1. Using these datasets, we reviewed the necessary conditions of terrestrial water, which shows negative Ce anomalies. We then examined how the Ce anomaly develops under such conditions. In conclusion, we suggest that the Ce anomaly appears due to Ce^{3+}/CeO_2 equilibrium in the absence of organic matter.

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Reference	Water sample	Filter	Referred item
Smedley (1991)	Groundwater	0.45 μm	Ce, Fe, pH, HCO$_3$, SO$_4$
Dupré *et al.* (1996)	River water	0.2 μm	Ce, Fe, pH, HCO$_3$, SO$_4$
Gaillardet *et al.* (1997)	River water	0.2 μm	Ce, Fe, pH, HCO$_3$, SO$_4$
Braun *et al.* (1998)	Groundwater	0.45 μm	Ce, Fe, pH, HCO$_3$, SO$_4$
Dia *et al.* (2000)	Groundwater	0.22 μm	Ce, Fe, Mn, pH, Eh, HCO$_3$, SO$_4$, DOC
Nakajima and Terakado (2003)	River and Groundwater	0.45 μm	Ce, Fe, Mn, pH, HCO$_3$, SO$_4$
Otsuka and Terakado (2003)	Groundwater	0.45 μm	Ce, Fe, Mn, pH, HCO$_3$, SO$_4$
Johannesson *et al.* (2004)	Surface water	0.45 μm	Ce, pH, HCO$_3$, SO$_4$, DOC
Gruau *et al.* (2004)	Groundwater	0.22 μm	Ce, Fe, Mn, pH, Eh, HCO$_3$, SO$_4$, DOC

DATA SOURCE DESCRIPTION

The data discussed in this paper are cited from nine publications (Table 1): Three references to riverwater (Dupré *et al.*, 1996; Gaillardet *et al.*, 1997; Nakajima and Terakado, 2003), five references to groundwater (Smedley, 1991; Braun *et al.*, 1998; Dia *et al.*, 2000; Otsuka and Terakado, 2003; Gruau *et al.*, 2004) and one reference to swamp water (Johannesson *et al.*, 2004). The nine publications cover most typical terrestrial waters ranging from a low (Dupré *et al.*, 1996; Gaillardet *et al.*, 1997) to high latitude (Dia *et al.*, 2000; Gruau *et al.*, 2004). For the data source descriptions, the reports and references therein are referred to.

Smedley (1991) investigated shallow groundwater samples from the Carnmenellis area, Cornwall, southwest England. Carnmenellis, at 252 m, is the highest point in an area, which has a windswept landscape with patches of moorland and is generally devoid of tree. The average annual temperature for most of Cornwall is about 10°C with slightly lower temperatures at higher altitude (http://www.metoffice.gov.uk/climate/uk/). The area includes the Carnmenellis granite and the immediately surrounding metasedimentary rocks (and some metabasite). 0.45 μm filtered samples were collected from shallow wells, boreholes, streams, and adits under low-flow conditions, during the autumn of 1988.

The area Dupré *et al.* (1996) surveyed is the Congo Basin in Central Africa, which is dominated by rain forests of high productivity and arborescent savannahs and the basin is submitted to a wet tropical climate that constantly experiences precipitation higher than 1500 mm/yr and temperatures above 25°C. Geologically, the central plain consists of Mesozoic sedimentary rocks and is bordered by Upper Proterozoic basement, composed of crystalline and metamorphic rocks associated with a shale-limestone system with a stratigraphic age of 900 Ma. The samples were collected from the Congo River and its tributaries between Bangui (Central African Republic) and Brazzaville (People's Republic of Congo) during the high water stage. Dissolved and suspended phases were isolated immediately after collection by filtration through 0.2 μm filters.

The Amazon River and its main tributaries in Brazil were studied by Gaillardet *et al.* (1997) and were sampled during the high water stage of May 1989. This basin is covered by tropical rainforests and savannas. These highly productive ecosystems benefit from high rainfall (2000–2300 mm/yr) and high mean temperature (25°C). The Amazon Basin can be divided in four major morphostructural units and be composed of different lithologic characters (see Gaillardet *et al.* (1997) and literature referred to there). Samples were filtered on site through 0.2 μm filters.

Braun *et al.* (1998) investigated groundwater in a lateritic soil cover in relation to a closed hydrographical system at Goyoum (East Cameroon). The region corresponds to the transition vegetation zone between rainforest and savannah. The altitude is between 600 and 700 m. At Goyoum, the subequatorial climate is characterized by the alternation between two wet and two dry seasons of variable intensity. The mean annual air temperature is about 24°C. In normal hydrological years, the mean annual rainfall is 1660 mm. The soils are developed on a gneissic basement belonging to the Upper Proterozoic Basal Complex (Bessoles and Lasserre, 1977). The 0.45 μm filtered samples were collected at different points of the hydrographical system and in groudwaers.

