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Article in *Geochimica et Cosmochimica Acta* · December 2000

DOI: 10.1016/S0016-7037(00)00494-4

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The distribution of rare earth elements in groundwaters: Assessing the role of source-rock composition, redox changes and colloidal particles

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(Received January 5, 2000; accepted in revised form June 27, 2000)

Abstract—Rare earth element (REE), dissolved organic carbon (DOC) and trace-element (Al, Mn, Fe, Sr, Ba, U and Th) concentrations were measured in fourteen well water samples (<0.22 μm) and one spring located along two transects set up in a catchment from Western Europe (Kervidy/Coët-Dan catchment, France). Previous hydrological and hydrochemical (NO_3^- , SO_4^{2-}) investigations demonstrated that three chemically and spatially distinct groundwater types are present in this catchment, which is fully confirmed by the REE and DOC results. These include: (i) a shallow, organic-rich groundwater ($4.4 < \text{DOC} < 34.6 \text{ mg/l}$) from the wetland areas, close to the river network. This first groundwater type, characterized by the development of temporary reducing conditions, records high and variable REE contents ($2 < \Sigma\text{REE} < 16 \text{ ppb}$) and displays slight or no negative Ce anomaly ($\text{Ce/Ce}^* = 0.8\text{--}1.05$); (ii) a shallow, organic-poor ($\text{DOC} < 3 \text{ mg/l}$), NO_3^- -rich groundwater type ($86.8 < \text{NO}_3^- < 155 \text{ mg/l}$) located in the weathered schists, below the hillslope domains. This second type corresponds to recently recharged, oxidized water and displays also high and variable REE concentrations ($2 \text{ ppb} < \Sigma\text{REE} < 15 \text{ ppb}$), but distinguish from the former by the occurrence of very strong negative Ce anomalies ($\text{Ce/Ce}^* = 0.05\text{--}0.10$); finally (iii) a deep, organic-poor ($\text{DOC} < 1 \text{ mg/l}$), nitrate-poor (NO_3^- close to 0.2 mg/l ; detection limit) groundwater. This third type corresponds to reduced water flowing into the deep fresh schists and yields low to very low REE contents ($\Sigma\text{REE} < 0.15 \text{ ppb}$) as well as slight negative Ce anomaly ($\text{Ce/Ce}^* = 0.8$ to 0.9).

Temporal REE concentration variations were assessed using samples regularly collected over a six month period. Results show that the spatially distributed Ce anomaly and REE pattern signatures are preserved throughout the studied period. By contrast, REE concentrations are quite variable through time, especially in the wetland waters where the REE concentrations are seen to vary in phase with both redox changes and DOC, Fe, U and Th content variations.

Three REE-rich water samples (one DOC-rich and two DOC-poor) were also filtered through membranes of decreasing pore size (100,000 D, 30,000 D, 5,000 D). The results show that between about 40% to 65% of the REE present in the shallow, DOC-poor groundwater samples are controlled by the colloidal fraction, which is likely to consist in these inorganic waters of a mixture of mineral phases. In the wetland groundwaters, the fraction of REE controlled by microparticles is higher than 65%, which confirms the predominant role of organic colloids as major REE carriers in wetland waters.

Using the above data set in conjunction with analyses of soil samples, we show that the deep Ce anomalies found in the upper non organic part of the aquifer are probably not source-rock inherited features: most likely, these anomalies arise from the oxidative precipitation of Ce. The very low REE content displayed by waters flooding the deep fresh schists is interpreted as due to the combined effects of (i) pH variation, (ii) secondary sulfate mineral precipitation and (iii) the trapping of colloids-borne REE by the aquifer-rock pores. Data from wetland groundwaters show that the REE, Fe, U and Th budgets of these waters are mainly controlled by seasonal changes in redox conditions and organic matter content. However, unlike organic-poor waters, it appears difficult to relate the Ce behaviour in these organic-rich waters solely to redox conditions. It is likely that the complexation of Ce by organic colloids in the organic-rich waters may mask redox changes by inhibiting the development of negative Ce anomalies. Copyright © 2000 Elsevier Science Ltd

1. INTRODUCTION

Although the rare earth elements (REE) have been extensively used during the past 30 years to study the differentiation and evolution history of the solid Earth and meteorites (Haskin et al., 1968; Gromet et al., 1984; Taylor and McLennan, 1985; Allègre, 1987; Hofmann, 1988), the low concentrations of these elements in waters (ppb level or less; see Sholkovitz, 1995 and references therein) have long prevented their use either as witnesses of water/rock interaction processes or as hydrological

tracers. The refinement of stable isotope dilution mass-spectrometry techniques and the recent development of high-sensitivity equipments—namely the Inductively Coupled Plasma Mass Spectrometers or ICP-MS (see for example Hall et al., 1995)—changed this situation. As a consequence there has now been an increasing number of studies dedicated to the chemistry of dissolved REE, including topics such as (i) the suitability of REE to be used as pertinent tracers of groundwater flows and mixing (Johannesson et al., 1997a; Johannesson et al., 1997b; Johannesson et al., 1999), (ii) the role of microparticles on the behaviour and transport mechanism of REE in rivers and groundwaters (Elderfield et al., 1990; Sholkovitz, 1993; Sholkovitz, 1995; Viers et al., 1997; Tricca et al., 1999),

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(iii) the effect of redox changes on the chemical coherence of REE with a particular attention being devoted to the significance of negative Ce anomalies (De Baar et al., 1988; Braun et al., 1990; Braun et al., 1998; Smedley, 1991).

Ample evidence has been already provided that the REE could be significantly mobilised during weathering, alteration and diagenesis processes (Hellman and Henderson, 1977; Nesbitt, 1979; Ward, 1986; Wood, 1990). However, the extent to which the distribution of REE in fresh water (i.e. absolute concentration, fractionation among the different REE...) is controlled by that of the REE in the parental rocks, is not fully assessed. For example, Smedley (1991) proposed that the large negative Ce anomaly observed in groundwaters from metasediments in the Carnmenellis area, England, was likely a source-related feature. By contrast, marked negative Ce anomalies for groundwaters in the lateritic system of Goyoum, Cameroon, (Braun et al., 1990) were interpreted as due to oxidation of Ce^{3+} to Ce^{4+} and subsequent secondary precipitation of cerianite (CeO_2). In fact, several other factors have been suggested as being important in controlling REE concentrations in rivers and groundwaters. The common decrease of REE concentrations upon successive filtrations of natural waters through decreasing pore size membranes indicates that a significant part of the so-called 'dissolved' REE pool does correspond to colloid-borne REE (Sholkovitz, 1995; Viers et al., 1997). This has to be related to the fact that the predominant REE aqueous species REE^{3+} is characterized by a high charge/ionic radius ratio which helps sorption onto suspended colloidal materials (such as Fe- and Mn-oxyhydroxides and organic matter). As previously suggested (Viers et al., 1997), the affinity of REE for organic matter implies that in fresh waters, the organic colloidal pool is probably of prime importance in term of its ability to complex them.

In this study, we investigated the temporal and spatial variations of REE, trace-element and dissolved organic content (DOC) in groundwaters of a small catchment. The studied catchment—the Kervidy/Coët-Dan catchment—was chosen as a suitable site for REE investigation because much information about its hydrogeology and hydrochemical setting was already available (Durand and Torres, 1996; Durand and Mérot, 1998; Curmi et al., 1998; Pauwels et al., 1998; Molénat, 1999; Molénat et al., 2000a). The primary aims of this work are: (1) to address the respective influence of source-rock composition, redox changes and organic matter on the distribution of REE in shallow groundwaters; and (2) to test whether these elements can be useful tracers of groundwater-rock interaction and groundwater flowpaths in small size catchments.

2. HYDROGEOLOGY AND PREVIOUS HYDROCHEMICAL DATA

The Kervidy/Coët-Dan catchment (5 km²) is located in the Coët-Dan drainage basin, about 100 km southwest of Rennes in Central Brittany, France (Fig. 1). The bedrock is made of fissured and fractured upper Proterozoic schists (Dabard et al., 1996). The soils, developed into a loamy material derived from bedrock weathering and eolian Quaternary deposits, exhibit facies variations, which are locally dominated by silt, clay or

sandstone materials (Pellerin and Van Vliet-Lanoë, 1994). The mineralogical composition of schist was determined from drill cutting analysis and includes (in decreasing relative proportion): quartz, muscovite, chlorite, K-feldspar and plagioclase (Pauwels et al., 1998). The soil horizons comprise a large number of secondary mineral phases including illite, smectite, kaolinite, various Fe-oxides and Fe-oxyhydroxides (hematite, goethite, ...) and Mn oxides (Pauwels et al., 1998; Curmi et al., 1995; Curmi et al., 1998). Pyrite is ubiquitous both in the unweathered and altered schists at a depth greater than about 7 m. Major and trace-element composition (including REE) of bulk soil and fresh schist samples recovered in the catchment are reported in Appendix A (see Table A).

The elevation range of the Kervidy/Coët-Dan catchment is between 93 and 135 m and gentle slopes predominate. The climate is humid temperate with a mean annual rainfall of 909 mm. The land use in the Kervidy/Coët-Dan catchment is intensive farming dominated by maize, wheat and temporary pastures for dairy production and a high density of indoor pig-stock breeding. This land use has caused heavy nitrate pollution of the waters of this catchment with a mean nitrate concentration in the river of roughly 70 mg.l⁻¹ NO₃⁻ (Molénat, 1999; Molénat et al., 2000a; Molénat et al., 2000b).