Dia *et al.* (2000) studied fourteen well water samples and one spring located along two transects set up in a catchment from Western Europe (Kervidy/Coët-Dan catchment, France). The elevation range of the Kervidy/Coët-Dan catchment is between 93 and 135 m and gentle slopes predominate. The land use in the catchment is intensive farming, which has caused heavy nitrate pollution of the waters of this catchment. The scale of the catch-

ment is recognized by two hydrologically contrasted domains: (i) the hill-slope domain which comprises well-drained soils and where infiltration is dominant; and (ii) the bottomland which comprises waterlogged soils. The climate is humid temperate with a mean annual rainfall of 909 mm. The bedrock is made of fissured and fractured upper Proterozoic schists. The samples used for determination of dissolved trace element and dissolved organic matter (DOC) concentrations were filtered on site using 0.22 μm filters.

Nakajima and Terakado (2003) analyzed ten stream waters and one groundwater from the Rokko granite area, Japan. The elevation range of the study site is between 200 and 600 m. Annual precipitation at Rokko Mountains is between 1200 to 1400 mm, and the mean annual temperature in the region varies between 10 and 15°C. The rocks and sediments in these sites were composed of the Rokko granite, which was a fine to coarse grained biotite granite of Mesozoic era. The water samples were immediately filtered through a 0.45 μm membrane filters.

The samples Otsuka and Terakado (2003) investigated were groundwaters from the southern Nishinomiya district near the sites of Nakajima and Terakado (2003). The alluvial plain on which the urban areas of Nishinomiya and neighboring cities lie is located in the southeast of the Rokko Mountains. This groundwater is characterized by its high PO_4 and low Fe concentrations. All the water samples were filtered through a 0.45 μm filters.

The water samples Johannesson *et al.* (2004) studied were from the Great Dismal Swamp in southeastern Virginia and northeastern North Carolina, USA. The study focused on Lake Drummond (and its watershed), which is a shallow (~2 m deep), blackwater lake located in the northern, Virginian section of the swamp. The samples are from its principal surface outflow waters. Annual precipitation at Lake Drummond is 1280 mm, and the mean annual temperature in the region varies between 15 and 15.4°C. Each water sample was immediately filtered on site using 0.45 μm filters.

A small cathment in Western France (Petit Hermitage catchment) was studied by Gruau *et al.* (2004). The Le Home toposequence belongs to the Petit Hermitage Catchment, a fourth-order stream drainage basin located roughly 350 km west Paris, France. The land use is intensive farming dominated by crops and grass fields. The recognition of two distinct groups of waters based on their spatial location: (i) DOC-poor groundwater flowing below the hillslope domains; (ii) DOC-rich groundwater from the wetland domains, close to the river network. Annual precipitation at the region is 850 mm, and the mean annual temperature is 11°C. The bedrock comprises altered Upper Proterozoic schist. The waters were filtered on site using 0.22 μm filters.

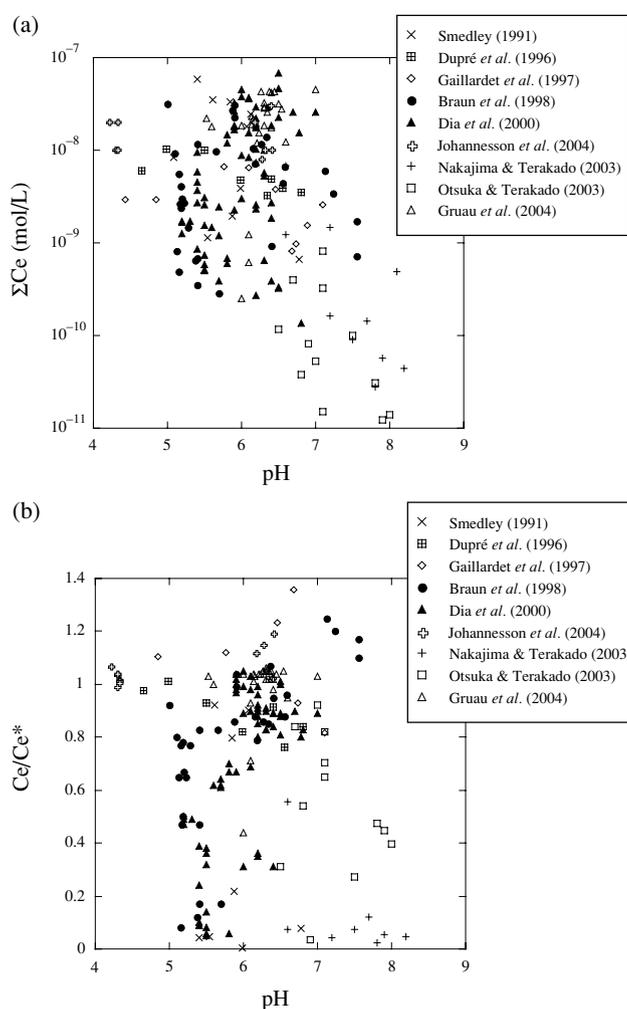*Fig. 1. Relationships between pH and (a) the concentration of ΣCe and (b) Ce anomaly (calculated from Eq. (1)) for the data sets from the 9 publications listed in Table 1.*

DISCUSSION

Effect of pH

Figures 1(a) and (b) show the observed values of ΣCe and the Ce anomaly against pH conditions, respectively. Ce data cited here are assumed to be the sum of (i) free Ce^{3+}, (ii) Ce(III) or Ce(IV) complexes with inorganic ions (e.g., HCO_3^- and OH^-) or dissolved organic matter, and (iii) small Ce particulates adsorbed on to organic colloids. It has been demonstrated that samples filtered with 0.45 and 0.22 μm filters included not only truly dissolved REE but also small particulate or colloidal phases (Lawrence and Kamber, 2006; Lawrence *et al.*, 2006; Pourret *et al.*, 2007a, b). We use here the term "ΣCe" as Ce that passes through the filters employed for each sampling, i.e., its truly dissolved, small particulate, and colloidal phases and the term "Ce^{3+}" as Ce concentration excluding the con-
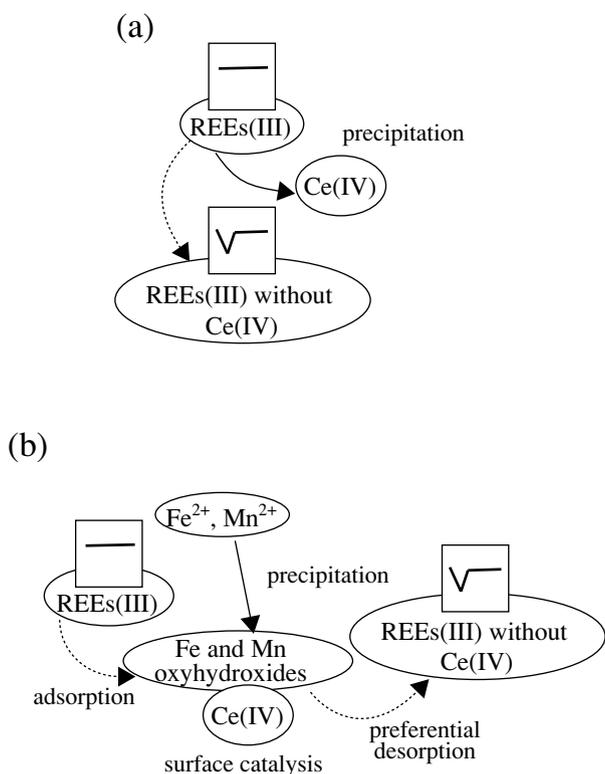
(a)

(b)

Fig. 2. Conceptual diagrams illustrating (a) independent precipitation of Ce and (b) oxidative scavenging of Ce.

tributions of inorganic ligands (see Appendix), although it does not actually mean the free Ce^{3+}.

The concentration of ΣCe roughly increases as pH decreases (Fig. 1(a)), implying that the absolute abundance of Ce is globally controlled by pH condition. This is consistent with previous studies, which revealed that the REEs, especially LREEs, dissolved concentrations decreased with increasing pH (Goldstein and Jacobsen, 1988; Byrne and Sholkovitz, 1996; Dupré et al., 1996; Gaillardet et al., 1997; Johannesson and Burdige, 2007).

By contrast, there is no overall relationship between Ce anomaly and pH. Deep negative Ce anomalies (<0.6) have been measured in 5 aquifers (Smedley, 1991; Braun et al., 1998; Dia et al., 2000; Nakajima and Terakado, 2003; Otsuka and Terakado, 2003). Smedley (1991) suggested that those observed in the groundwaters that flood the metasediments from the Carmenellis region mirror the trends observed in their host-rocks and appear to be inherited from them by water-rock interaction involving chiefly REE enriched minerals. Alternatively, the anomaly has been interpreted as due to the selective removal of Ce from the waters by means of secondary cerianite (CeO_2) precipitation (Braun et al., 1998; Dia et al., 2000; Nakajima and Terakado, 2003; Otsuka and Terakado, 2003). We examine the condition in which negative Ce anomaly can develop by Ce(III) oxidation and fractionation using existing data sets.
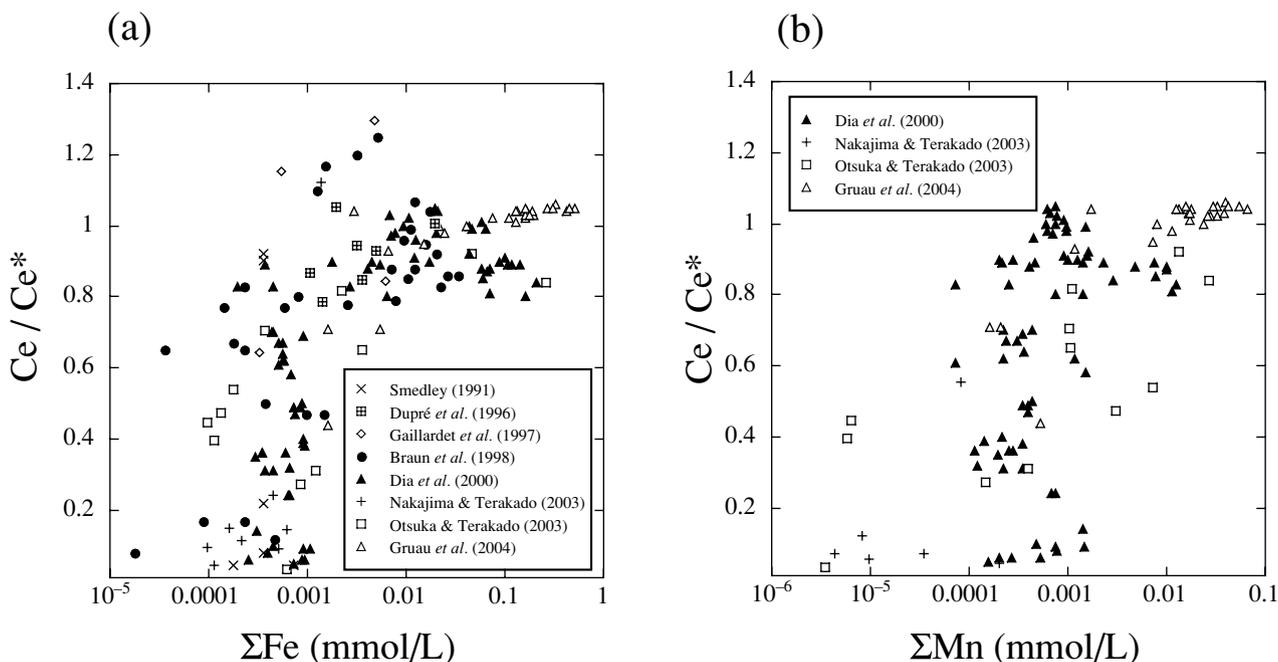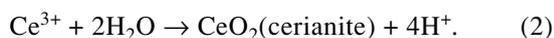