Previous studies (Cann, 1990; Durand and Torres, 1996; Pauwels et al., 1998; Molénat, 1999; Molénat et al., 2000a; Molénat et al., 2000b) established that the hydrological setting of the Kervidy/Coët-Dan catchment has to be divided into two contrasted aqueous domains: (i) an upper compartment located in the weathered schists with interstitial porosity that has a captive role; and (ii) a lower compartment located in the fresh schists that has a transmissive role. In the hillslope domains, the water table always remains a few meters below the soil surface, while in the bottomland area it usually reaches the soil surface during the wet season, namely winter and spring (Molénat, 1999; see Fig. 1). This difference in groundwater/soil surface relationship leads to the recognition of two hydrologically contrasted domains at the scale of the catchment: (i) the hillslope domain which comprises well-drained soils and where infiltration is dominant; and (ii) the bottomland which comprises waterlogged soils.

The investigation of groundwater composition in the basin has so far concerned only a limited number of anions (Cl⁻, NO₃⁻, SO₄²⁻) (Durand and Torres, 1996; Molénat et al., 2000b) and cations (Si, Fe) together with a few DOC data (Jaffrézic, 1997). These results showed that the Kervidy/Coët-Dan groundwater can be summarized by the contrast of three spatially-distributed chemical domains. These include: (i) the uppermost part of the groundwater, sampled below the hillslope, and which is colourless, slightly acidic, always oxidized and nitrate-contaminated (up to 200 mg.l⁻¹ NO₃⁻ (Molénat et al., 2000b). (ii) The deep groundwater domain, where NO₃⁻ concentrations decrease drastically; this drop appears to be in phase with a decline of the redox potential and coincides with an increase of the dissolved Fe (as Fe²⁺) and SO₄²⁻ contents, so that it is believed to be in part due to a denitrification reaction involving direct oxidation of pyrite present in the aquifer (Pauwels et al., 1998). (iii) The shallow groundwater domain located in the wetlands where the water table reaches the organic-rich upper soil horizons.

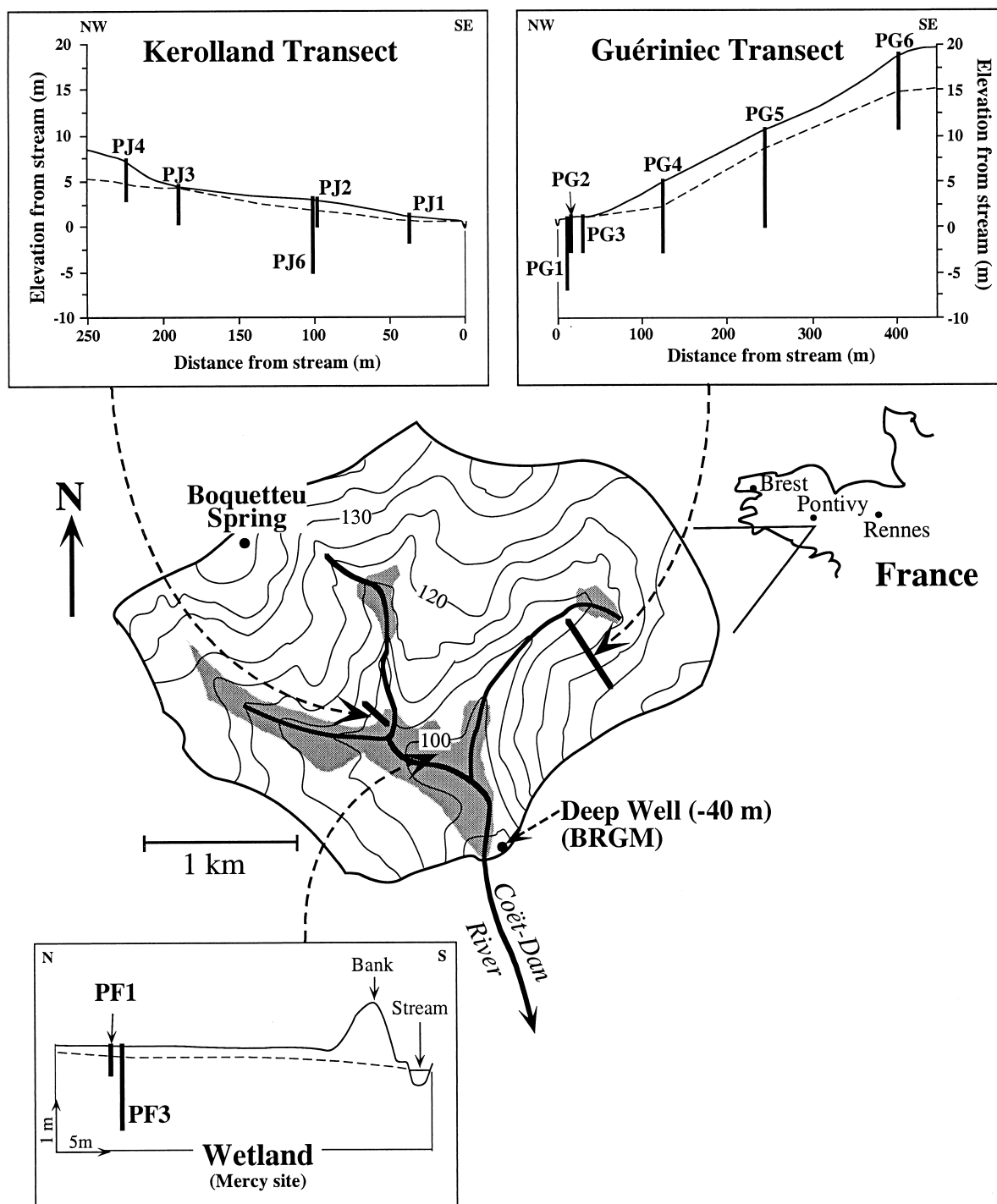


Fig. 1. Location map of the Kervidy catchment (Brittany, France) showing the different sampling sites (wells and spring), and the well water sampling placements set up at both, Kerolland and Guériniec transects and within the wetland of the Mercy site. The measured groundwater levels (dashed lines in the three insert figures) are indicated for a wet period (February). Discontinuous patterned areas located near the channel network indicate the location of wetland zones.

This third groundwater component is coloured, DOC-rich and exhibits variable nitrate concentrations (Durand and Torres, 1996; Jaffrézic 1997). In addition, these waters are characterized by the development of periodic reducing con-

ditions mostly in late winter and spring, which is a direct consequence of the waterlogging of the uppermost soil horizon (Jaffrézic, 1997). The analytical procedure followed during this study is detailed in Appendix B.

Table 1. Trace-element and dissolved carbon concentrations in the <0.22 μm “dissolved” fractions.

Well N°	PF1 (Mercy Wetland)													
Sample N°	PZ 254	PZ 264	PZ 273	PZ 282	PZ 293	PZ 307	PZ 319	PZ 331	PZ 347	PZ 1001	PZ 1005	PZ 357	PZ 367	PZ 387
Sampling Date	12/17/97	1/7/98	1/14/98	1/21/98	2/3/98	2/18/98	3/5/98	3/17/98	4/1/98	4/3/98	4/8/98	4/22/98	5/6/98	5/20/98
La (ppt)	377	555	607	498	381	771	1251	1264	1509	1747	1771	1571	1312	1122
Ce	801	1171	1245	1033	747	1444	2594	2712	3140	3591	3577	3151	2574	2163
Pr	116	168	178	150	117	232	364	377	436	494	494	434	395	354
Nd	492	719	754	643	503	992	1570	1592	1859	2070	2066	1825	1521	1396
Sm	93	135	150	125	94	187	299	306	355	393	405	364	311	282
Eu	18	26	29	24	18	38	59	60	70	79	79	69	62	59
Gd	70	107	114	95	70	145	225	234	257	293	292	276	251	232
Tb	—	13	14	12	—	19	29	30	35	39	39	34	30	27
Dy	34	57	61	52	38	84	124	135	151	168	168	153	136	125
Ho	—	10	12	10	—	16	24	26	29	31	32	29	27	25
Er	20	31	34	29	20	46	71	72	87	96	95	83	74	70
Tm	—	—	—	—	—	—	—	10	11	12	12	11	14	12
Yb	19	27	32	26	21	41	60	64	75	79	83	73	66	59
Lu	—	—	—	—	—	—	10	12	13	13	14	13	13	11
ΣREE (ppb)	2.04	3.02	3.23	2.70	2.01	4.02	6.68	6.89	8.03	9.11	9.13	8.08	6.79	5.94
Ce/Ce*	0.90	0.90	0.89	0.88	0.83	0.80	0.90	0.92	0.91	0.90	0.89	0.89	0.84	0.80
La _N /Yb _N	2.0	2.0	1.9	1.9	1.9	1.9	2.1	2.0	2.0	2.2	2.1	2.2	2.0	1.9
Al (ppb)	100	140	202	151	110	202	314	278	312	298	353	285	196	150
Mn	11.1	15.1	25.3	22.8	13.9	41.0	54.8	87.6	87.0	69.9	79.3	127.2	156.8	77.8
Fe	101	248	307	231	149	362	976	2468	5645	4969	6466	8070	11660	9086
Sr	40.7	31.5	31.0	29.8	34.2	31.9	31.3	38.4	46.5	42.0	41.7	51.3	59.2	57.5
Ba	5.41	6.20	8.16	6.74	6.55	7.13	6.81	7.64	11.2	10.4	8.36	8.88	8.59	7.16
Th (ppt)	25	54	86	58	31	77	161	183	244	249	295	246	207	157
U	34	44	46	42	39	72	119	134	155	162	160	141	112	118
pH	6.3	6.1	6.0	6.2	6.3	6.2	6.2	6.2	6.2	6.7	7.0	6.5	6.40	6.78
T (°C)	4.7	8.9	8	9.6	5.1	8.8	11.4	12	12.6	11.9	11.3	11.8	12.5	19.8
Eh (mV)	398	353	408	395	403	406	356	330	283	352	318	291	259	255
DOC (mg/l)	16.7	15.4	15.0	12.5	10.1	14.3	n.m.	25.0	29.6	33	34.6	31.2	27.0	25.9
NO ₃ ⁻ (mg/l)	3.10	15.04	36.27	16.06	22.56	2.91	3.04	n.m.	n.m.	n.m.	n.m.	2.76	3.71	3.20
SO ₄ ²⁻ (mg/l)	26.45	12.64	12.41	8.79	8.33	9.41	8.26	7.32	15.94	n.m.	n.m.	3.03	3.22	3.20

n.m.: not measured.