Fig. 3. Relationships between Ce anomaly and the concentrations of (a) ΣFe and (c) ΣMn for the data sets from the 9 publications listed in Table 1.

Relationship between Ce anomaly and Fe, Mn and DOC

Two possible reactions have been considered to lead to Ce oxidation and fractionation (Fig. 2). The first is described in Braun *et al*. (1990) (see Fig. 2(a)):

$$Ce^{3+} + 2H_2O \rightarrow CeO_2(cerianite) + 4H^+. \quad (2)$$

The reaction strongly depends on *in situ* Eh-pH condition and easily proceeds in the usual stream waters (Akagi and Masuda, 1998).

The second is the "oxidative scavenging" that is composed of three-stage process (Bau, 1999) (see Fig. 2(b)): (i) an initial sorption of Ce(III) together with the other REEs(III) onto Mn and Fe oxyhydroxides, followed by (ii) Ce oxidation due to surface catalysis on Mn (hydr)oxides (Koppenkastrop and De Carlo, 1992; Koppi *et al*., 1996) and Fe oxyhydroxides (Bau, 1999; Ohta and Kawabe, 2001), e.g.,

$$Ce^{3+} + MnOOH \rightarrow CeO_2(cerianite) + Mn^{2+} + 4H^+ \quad (3)$$
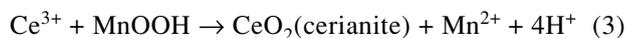
and (iii) the preferential desorption of REEs (III) including Ce(III) over Ce(IV).

We first examined contributions of Fe and Mn to the appearance of Ce anomaly. The concentrations of Fe were reported in 8 publications (Smedley, 1991; Dupré *et al*., 1996; Gaillardet *et al*., 1997; Braun *et al*., 1998; Dia *et al*., 2000; Nakajima and Terakado, 2003; Otsuka and Terakado, 2003; Gruau *et al*., 2004), Mn in 4 publications (Dia *et al*., 2000; Nakajima and Terakado, 2003; Otsuka and Terakado, 2003; Gruau *et al*., 2004).

Figures 3(a) and (b) display the relationships between the extent of Ce anomaly and the concentrations of ΣFe and ΣMn. The terms "ΣFe" and "ΣMn" are here defined as the same as ΣCe, consisting of both colloidal and dissolved fractions of respective elements. It is clear that the negative Ce anomaly develops when ΣFe and ΣMn concentrations are low (ΣFe and ΣMn $< 5 \times 10^{-5}$ mol/L), implying that Ce anomaly may not reflect the REE patterns of parental rocks but rather reflect the extent of Ce(III) oxidation. This could result both (i) from "independent" precipitations of Ce(IV) from Fe(III) or Mn(IV) precipitation, reflecting *in situ* pH-Eh condition and (ii) from the oxidative scavenging of Ce with Fe and Mn oxyhydroxides. It will be again discussed in the following section.

Dia *et al*. (2000) and Gruau *et al*. (2004) explained the lack of Ce anomaly at high concentrations of Fe(II) and Mn(II) has something to do with the presence of organic compounds. They mentioned that Eh decreases coincided with increases of dissolved organic carbon (DOC), and Mn and Fe concentrations. They proposed two hypotheses to explain the absence of a negative Ce anomaly at a high DOC concentration. The first hypothesis is that
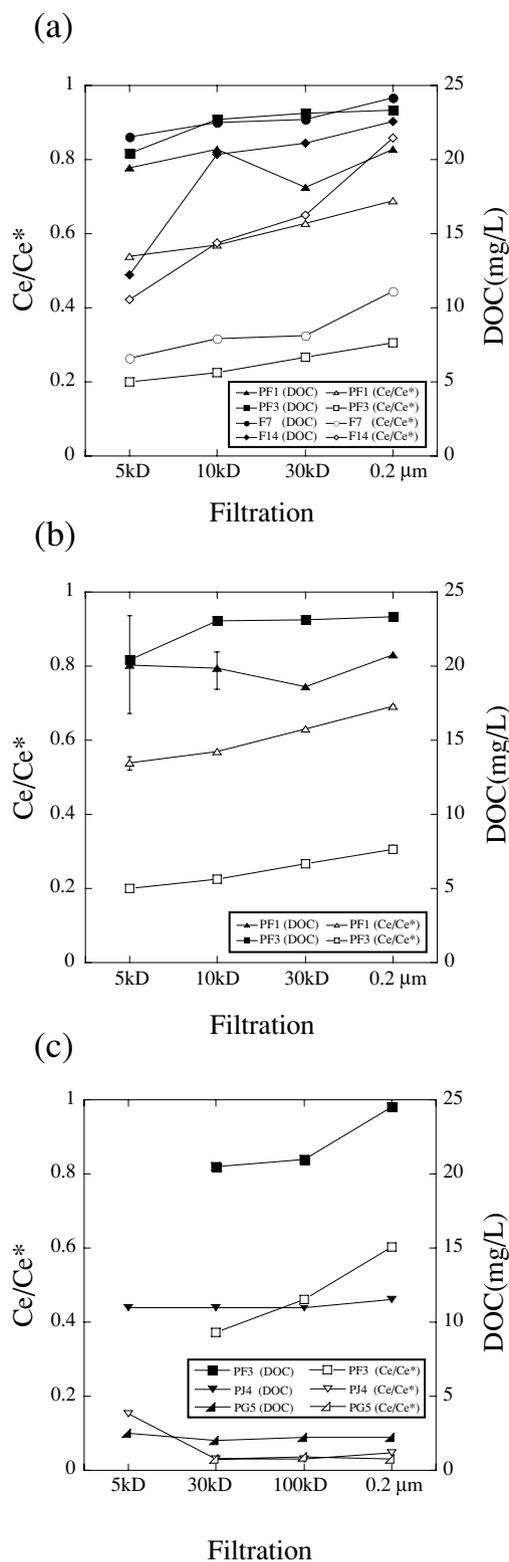

Fig. 4. Ce anomaly and DOC concentrations of filtrates using the data reported by Dia et al. (2000) (a), Pourret et al. (2007a) (b) and Pourret et al. (2007b) (c).
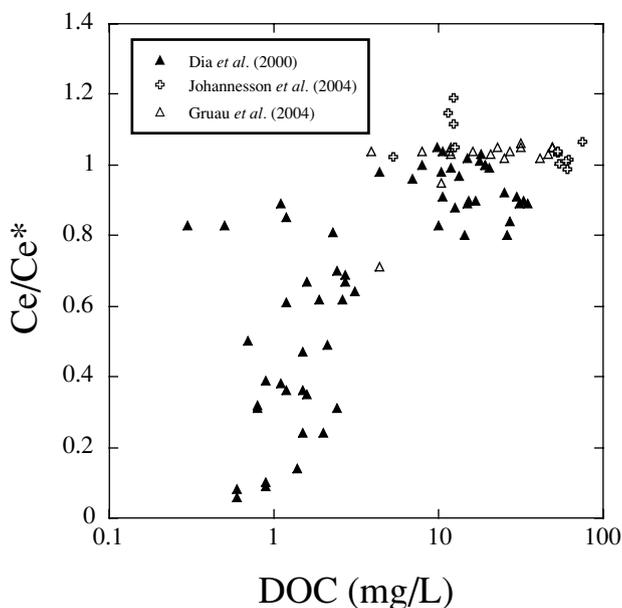
Fig. 5. Relationships between Ce anomaly and the DOC concentration for the data sets from the 3 publications listed in Table 1.

cerianite precipitation becomes impossible because of stabilization of Ce^{4+} (as other REE^{3+}) by complexation with organic matter. It has been considered that REE complexation with organic matter could diminish negative Ce anomalies (Davranche *et al.*, 2004, 2005). Recent experimental and modeling works have revealed that REE-HS (humic substance) complexes predominantly occur in natural water especially at pH from 6 to 10 (Tang and Johannesson, 2003; Sonke and Salters, 2006; Pourret *et al.*, 2007a, c; Stern *et al.*, 2007).