— indicates concentration below detection limits.

3. RESULTS

3.1. Chemical Composition of the 0.22 μm Filtrates

3.1.1. Field measurement and DOC and major anion concentrations

Field measurements (i.e. pH, Eh, temperature and conductivity) and DOC concentrations are presented in Table 1 along with earlier reported NO₃⁻ and SO₄²⁻ concentrations (Molénat et al., 2000b). The nitrate and DOC results are displayed further on Figure 2. These results confirm the existence of the here-above mentioned three chemical groups of water: (i) the shallow groundwaters from the hillslope domains (‘shallow weathered schist groundwater’ in Fig. 2) exhibit the highest NO₃⁻ concentrations (>34.1 mg/l) but have very low DOC content (<3.1 mg/l); (ii) in the deepest part of the aquifer concentrations of both species are close to the detection limit; (iii) the shallow organic waters from the Mercy site wetland yield moderate to low NO₃⁻ concentrations (53.9 to 3.1 mg/l) but high DOC values (4.4 to 34.6 mg/l). The maximum DOC content found in the latter waters are comparable to previously reported values for natural wetlands, as for example the swampy zone of the Nsimi-Zoétélé site (Cameroon) (24 mg/l) (Viers et al., 1997), or the swampy zone of Mont St Hilaire

catchment (Canada) (47 mg/l) (Dalva and Moore, 1991). NO₃⁻ concentrations in the shallow, organic-poor groundwaters from both the Kerolland and Guériniec transects progressively increase from bottom to top (from about 86.8 to 155 mg/l at Kerolland and from about 34.1 to 109.1 mg/l at Guériniec (see also Molénat et al., 2000b). By contrast, SO₄²⁻ decrease from 11.52 to 0.96 mg/l at Guériniec, while concentrations remain nearly constant along the Kerolland transect.

PH and Eh data also evidence contrasted domains. Shallow, colourless groundwaters from the hillslope domains are slightly acidic (5.2 < pH < 6.8) and oxidized (Eh values ranging from 344 to 544 mV). As for the major anions, the pH of these waters appears to show spatial variations: the waters from uphill wells (e.g. PJ4 and PG6) are slightly more acidic (5.2 to 5.4) than the waters from wells located closer to the stream (e.g. PJ1 and PG2; pH = 6.0–6.4). Organic-rich waters from the Mercy wetland are also slightly acidic (pH = 6 to 6.5). Moreover, these waters distinguish themselves from the former by their variable Eh values, especially those from PF1 well for which a marked decrease of Eh values was recorded at the end of the sampling period (from about 400 mV in winter down to 250 mV in spring). During this Eh decline time range, the waters were characterized by a simultaneous DOC content increase (up to 35 mg/l).

Table 1. (Continued)

Well N°	PF3 (Mercy Wetland)													
Sample N°	PZ 255	PZ 265	PZ 275	PZ 284	PZ 295	PZ 309	PZ 321	PZ 333	PZ 349	PZ 1003	PZ 1008	PZ 359	PZ 369	PZ 389
Sampling Date	12/17/97	1/7/98	1/14/98	1/21/98	2/3/98	2/18/98	3/5/98	3/17/98	4/1/98	4/3/98	4/8/98	4/22/98	5/6/98	5/20/98
La (ppt)	1986	975	1108	1550	610	1851	944	2705	2103	4018	2717	1774	1023	1019
Ce	5040	2317	2587	3755	1390	4556	2174	6289	5253	9596	6590	4157	2525	2432
Pr	664	323	332	481	207	563	283	816	646	1254	865	546	352	344
Nd	2856	1422	1401	2082	888	2338	1166	3391	2729	5129	3500	2143	1326	1295
Sm	494	263	249	374	159	410	213	604	467	968	661	399	249	246
Eu	89	49	46	69	33	78	42	113	84	188	126	77	47	46
Gd	342	191	184	276	122	307	167	424	321	717	488	300	184	179
Tb	38	23	22	32	13	29	17	53	38	73	49	31	19	19
Dy	145	91	84	127	59	136	83	208	148	321	217	131	79	82
Ho	27	17	16	23	12	24	15	39	27	58	42	26	16	16
Er	79	51	46	67	33	67	44	112	81	160	109	69	41	40
Tm	—	—	—	—	—	—	—	13	10	24	18	11	—	—
Yb	65	43	37	56	30	53	36	88	64	133	98	57	34	35
Lu	11	—	—	10	—	—	—	15	11	24	17	11	—	—
ΣREE (ppb)	11.8	5.77	6.11	8.90	3.56	10.41	5.18	14.9	12.0	22.7	15.5	9.73	5.89	5.75
Ce/Ce*	1.03	0.97	1.00	1.02	0.91	1.04	0.98	0.99	1.05	1.00	1.01	0.99	0.98	0.96
La _N /Yb _N	3.1	2.3	3.0	2.8	2.1	3.5	2.6	3.1	3.3	3.0	2.8	3.1	3.0	3.0
Al (ppb)	101	148	95.2	163	107	112	142	241	80.3	173.8	149.3	86.3	24.3	25.4
Mn	36.0	38.6	32.9	42.2	50.0	33.9	52.9	53.0	40.9	41.3	50.3	82.6	33.6	24.5
Fe	377	399	529	595	669	1177	1146	2573	1093	2412	3207	3614	431	701
Sr	46.9	35.2	42.4	33.0	37.4	38.8	46.6	47.8	51.4	49.9	54.4	49.9	51.5	54.3
Ba	7.23	7.60	7.16	6.87	7.94	6.01	9.54	7.87	7.35	7.24	8.62	7.77	6.70	7.32
Th (ppt)	51	69	39	94	55	71	84	167	76	173	157	91	44	48
U	64	60	39	75	42	76	53	136	96	193	138	73	53	56
pH	6.1	5.9	5.9	5.9	6.3	5.9	6.1	6.0	6.0	6.5	6.5	6.2	5.9	6.2
T (°C)	9.5	6.3	8.8	9.0	4.9	10.4	11.6	11.3	12.1	12.7	12.0	11.7	12.4	17.2
Eh (mV)	392	363	380	371	370	339	366	321	340	353	361	328	345	347
DOC (mg/l)	18.1	13.3	7.9	15.1	10.6	10.7	10.5	20.2	9.8	19.3	17.8	11.8	4.4	6.9
NO ₃ ⁻ (mg/l)	2.89	16.94	15.73	12.40	13.02	12.40	2.91	25.84	46.99	n.m.	n.m.	34.56	53.88	25.21
SO ₄ ²⁻ (mg/l)	33.39	13.89	9.52	11.91	8.50	13.54	5.66	9.09	8.30	n.m.	n.m.	7.73	7.57	2.58

n.m.: not measured.

— indicates concentrations below detection limits.

3.1.2. REE concentrations and patterns

REE concentrations are reported in Table 1. Normalized patterns with respect to the estimated average composition of the North American Shale Composite (Haskin et al., 1968; Gromet et al., 1984) are displayed further on Figs. 3a, 3b and 4. As regards the REE concentrations and patterns, two important points should be mentioned as follows:

1. Samples from the three previously identified groundwater domains based on nitrate concentrations, DOC data and redox status (Jaffr  zic, 1997; Pauwels et al., 1998; Mol  nat et al., 2000b; see Fig. 2) tend to have distinct REE signatures. Specifically, colourless waters from the deep part of the aquifer (wells PG1, PJ6 and 40-m-deep BRGM) yield distinctly low to very low REE concentrations ($0.04 < \Sigma\text{REE} < 0.15$ ppb) as compared to the oxidized, colourless waters from the two investigated hillslope transects which have higher REE concentrations (wells PJ1 to PJ4 and PG2 to PG6; $0.17 < \Sigma\text{REE} < 16.8$ ppb). The low REE content registered in the deep samples has probably to be related to higher pH (Pauwels et al., 1998). Moreover, while the latter commonly have pronounced negative Ce anomalies ($0.06 < \text{Ce}/\text{Ce}^* < 0.9$), the deepest samples show Ce/Ce* ratio closer to 1.0 (i.e. no Ce anomaly). The organic waters from

the Mercy wetland (wells PF1 and PF3; see Fig. 4) distinguish themselves from the colourless ones by having variable REE concentrations and S-shaped patterns showing no, or only very slight negative Ce anomalies ($0.8 < \text{Ce}/\text{Ce}^* < 1.05$; see Fig. 4). The shallow, organic-poor groundwaters tend to show systematic variations of their REE signatures depending on the position of wells along the catena (Figs. 3a and 3b). Along the Gu  riniec transect, the Ce anomaly size progressively decreases from uphill wells (Ce/Ce* around 0.08) down to bottomland well PG2 ($0.61 < \text{Ce}/\text{Ce}^* < 0.89$). Moreover, this progressive disappearance of the Ce anomaly along the hillslope is accompanied by a regular decrease of the (La/Yb)_N ratio (from 15.9 to 0.4). Along the Kerolland transect, the Ce anomaly size is also maximum at the top of the hillslope (i.e. Boquetteu spring; Ce/Ce* = 0.06; Fig. 3a).