The second hypothesis is that cerianite is adsorbed onto colloids being then measured as a part of the solutions. Ultrafiltration experiments for the samples taken from the sites reported that a part of the REEs was controlled by the colloidal fraction (Dia *et al.*, 2000; Pourret *et al.*, 2007a, b). Figures 4(a), (b) and (c) show Ce/Ce* and DOC concentrations of filtrates using the data reported by Dia *et al.* (2000) and Pourret *et al.* (2007a, b). For the organic-rich sites (PF1, PF3, F7, F14), the Ce/Ce* of the filtrates decreased as the pore size of filters was smaller, implying that Ce(IV) complexed and/or adsorbed onto the organic and partly inorganic colloids (Figs. 4(a) and (b)). By contrast, the Ce anomaly and DOC concentration were independent of pore size for the organic-poor sites (PJ4, PG5) (Fig. 4(c)). This suggests that the colloidal and dissolved organic matter cannot diminish the Ce anomaly when DOC concentration is low (<10 mg/L). In a such case REEs might be predominantly affected by other factors and be approximated as a dis-

solved fraction.

Figure 5 displays the relationships between the extent of Ce anomaly and the concentration of DOC reported by Dia *et al.* (2000), Gruau *et al.* (2004) and Johannesson *et al.* (2004). No Ce anomaly is seen for all the sites at which DOC > 10 mg/L, whereas it sometimes develops at the sites of DOC < 10 mg/L. It implies that Ce cannot be considered as a good tracer of redox conditions in organic-rich waters as previously suggested by Dia *et al.* (2000), but may be used as it in organic-poor conditions.

Relationship between a Ce anomaly and redox condition

Ce anomaly may indicate *in situ* redox conditions both (i) by Ce^{3+}/CeO_2 reaction and (ii) by oxidative scavenging of Ce by Fe and Mn oxyhydroxides. As demonstrated by Akagi and Masuda (1998), assuming simply that cerianite (CeO_2) is a unique species of Ce(IV) in the water system and that the activity of solid phase is unity, the maximum activity of Ce^{3+} can be written as function of Eh and pH as follows.

$$Ce^{3+} + 2H_2O = CeO_2 + 4H^+ + e^- \qquad K = 10^{-21.32} \qquad (4)$$
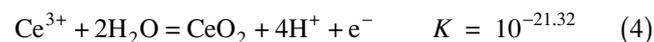
$$cCe^{3+} = 10^{\left(-4pH - \frac{F(Eh - E^\circ)}{2.3RT}\right)} \qquad E^\circ = 1.258V \qquad (5)$$

where the prefix "c" means that the calculated value of Ce^{3+} from Eh and pH. The equilibrium constant K is from Schumm *et al.* (1973) (Table 2) and then E° is calculated. We can understand whether chemical thermodynamics determined the behavior of Ce by comparing the concentrations of Ce(III) and cCe^{3+}. All the data sets we examined had pH data, but only two publications (Dia *et al.*,
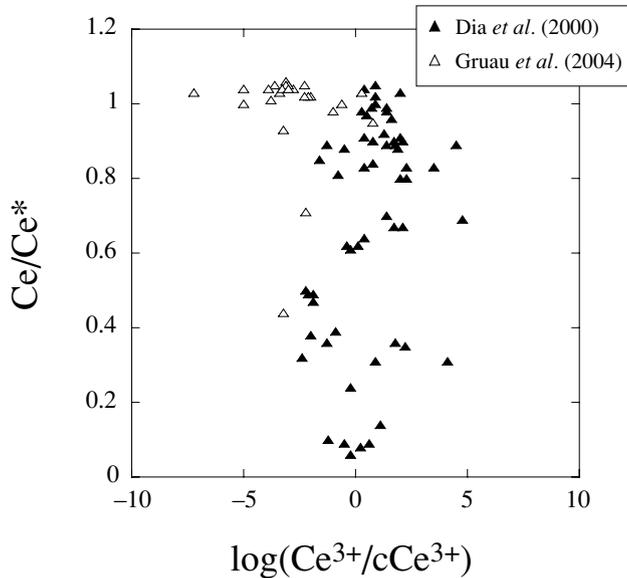
Fig. 6. Ce anomaly vs. Ce^{3+}/cCe plot using the data reported by Dia et al. (2000) and Gruau et al. (2004) illustrating better consistency of actual and calculated Ce concentrations as Ce anomaly becomes deeper.

2000; Gruau *et al*., 2004) showed Eh data. The Eh values reported by Dia *et al*. (2000) ranged 250 mV to 550 mV, while by Gruau *et al*. (2004) ranged 150 mV to 400 mV. Figure 6 shows Ce anomalies plotted against Ce^{3+}/cCe, which is an indicator whether Ce^{3+} is saturated or not when all the assumptions introduced are appropriate, with the calculated data from two publications (Dia *et al*., 2000; Gruau *et al*., 2004). The ratio is an indicator of the discrepancy from the equilibrium of the reaction expressed in Eq. (2) and, when it is unity, the system may be at equilibrium. The value of Ce^{3+}/cCe tends to become 1 as Ce anomaly becomes more negative, while the value widely scatters as negative Ce anomaly disappears. The accurate measurement of Eh in natural water is normally difficult (Bartlett, 1999). When the inaccuracy of Eh values is discounted, these results may imply the following. The concentration of Ce^{3+} may be determined more strictly by the Ce^{3+}/CeO_2 equilibrium when the deeper negative Ce anomaly appears; organic matter, however, might govern the Ce^{3+} concentration when there is no Ce anomaly.

To debate the relationship between negative Ce anomaly and redox condition for all data sets, we indirectly calculated Eh using Eq. (6), which is derived from Eq. (5), assuming the Ce^{3+}/CeO_2 equilibrium.

$$cEh\left(pH, Ce^{3+}\right) = E° - \frac{2.3RT}{F}\left(4pH - \log\left[Ce^{3+}\right]\right)$$
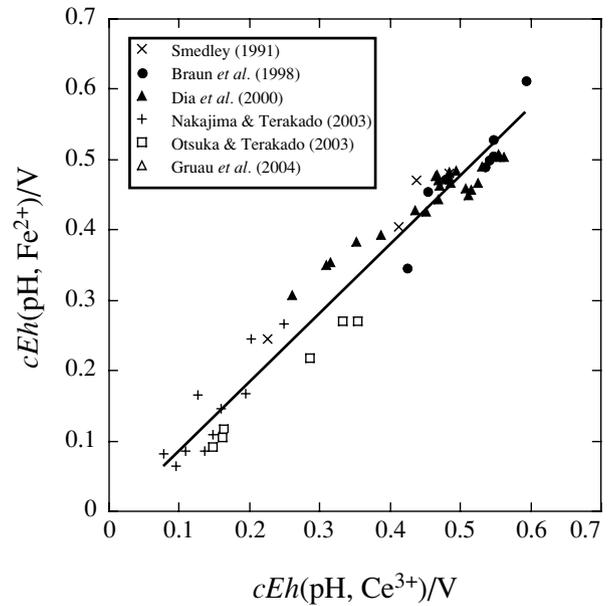$$E° = 1.258V. \quad (6)$$

Fig. 7. Relationship between $cEh(pH, Ce^{3+})$ and $cEh(pH, Fe^{2+})$ for data set showing sharpe negative Ce anomaly ($Ce/Ce^* < 0.6$). The lower cEh corresponds to the higher concentration of Ce or Fe, whereas the higher cEh corresponds to the lower concentration of Ce or Fe. The solid line shows a regression line for all data: $cEh(pH, Ce^{3+}) = 0.976 \ cEh(pH, Fe^{2+}) - 0.012$, $r^2 = 0.95$.

Furthermore, assuming at a low Fe concentration that Fe is in equilibrium following $Fe^{2+}/Fe(OH)_3(am)$ reaction (Eq. (7)), Eh can also be calculated in a similar manner to $cEh(pH, Ce^{3+})$ using Eq. (8).

$$Fe^{2+} + 3H_2O = Fe(OH)_3(am) + 3H^+ + e^-$$
$$K = 10^{-25.59} \quad (7)$$
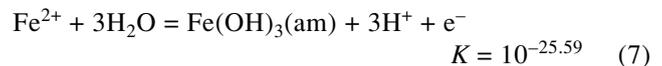
$$cEh\left(pH, Fe^{2+}\right) = E° - \frac{2.3RT}{F}\left(3pH - \log\left[Fe^{2+}\right]\right)$$
$$E° = 1.065V. \quad (8)$$

The equilibrium constant K and the standard redox potential $E°$ are from Langmuir (1997) (Table 2). If the slope ($cEh(pH, Fe^{2+})/cEh(pH, Ce^{3+})$) = 1, the concentrations of Fe^{2+} and Ce^{3+} are determined by *in situ* pH and Eh with the assumed equilibrium $Fe^{2+}/Fe(OH)_3(am)$ and Ce^{3+}/CeO_2, respectively. Whereas, if cEhs depend more on pH (one of the explanatory variables), in other words, the concentrations of Ce and Fe are independent of Eh, the slope would be close to 1.33. Ce oxidation or scavenging of Ce is considered to take place during the initial precipitation of iron, where amorphous $Fe(OH)_3$ is a major phase. FeOOH is a stable solid phase, which must be considered in the case of the dissolution process of iron.

Chemical condition for the appearance of Ce anomaly   377

Here, the FeOOH phase has not been considered, as we are not looking at the reaction associated with the dissolution of iron ions. Iron carbonate species have also not been considered. The stability constant of $FeCO_3$ reported by Langmuir (1997) indicates the carbonate phase can be important only when pH is greater than 7.5. Such high pHs are not seen in the data we cited except for one ground water sampled in Japan (Nakajima and Terakado, 2003; Otsuka and Terakado, 2003).