2. Despite large REE concentration variations, the REE pattern shape (amplitude of Ce anomaly and (La/Yb)_N ratio) remains constant through time. This temporal stability of the REE pattern shape is well illustrated by the organic waters from well PF1 for which the Ce/Ce* and (La/Yb)_N ratios are nearly constant through the entire studied period (0.8–0.92 and 1.9–2.2) while the sum of the REE is multiplied by a factor of 4.5 (Fig. 4).

Table 1. (Continued)

Well N°	PJ1 (Kerrolland)				PJ2 (Kerrolland)				PJ3 (Kerrolland)				PJ4 (Kerrolland)							
Sample N°	PZ 257	PZ 267	PZ 286	PZ 335	PZ 370	PZ 258	PZ 268	PZ 287	PZ 336	PZ 371	PZ 259	PZ 269	PZ 288	PZ 337	PZ 372	PZ 260	PZ 270	PZ 289	PZ 337	PZ 372
Sampling Date	12/17/97	1/7/98	1/21/98	3/17/98	5/6/98	12/17/97	1/7/98	1/21/98	3/17/98	5/6/98	12/17/97	1/7/98	1/21/98	3/17/98	5/6/98	12/17/97	1/7/98	1/21/98	3/17/98	5/6/98
La (ppt)	571	465	534	646	724	174	234	200	161	126	699	162	133	172	115	121	253	233	179	244
Ce	418	327	365	377	420	274	343	321	207	168	654	102	72	120	83	149	239	233	175	240
Pr	128	100	108	125	141	49	67	62	38	32	213	27	21	30	23	30	51	51	40	59
Nd	550	416	453	496	548	214	299	264	165	137	1062	120	96	130	90	146	237	230	174	262
Sm	71	55	62	70	76	40	58	48	33	26	283	28	22	31	23	34	58	53	45	67
Eu	14	11	12	14	16	—	11	—	—	—	67	6	—	11	10	10	17	18	19	27
Gd	61	44	50	58	65	36	52	40	29	22	346	43	38	47	32	51	100	102	76	111
Tb	—	—	—	—	—	—	—	—	—	—	43	6	—	—	—	—	17	20	12	18
Dy	24	19	22	25	28	19	30	23	18	11	215	35	31	34	22	41	102	118	77	114
Ho	—	—	—	—	—	—	—	—	—	—	48	—	—	—	—	—	23	26	17	26
Er	—	—	—	13	16	14	18	19	12	10	133	19	18	20	15	27	63	66	46	67
Tm	—	—	—	—	—	—	—	—	—	—	16	—	—	—	—	—	—	—	—	—
Yb	—	—	—	10	—	12	15	14	10	—	91	12	10	12	10	21	40	41	30	42
Lu	—	—	—	—	—	—	—	—	—	—	16	—	—	—	—	—	—	—	—	—
Y	186	155	176	230	238	145	221	164	169	110	1444	287	255	326	213	318	803	878	711	1011
ΣREE (ppb)	1.84	1.44	1.61	1.83	2.03	0.83	1.13	0.99	0.67	0.53	3.89	0.56	0.44	0.61	0.42	0.63	1.20	1.19	0.89	1.28
Ce/Ce*	0.36	0.35	0.36	0.31	0.31	0.70	0.64	0.67	0.62	0.62	0.40	0.36	0.32	0.39	0.38	0.58	0.49	0.50	0.49	0.47
La _N /Yb _N	—	—	—	6.8	—	1.5	1.5	1.5	1.6	—	0.8	1.4	1.3	1.4	1.2	0.6	0.6	0.6	0.6	0.6
Al (ppb)	1.35	1.20	9.53	5.69	3.22	11.1	10.5	10.0	13.1	8.65	31.7	20.3	22.7	26.0	23.5	32.0	60.4	66.1	50.9	69.1
Mn	15.3	10.7	13.8	12.3	19.4	12.4	19.6	12.9	12.3	65.5	12	6.3	6.7	7.8	19	84	22	24	19	22
Fe	19.4	16.4	19.2	25.4	20.8	24.5	31.3	28.8	31.7	32.2	51	34	37	51	52	38	40	50	48	42
Sr	94.7	92.4	77.3	86.8	89.8	98.4	119	84.6	93.5	94.7	232	190	181	173	179	217	239	220	187	219
Ba	14.9	14.3	13.9	14.3	14.6	14.0	16.3	12.1	15.1	13.1	41.5	26.8	27.0	30.8	28.2	73.9	80.8	85.0	68.2	81.1
Th (ppt)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	15	—	—	—	—	—
U	10	10	10	12	11	—	10	—	10	10	11	—	—	—	—	—	—	—	—	—
pH	n.m.	6.2	6.2	6.4	6.0	n.m.	5.7	5.9	5.6	5.7	n.m.	5.5	5.5	5.4	5.5	n.m.	5.3	5.2	5.2	5.2
T (°C)	9	10.4	8.8	9.7	14.0	7.6	10.3	7.7	12.0	12.1	8.5	10.7	8.5	12.2	11.8	7.6	10.7	8.2	12.9	13.0
Eh (mV)	436	437	413	497	400	454	453	483	465	418	433	425	367	462	387	460	403	417	441	432
DOC (mg/l)	n.m.	1.6	1.5	0.8	2.4	n.m.	3.1	1.6	2.6	1.9	n.m.	1.2	0.8	0.9	1.1	n.m.	n.m.	0.7	2.1	1.5
NO ₃ ⁻ (mg/l)	93.90	92.14	94.42	92.79	85.56	91.47	102.25	104.70	102.26	78.21	163.67	121.46	120.42	133.24	118.25	117.88	152.71	147.19	133.72	134.53
SO ₄ ²⁻ (mg/l)	10.95	9.04	6.61	5.48	5.14	7.40	15.47	11.88	10.04	11.16	12.74	6.38	5.10	5.97	5.21	7.41	5.58	5.66	4.91	5.73

n.m.: not measured.

— indicates concentrations below detection limits.

v Calculated using Nd concentrations instead of Pr contents.

Table 1. (Continued)

Well N°	PJ6 (Kerrolland)					Boquetteu Spring		
Sample N°	PZ 262	PZ 272	PZ 291	PZ 340	PZ 375	671	678	695
Sampling Date	12/17/97	1/7/98	1/21/98	3/17/98	5/6/98	9/12/96	11/05/96	1/14/97
La (ppt)	24	25	22	20	27	571	627	617
Ce	50	47	45	38	55	85	96	71
Pr	—	—	—	—	—	187	245	207
Nd	29	28	26	22	30	830	1107	909
Sm	—	—	—	—	—	163	229	176
Eu	—	—	—	—	—	33	45	41
Gd	—	—	—	—	—	133	181	161
Tb	—	—	—	—	—	17	21	18
Dy	—	—	—	—	—	67	87	79
Ho	—	—	—	—	—	13	16	15
Er	—	—	—	—	—	39	46	43
Tm	—	—	—	—	—	—	—	—
Yb	—	—	—	—	—	32	36	32
Lu	—	—	—	—	—	—	—	—
ΣREE (ppb)	0.124	0.122	0.113	0.102	0.146	2.17	2.73	2.37
Ce/Ce*	0.87 ^V	0.81 ^V	0.88 ^V	0.85 ^V	0.89 ^V	0.06	0.06	0.05
La _N /Yb _N	—	—	—	—	—	1.8	1.8	1.9
Al (ppb)	—	n.m.	—	—	—	12.9	10.1	15.2
Mn	546	618	553	427	417	11.2	29.1	8.6
Fe	3654	3920	3919	3318	5931	49	52	40
Sr	43	40	38	39	38	n.m.	93.9	91.8
Ba	7.5	6.6	7.1	7.8	7.0	27.7	27.0	23.0
Th (ppt)	—	—	—	—	13	—	—	—
U	25	19	22	18	18	12	11	11
pH	n.m.	6.5	6.5	6.2	6.4	5.8	5.8	5.5
T (°C)	7.2	10.8	8.4	12.5	12.6	14.5	11.9	8.8
Eh (mV)	n.m.	249	269	279	243	n.m.	n.m.	n.m.
DOC (mg/l)	n.m.	2.3	0.0	1.2	n.m.	n.m.	n.m.	n.m.
NO ₃ ⁻ (mg/l)	—	—	—	n.m.	1.36	n.m.	n.m.	n.m.
SO ₄ ²⁻ (mg/l)	15.05	15.49	14.14	15.93	15.90	n.m.	n.m.	n.m.

n.m.: not measured.

— indicates concentration below detection limits.

^V Calculated using Nd concentrations instead of Pr contents.