Figure 7 shows the relationship between cEh(pH, Ce^{3+}) and cEh(pH, Fe^{2+}) when only data displaying deep negative Ce anomalies (Ce/Ce* < 0.6) are considered. The slope of the regression line is almost 1 (cEh(pH, Ce^{3+}) = 0.976 cEh(pH, Fe^{2+}) − 0.01, r^2 = 0.95), implying that solubilities of both Ce and Fe in waters similarly reflected pH and Eh of the waters. It should be noted that the intercept of the regression line is zero considering the range of uncertainty. This suggests that the concentration of Ce may be determined by the simple Ce^{3+}/CeO_2 reaction in water with a Ce anomaly. The good agreement of cEh(pH, Fe^{2+}) and cEh(pH, Ce^{3+}) may be an indication that the solid phases are much simpler than we have considered when Ce anomaly is seen with void of complicated DOC in systems.

CONCLUSIONS

As far as the nine publications are considered, conditions where terrestrial water develops a negative Ce anomaly must satisfy all the following conditions: (i) Fe and Mn < 10^{-5} mol/L and (ii) DOC < 10 mg/L. Although more detailed investigations are necessary to obtain a more general conclusion, we consider that the negative Ce anomaly may reflect water chemistry only at organic-poor conditions.

The agreement between cEh(pH, Ce^{3+}) and cEh(pH, Fe^{2+}) in terrestrial water may imply the following: when Ce anomaly appears, the solubility of Ce can be determined by Ce^{3+}/CeO_2 equilibrium. It implies that the absolute concentration of Ce might possess meaningful *in situ* redox information. Therefore, most discussions based on Ce anomaly, a concentration relative to those of neighboring elements, would lead us to irrelevant discussion. Although it should be noticed that Ce is not an accurate indicator of *in situ* pH and Eh condition with quite a wide range of uncertainty involved, as shown in Fig. 3, the agreement of cEh(pH, Ce^{3+}) and cEh(pH, Fe^{2+}) is worth discussing. Bartlett (1999) pointed out that a Pt electrode may not reflect changes in some species involved in redox reactions and that neither Mn or Fe oxides nor nitrate had the expected quantitative effect on the Pt electrode measurement. It implies that the redox condition of natural water could be better understood by Ce and Fe data than *in situ* Eh measurement.

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APPENDIX

The observed values of Ce concentrations in the reports represent not the free Ce^{3+} concentrations, but the total trivalent and tetravalent cerium concentrations, $\sum Ce$ of the water studied. We assumed that dissolved Ce fraction could be approximated by $\sum Ce$ in a organic-poor condition and the free Ce^{3+} concentrations were approximated from complexation mass-balance and equilibria equations (Langmuir, 1997):

$$\left[Ce^{3+}\right] = \sum Ce \Big/ \Big\{ 1 + 10^{3.59}\left[SO_4^{2-}\right] + 10^{2.31}\left[HCO_3^-\right] + 10^{7.06}\left[CO_3^{2-}\right] + 10^{11.76}\left[CO_3^{2-}\right]^2 + 10^{-8.34}\left[10^{-pH}\right] + 10^{-15.0}\left[10^{-pH}\right]^2 \Big\}.$$

$$(A1)$$

The thermodynamic constants used in this study are listed in Table 2. Although the stability constants are a function of ionic strength and temperature (e.g., Millero, 1992), we thoroughly used stability constants at 25°C and zero ionic strength as we only referred the data for fresh water sites, which ionic strengths are low (majority of the samples had $I < 0.01$). The possible species $CeSO_4^+$, $CeHCO_3^{2+}$, $CeCO_3^+$, $CeOH_2^+$ and $Ce(OH)^{2+}$ were considered. The fraction of free Ce^{3+} calculated from Eq. (A1) for the waters we have used ranged from 0.1 to 80% of $\sum Ce$, whereas that of free Fe^{2+} (calculated using (A2)) was always greater than 60%. The error in Eh resulting from the error in the estimation of free Ce^{3+} is considered to be insignificant considering the range of uncertainty in discussion, since an error by one order of magnitude in the free Ce^{3+} fraction corresponds to only 0.026 V error in cEh(pH, Ce^{3+}). Some samples void of SO_4^{2-} data were excluded in the discussions, as SO_4^{2-} complex may become quite significant in certain environments (Schijf and Byrne, 2004). If the data sets did not include carbonate ion, the concentration of HCO_3^- and CO_3^{2-} were estimated from pH assuming the equilibrium with 300 ppmVCO_2 air at each site. The complexation with dissolved organic matter (DOM) was not considered due to the ambiguous information of DOM and the complication involved in the reaction between Ce and DOM, although REEs can be strongly complexed by organic matter due to their high stability constants with some specific compounds (Ohta and Kawabe, 2001; Tang and Johannesson, 2003). We also considered that the Ce complex with DOC is negligible when DOC < 10 mg/L.

The observed values of Fe concentrations in the reports represent not the free Fe^{2+} concentrations but the $\sum Fe$ that includes dissolved, colloidal and small particulate. Free Fe^{2+} was obtained in a similar manner to that for free Ce^{3+} introducing similar assumptions

$$\left[Fe^{2+}\right] = \frac{\sum Fe}{1 + 10^{2.25}\left[SO_4^{2-}\right] + 10^{2.0}\left[HCO_3^-\right] + 10^{5.1}\left[CO_3^{2-}\right]}.$$

$$(A2)$$