3.1.3. Fe, Mn, Al, Th, U, Sr and Ba data

The concentrations of other trace elements are presented in Table 1 and compared to the REE concentration fluctuations in Figures 5a–f. High Fe concentrations are observed both in the deepest waters and in the organic-rich waters from the Mercy wetland (Fig. 5e). In the latter samples Fe concentrations vary in phase with REE contents (Table 1). The high iron concentrations (up to 6000 ppb) found in PJ6 and 'BRGM' deep well waters are consistent with previously reported data for deep water samples collected farther south in the Coët-Dan catchment (Pauwels et al., 1998). Mn exhibits a different behaviour, the only Mn-rich waters being deepest groundwaters (265 to 618 ppb; Fig. 5f). Concentrations in the shallow organic-rich and organic-poor waters are low, from 11 to 157 ppb and from 4 to 84 ppb, respectively (Table 1).

The behaviour of U, Th and Al is clearly dependent on the DOC content. With very few exceptions, concentrations in these three elements are indeed systematically higher in the organic-rich waters than in DOC-poor waters (Fig. 5c and 5d). Even though the correlation slopes seem to be different in PF1 and PF3 waters, Th, U, Al and REE concentrations in these waters appear to be strongly linked. The Th concentrations measured in the Mercy organic-rich waters are comparable to

the concentrations registered in wetland waters from the Nsimi-Zoetele site in Cameroon (maximum Th concentration of 140 ppt; Viers et al., 1997).

Strontium and barium show the same behaviour, though markedly different from that of U, Th and Al. Concentrations in the deepest parts of the aquifer are low and remain constant (<58 ppb for Sr and 11 ppb for Ba), while concentrations are higher and more variable in the shallow, organic-poor waters from the Kerolland and Guériniec transects. Along the Kerolland transect both the Sr and Ba contents of the waters are seen to increase regularly from the bottom to the top of the hillslope (see Table 1).

3.2. Effect of Successive Filtration on REE Patterns and Trace-Element Distributions

In order to establish the role of colloids, three samples—two organic-poor waters from PJ4 and PG5 wells and one organic-rich water from PF3 well—were successively filtered through membranes of smaller pore size (see Table 2). The following results are obtained:

1. In the three cases, REE concentrations are lowered upon successive filtrations at decreasing pore size. However, and

Table 1. (Continued)

Well N°	PG1 (Guériniec)				PG2 (Guériniec)				PG3 (Guériniec)				PG4 (Guériniec)				PG5 (Guériniec)				PG6 (Guériniec)				40-m-Deep
Sample N°	PZ 276	PZ 277	PZ 343	PZ 378	PZ 278	PZ 344	PZ 379	PZ 279	PZ 345	PZ 380	PZ 280	PZ 346	PZ 381	PZ 281	PZ 382	PZ 319									
	PZ																								
	3/17/																								
Sampling Date	1/14/98	1/14/98	3/17/98	5/6/98	1/14/98	3/17/98	5/6/98	1/14/98	98	5/6/98	1/14/98	3/17/98	5/6/98	1/14/98	5/6/98	2/24/98									
La (ppt)	8	104	41	37	3195	1292	1010	1429	1129	2128	2618	1883	1596	5075	2432	18									
Ce	19	257	54	90	5223	2084	1694	430	640	1349	513	379	217	811	365	38									
Pr	—	44	10	17	973	411	317	357	345	839	628	451	386	938	426	—									
Nd	14	251	47	95	4480	1844	1472	1439	1516	3774	2535	1808	1531	3494	1533	22									
Sm	—	69	10	28	840	363	288	271	305	821	453	318	271	508	205	—									
Eu	—	17	—	—	181	79	64	59	67	175	87	66	55	88	39	—									
Gd	—	91	10	34	854	345	284	229	229	557	319	232	198	363	152	—									
Tb	—	10	—	—	94	33	29	32	25	63	37	24	19	41	14	—									
Dy	—	48	—	19	398	164	136	148	129	320	146	109	82	143	54	—									
Ho	—	10	—	—	82	32	27	29	26	63	27	20	16	27	10	—									
Er	—	30	—	12	236	92	78	81	76	180	78	54	41	79	26	—									
Tm	—	—	—	—	28	12	10	10	11	26	—	—	—	—	—	—									
Yb	—	24	—	10	178	73	63	58	67	164	57	42	31	49	15	—									
Lu	—	—	—	—	35	15	13	—	12	29	—	—	—	—	—	—									
ΣREE (ppb)	0.04	0.95	0.17	0.34	16.8	6.84	5.49	4.57	4.58	10.5	7.50	5.39	4.44	11.6	5.27	0.08									
Ce/Ce*	0.83 ^v	0.89	0.61	0.83	0.69	0.67	0.70	0.14	0.24	0.24	0.09	0.10	0.06	0.09	0.08	0.88 ^v									
La _N /Yb _N	—	0.4	—	0.4	1.8	1.8	1.6	2.5	1.7	1.3	4.6	4.4	5.2	10.5	15.9	—									
Al (ppb)	2.7	5.4	10.4	2.6	32.8	21.4	17.4	25.3	37.1	49.9	38.2	34.7	21.0	41.8	21.2	6.9									
Mn	678	12	4	4	19	17	24	78	38	41	41	26	15	81	43	265									
Fe	25	21	29	11	51	31	25	17	37	36	51	25	14	60	22	3206									
Sr	41	51	47	51	53	50	50	57	74	70	66	73	62	101	85	27.2									
Ba	1.8	2.8	2.9	2.3	10.7	10.4	11.6	20.0	34.4	30.5	28.2	30.2	18.2	43.2	29.2	3.9									
Th (ppt)	—	—	—	—	—	—	—	—	—	10	—	—	—	—	—	13									
U	65	22	10	15	61	34	40	—	11	23	—	12	—	—	—	38									
pH	6.8	6.4	5.7	6.3	6.1	5.8	5.8	5.5	5.4	5.4	5.4	5.4	5.5	5.4	5.5	n.m.									
T (°C)	11.5	10.7	11.6	11.4	10.7	11.2	11.6	11.1	11.5	11.5	11.3	12.5	11.6	11.8	12.5	n.m.									
Eh (mV)	458	535	458	344	544	474	439	522	463	446	447	414	462	499	474	n.m.									
DOC (mg/l)	0.5	1.1	1.2	0.3	2.7	2.7	2.4	1.4	1.5	2.0	0.9	0.9	0.6	n.m.	0.6	n.m.									
NO ₃ ⁻ (mg/l)	—	34.10	36.58	35.96	76.88	86.79	68.10	99.91	113.89	91.71	109.22	105.82	86.49	99.36	92.40	2.65									
SO ₄ ²⁻ (mg/l)	14.40	11.52	7.68	7.68	8.64	6.18	4.48	3.63	6.64	6.66	2.17	3.12	1.75	0.00	1.10	20.76									

n.m.: not measured.

— indicates concentration below detection limits.

^V Calculated using Nd concentrations instead of Pr contents.

Mean trace-element contents (in ppb) of the SLRS-3 Canadian water standard, performed in the Geochemistry Laboratory of the University of Toulouse (France) by ICP-MS measurements, and comparison of the analytical accuracy with values obtained by Louvat (1997), Viers et al. (1997) and Ollivier-Lauquet et al. In prep.). The reproducibility is indicated by the σ error in %.

taking into account the analytical uncertainties, the shape of the REE patterns remains globally unchanged, even though a slight decrease of the Ce/Ce* ratio of the organic-rich sample may be noticed.

- In the organic-rich sample, the REE concentration decrease occurred at coarse filter size (100 kD) and was accompanied by a decrease in DOC and in Al, U, Th, Mn and Fe contents. In the organic-poor samples, decreases in Al, Fe and Mn contents were also observed.
- As a general rule, Sr and Ba concentrations were little affected in the organic-rich sample, while a content decrease was obtained for both elements (see Table 2) in the organic-poor waters in the two last filtrations.

4. DISCUSSION

The analyzed groundwater samples display strong variations in both REE patterns and concentrations which appear to be correlated with variations in DOC, major anions and other trace

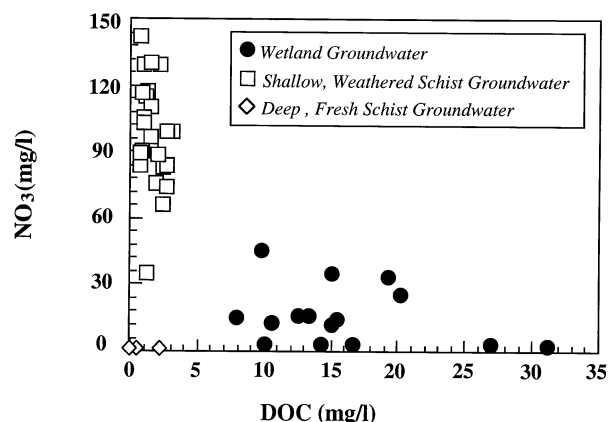


Fig. 2. NO₃⁻ concentrations (expressed in mg/l) plotted against dissolved organic contents (DOC) (mg/l) for the Kervidy/Coët Dan groundwaters.

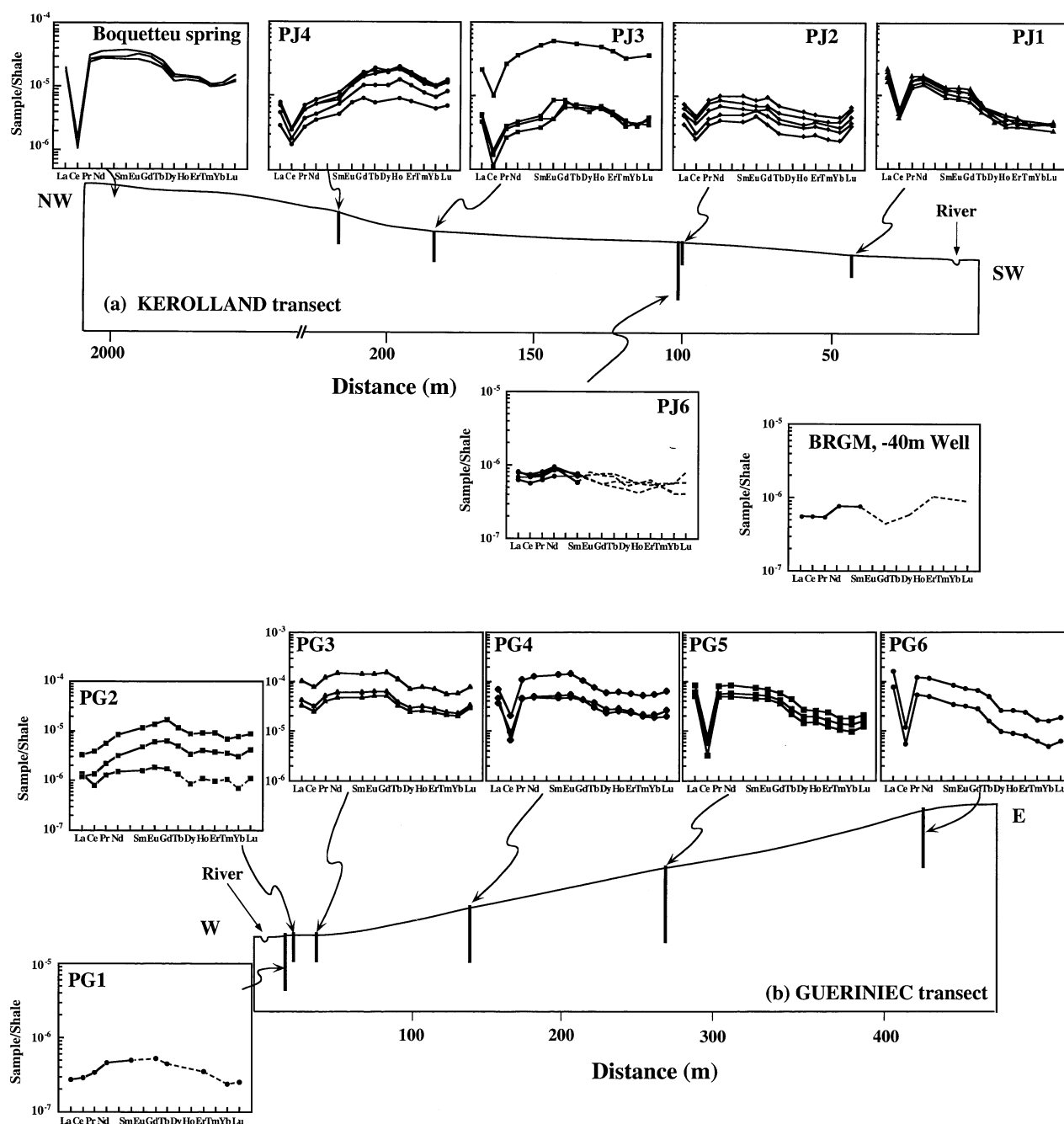


Fig. 3. Sketch diagram showing downslope evolution of shale-normalized REE profiles for the sampled wells and springs from the Kerolland (a) and Guériniec (b) transects. Middle and heavy REE concentrations for PJ6, PG1 and 40 m deep BRGM wells were close to, or below the detection limits (<10 ppt) and are reported using dashed lines.

element characteristics. The dataset is especially significant since the observed differences in REE signatures are not randomly distributed within the aquifer but correspond closely to the three previously identified chemical and hydrological domains (Curmi et al., 1998; Pauwels et al., 1998; Molénat, 1999; Molénat et al., 2000a; Molénat et al., 2000b; Riou, 1999). In addition, while the REE characteristics of some samples appear to be invariant through time, other show seasonal variability which are linked to several other physico-chemical parameter

changes, notably DOC content and redox conditions (Table 1). By measuring both the REE pattern and concentration variations along groundwater flow paths and identified redox condition changes, we may be able to: (i) evaluate the true control of the rock REE composition on the shallow groundwater REE patterns; the discussion will be particularly focussed on the negative Ce anomaly problem; (ii) assess the effects of both heterotrophic and autotrophic reduction processes on the hydrochemistry of these elements; and finally (iii) test whether the

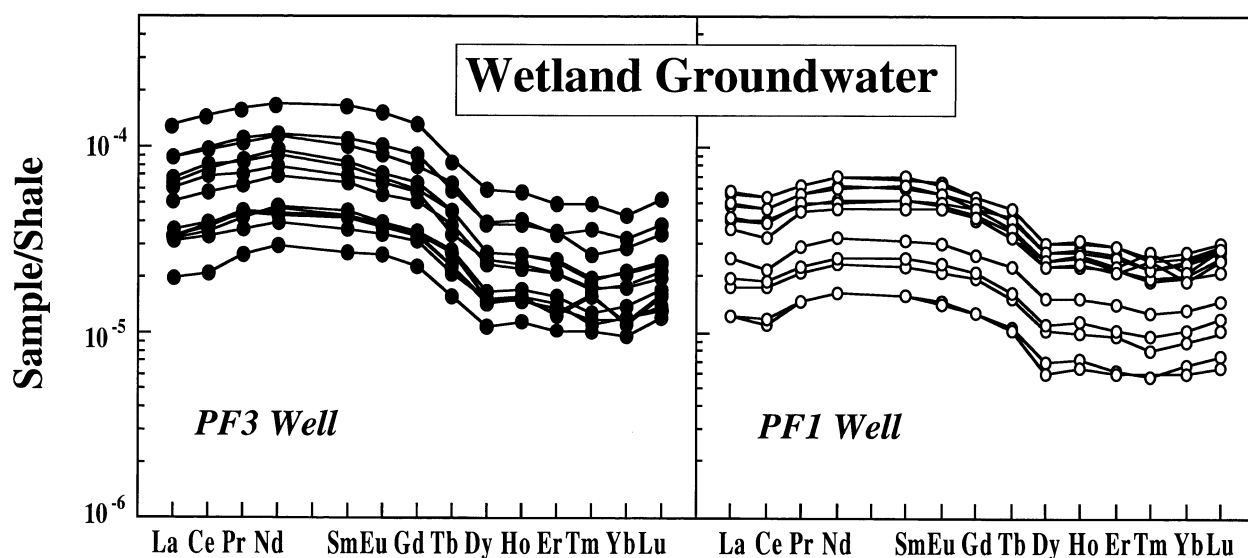


Fig. 4. Shale-normalized REE profiles for the organic-rich waters from the Mercy wetland (PF1 and PF3 wells).

REE behave as conservative species in groundwaters which could help in reconstructing groundwater flow path and groundwater mixing. Three important questions in this context are: (1) What are the origin and significance of the variable Ce anomalies recorded in the Kervidy/Coët-Dan organic-poor groundwaters? (2) Which kind of process(es) may account for the very low REE concentrations measured in the deepest part of the aquifer? (3) What are the relative roles played by DOC fluctuations, seasonal redox variations and soil-forming minerals in the specific REE signatures and REE dynamics which are seen in wetland groundwaters? In the following sections, we attempt to answer these questions.

4.1. Origin of Large Negative Ce Anomalies in Shallow Groundwaters: Source-Related Characteristic or Oxidation Effect?

One of the most striking results stemming from the present dataset is that the nitrate-rich and organic-poor, oxidizing waters from the hillslope domain show deep negative Ce anomalies whose amplitude appears to be constant through time. Given the high nitrate concentrations of these waters, it is inferred that these waters do probably correspond to the most recently recharged part of the Kervidy/Coët-Dan aquifer. Ce/Ce* ratios as low as 0.05–0.10 (PG5 and PG6 wells and the Boquetteu spring) may be among the lowest Ce/Ce* measured in groundwater samples, worldwide. To our knowledge, the only two aquifers in which similarly low ratios have been so far measured are located in the Carnmenellis and Goyoum catchments, South England and Cameroon, respectively (Smedley, 1991; Braun et al., 1998). As already mentioned in the introduction, the interpretation of large negative Ce anomalies in groundwaters is still a controversial issue. Smedley (1991) suggested that those observed in the groundwaters that flood the metasediments from the Carnmenellis 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. By contrast, those measured in the Goyoum aquifer were interpreted by Braun et al. (1998) as due to the selective removal of Ce from the waters by means of secondary cerianite (CeO_2) precipitation. In the present case, however, we think that the large negative Ce anomalies are unlikely to represent inherited aquifer-rock REE signatures for two reasons:

1. Based on preliminary investigation of bulk soil samples, no evidence can be found for the presence of negative Ce anomalies in any of the rock units that compose the Kervidy/Coët-Dan catchment (see Fig. 6 and Appendix A). Moreover, we stress that the soils from the Kervidy/Coët-Dan wetlands (no Ce-anomaly waters) and Kervidy/Coët-Dan hillslope domains (large Ce-anomaly waters) exhibit comparable major and trace-element compositions (see Appendix A).
2. Figure 7 compares the amplitude of the negative Ce anomalies found in the Kervidy, Carnmenellis and Goyoum groundwaters with that of the anomalies found in a large numbers of soil and paleosol samples (whole-rock data) from Africa (Braun et al., 1998), Europe (Gallet et al., 1998; this study), China (Gallet et al., 1996; Gallet et al., 1998), Argentina (Gallet et al., 1998) and New Zealand (Rankin and Childs, 1976). As can be seen, many soils and paleosols do exhibit Ce-anomalies, the latter being either positive or negative. However, it is clear from Figure 7 that none shows a negative Ce anomaly as deep as those found in the Kervidy, Carnmenellis and Goyoum groundwaters.

The only plausible explanation is thus that the large negative Ce anomalies which we observe in hillslope groundwaters are due to oxidative removal of Ce from the aqueous solution. Ce behaves differently from the neighbouring trivalent REE as a result of its Ce(IV)/Ce(III) redox couple (De Baar et al., 1988; Braun et al., 1990; Braun et al., 1998), which can lead to the precipitation of Ce in oxidizing groundwaters as CeO_2 . Pe-pH

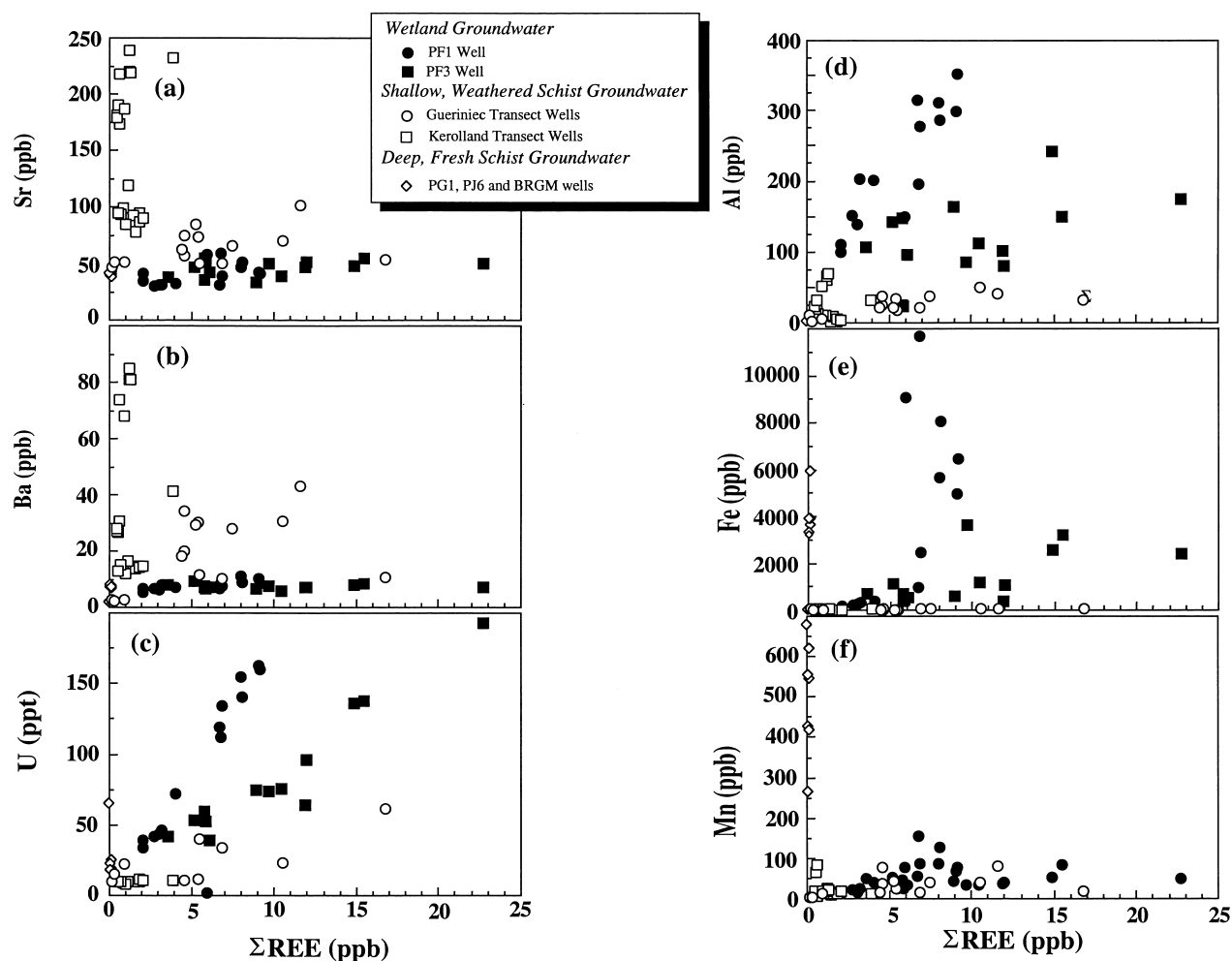


Fig. 5. Relationships between REE and Sr, Ba, U, Al, Fe and Mn concentrations for the different Kervidy/Coët-Dan groundwaters. The data are expressed in ppb except those of U expressed in ppt. Corresponding sampling dates can be found in Table 1.

diagrams (e.g. De Baar et al., 1988; Braun et al., 1990) indicated that cerium oxide precipitation appears to fall within the ranges of pe and pH typical for natural waters. Alternatively, Ce may be removed from natural waters due to its oxidative scavenging on the surface of soil-forming Mn or/and Fe oxyhydroxides. This latter process was recently confirmed by Bau (1999) who reported positive anomalies for experimentally determined Ce partition coefficient between Fe oxyhydroxides and REE-bearing solutions. According to Bau (1999), such an oxidative scavenging of Ce may be regarded as a three stage process consisting of (i) an initial sorption of Ce(III) together with the other REE(III), followed by (ii) the partial oxidation of Ce(III) to Ce(IV) on the Fe-oxyhydroxide surface, and (iii) the preferential desorption of Ce(III) and the other REE(III) compared to Ce(IV). Although the global physico-chemical environment in which the present hillslope groundwaters occur (i.e. elevated Eh, high nitrate concentrations, presence of abundant Fe and Mn oxyhydroxides in the soils) appears consistent with an hypothesis based on an oxidative removal of Ce, it remains however that we have currently no argument to decide which of the above two processes (oxidation of Ce(III) in Ce(IV) in

solution followed by cerianite precipitation or oxidative scavenging of Ce(III) on Fe-Mn oxyhydroxides) do control the chemistry of Ce in these waters.

Beside the presence of marked negative Ce anomalies, other common characteristics of hillslope groundwaters include a low pH (down to 5.4) as well as a high concentration in REE, Sr and Ba (see Table 1). The ultrafiltration experiments performed on PG5 and PJ4 waters have shown that between 40% (PJ4) and 65% (PG5) of the REE initially present in the 0.22 μm filtrates are removed when these waters are filtered through decreasing pore size membranes (Table 2). This result demonstrates that part of the REE are controlled in these solutions by the colloidal fraction, which fully confirms the emerging view that microparticles are likely to be major REE carriers in natural, fresh water systems (Elderfield et al., 1990; Sholkovitz, 1993; Sholkovitz, 1995; Viers et al., 1997; Tricca et al., 1999). As regards to the low DOC concentrations the nature of the microparticles is expected to be an assortment of clay particles, Al-oxides and Fe-, Mn-oxyhydroxides, which would explain why the REE content decrease is accompanied by drops in Al, Mn and Fe (PG5 only) concentrations (see Table 2). A more

Table 2. Trace-element and dissolved organic concentrations in the different filtrates (<0.2 μm , <100,000 D, <30,000 D, <5,000 D).

Well N°	PJ4				PG5				PF3		
Sampling date	3/17/98				3/17/98				1/22/98		
Filtration	<0.2 μm	<100 kD	<30 kD	<5 kD	<0.2 μm	<100 kD	<30 kD	<5 kD	<0.2 μm	<100 kD	<30 kD
La (ppt)	54	49	49	39	394	342	317	174	1078	748	370
Ce	47	36	36	27	68	55	44	27	2580	1552	773
Pr	11	7	7	5	82	61	51	25	348	248	130
Nd	48	33	33	22	338	239	200	96	1537	1099	629
Sm	12	—	—	—	58	37	31	14	267	196	121
Eu	—	—	—	—	12	—	—	—	54	37	23
Gd	19	13	13	—	40	32	25	13	216	150	89
Tb	—	—	—	—	—	—	—	—	25	18	—
Dy	21	14	13	10	23	15	13	—	102	72	38
Ho	—	—	—	—	—	—	—	—	18	13	—
Er	15	12	11	—	16	10	—	—	58	39	24
Tm	—	—	—	—	—	—	—	—	—	—	—
Yb	12	—	—	—	13	10	—	—	48	37	24
Lu	—	—	—	—	—	—	—	—	—	—	—
ΣREE (ppb)	0.25	0.19	0.19	0.14	1.06	0.8	0.71	0.37	6.35	4.22	2.25
Ce/Ce*	0.46	0.44	0.44	0.44	0.09	0.09	0.08	0.10	0.98	0.84	0.82
La _N /Yb _N	0.45	—	—	—	3.14	3.36	—	—	2.24	2.04	1.53
Al (ppb)	43.7	42.4	37.7	36.6	23.0	25.0	24.2	15.0	174	83.1	33.8
Mn	24.1	23.7	19.7	17.1	26.4	26.3	20.7	16.7	32.4	30.5	23.8
Fe	58	58	64	57	30	31	30	20	453	155	51.7
Sr	203	202	174	155	70.6	70.6	71.0	45.0	25.9	27.0	28.8
Ba	73.4	73.3	57.3	65.7	30.5	30.3	29.9	18.7	9.7	15.0	13.1
Th (ppt)	—	—	—	—	—	—	—	—	93	50	23
U	—	—	—	—	—	—	—	—	61	33	14
DOC (mg/l)	1.2	0.8	0.8	3.8	0.8	0.9	0.8	n.m.	15.1	11.5	9.3

n.m.: not measured.

— indicates concentrations below detection limits.

Detection limits from Viers et al. (1997) and blank levels in the 0.2 μm , 100,000 D, 30,000 D and 5,000 D filtrates.

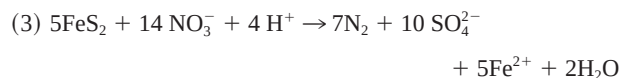
precise determination of the microparticle composition would require saturation index calculations with respect to minerals such as kaolinite or/and goethite, or characterization of the colloidal fraction using for example transmission electronic microscope (TEM) observations (Oliv  -Lauquet, 1996). These two latter approaches remain to be developed in the case of the Kervidy/Co  t-Dan aquifer.

4.2. Processes Controlling the Behaviour of REE Along Groundwater Flow Paths

One of the key characteristics of the Kervidy/Co  t-Dan aquifer is the presence of correlated variations of nitrate and sulfate concentrations, which appear to occur following two different groundwater circulation paths (Fig. 8). The first path is nearly vertical and corresponds to the infiltration of water from the upper compartment of the aquifer located in the weathered schists into the deeper compartment located in the fresh schist (flow path N   1 in Fig. 8). As shown in Table 1 and as further discussed by Pauwels et al. (1998) and Mol  nat et al. (2000b), this first path is characterized by a progressive decrease of the NO_3^- concentrations, and by a build up of the SO_4^{2-} and Fe contents. The second groundwater flow path follows the topographic surface and appears to be limited to the weathered schist aquifer (flow path N   2 in Fig. 8). This flow corresponds to the downslope transfer of part of the water that is steadily recharged in the upland domains by infiltration.

Shallow wells PG2 to PG6 and PJ1 to PJ4 sampled this sub-surface flow which is characterized by a regular decrease of the nitrate content from uphill down to bottomhill wells, while the sulfate concentration progressively increases along the same flow path (Fig. 8, Table 1).

The REE distribution and content variations already indicated that migration of the groundwater along flow path N   1 leads to a REE content fall as well as a Ce anomaly decrease at depth (Fig. 8; see also Fig. 9). As already pointed out, Pauwels et al. (1998) proposed that part of the nitrate depletion, which is observed along flow path N   1, may be due to a denitrification reaction, mediated by the autotrophic bacteria *Thiobacillus denitrificans*, and involving the oxidation of pyrite (FeS_2) as follows:



As assessed by the comparison of the deep and surface water chemical composition (Table 1), this denitrification reaction which is a common process in nitrate-contaminated aquifers (e.g., Frind et al., 1990; B  ttcher et al., 1992), increases both the pH and SO_4^{2-} and Fe contents of the solution. The reducing conditions which prevail in these denitrified Fe- and sulfate-rich waters may explain the smaller negative Ce anomalies as compared to their shallow, oxidized counterparts. Similarly, the

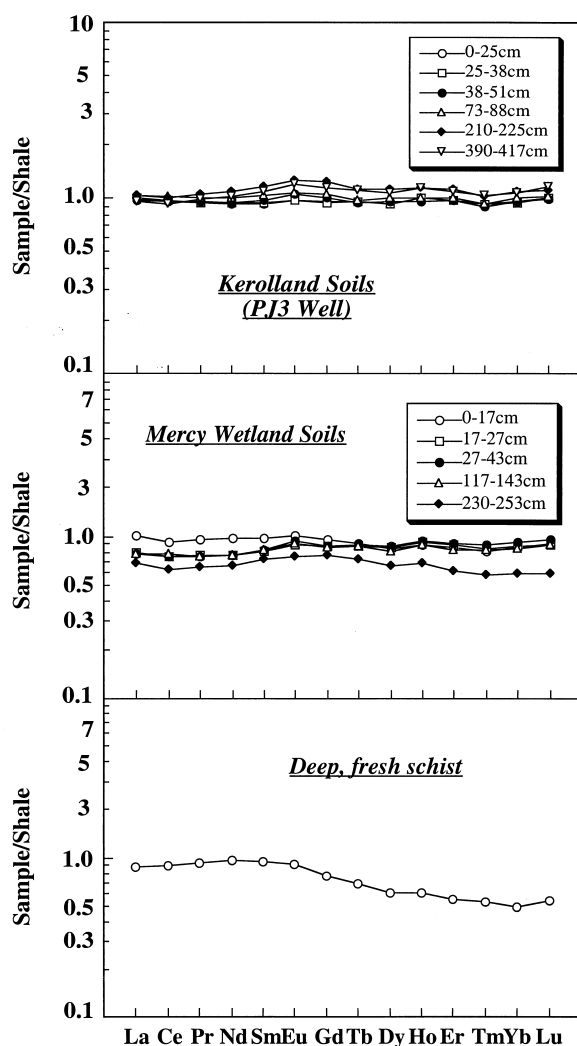


Fig. 6. Shale-normalized REE patterns illustrating the lack of Ce anomaly in the soils and basement schist of the Kervidy/Coët-Dan catchment. The corresponding data are reported in Appendix A.

pH increase resulting from this reaction could favour surface complexation and sorption of the REE, especially of the LREE for which solid-liquid partitioning coefficients are known to increase with pH (Sholkovitz, 1995). As a consequence, the pyrite oxidation reaction could also indirectly account—by adsorption on soil particles—for both the REE content drop and pattern shape flattening which are observed between shallow and deep waters.

However, other processes could also enhance the removal of REE during the downward water migration. The first relates to the precipitation of sulfate minerals in the deep aquifer. Study of rock matrix revealed indeed the presence of jarosite ($\text{KFe}(\text{SO}_4)(\text{OH})_6$) and natroalunite ($\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$) which are both thought to be secondary crystallisation products of the above denitrification reaction (Pauwels et al., 1998). Although the capacity of these two mineral phases to accept REE in their crystal lattice or to adsorb these elements on their crystal surfaces remains to be quantitatively investigated, it is to be noted that other sulfate minerals such as barite have been

shown to contain REE up to the ppm level (e.g. Guichard et al., 1979). A second possible mechanism relates to the role of colloids. As shown above, between about 40% and 65% of the REE present in the nitrate-rich, shallow groundwaters are carried by colloidal microparticles. Although the size of these particles can be expected to be much smaller than the size of the pores (that are important for water drainage), it remains however that some might aggregate to form larger particles during transport or be pumped by adsorbing on the solid phase (O'Melia, 1980; Buffle and Leppard, 1995). Note that this second process of colloid trapping is independent of the denitrification reaction, which is not the case in the hypothesis of a REE drop due to pumping of these elements by secondary sulfate mineral precipitation.

We now turn to discussing the origin and significance of the REE variations observed along shallow water flow path N° 2 (Fig. 8). Looking at the Guériniec transect waters which exhibit the most regular variation, it can be seen that the dominant feature of this second flow path is the emergence of a regular decrease of the negative Ce anomaly while the groundwater is flowing downslope (Fig. 3b). As with flow path N° 1, the Ce anomaly size decrease appears to be in phase with a drop and build up in NO_3^- and SO_4^{2-} concentrations, respectively (Table 1). However, we note two major differences when comparing flow paths N° 1 and N° 2. Firstly, the Ce anomaly drop and concomitant build up of SO_4^{2-} concentrations is not accompanied by an increase of the Fe content of the water. In fact, the Fe concentrations remain always very low along flow path N° 2 (i.e., <52 ppb against >3000 ppb for the deep, denitrified waters), whichever the Ce/Ce* ratio may be (see Fig. 10). Secondly, the Eh values remain high, ranging between 344 and 544 mV along the Guériniec transect. This marked difference suggests that both the drop in Ce anomaly amplitude and nitrate contents might not arise in response to denitrification as assumed in the case of flow path N° 1. As suggested by preliminary hydrological modelling, the observed trend may indicate a progressive mixing phenomenon along the hillslope between a nitrate-rich water coming from the recharge zone in the upland domain (flow path N° 2; Fig. 8) and a return flow water comprising deep, denitrified water (flow path N° 3 in Fig. 8). In this case, the low Fe content in the shallow groundwaters could be explained by the re-oxidation of Fe^{2+} during water mixing and its precipitation as secondary iron oxyhydroxide.

4.3. Control of DOC and Heterotrophic Redox Processes on the REE Budget of Wetland Waters

Thorough interpretation of the wetland water REE signatures and REE dynamics requires elucidation of three important questions: (i) what is the role played by dissolved organic matter on the REE and other trace-element budget of these waters? (ii) How explain the lack of Ce anomaly despite the observed marked changes in redox conditions? Finally (iii) what is the exact relationship between the development of temporary reducing conditions, build up of DOC content and the seasonal variability of REE and trace-element concentrations?

Let us moved to the first question. As previously suggested (Sholkovitz, 1995; Viers et al., 1997), the behaviour of many trace elements in natural waters appears to be linked with that

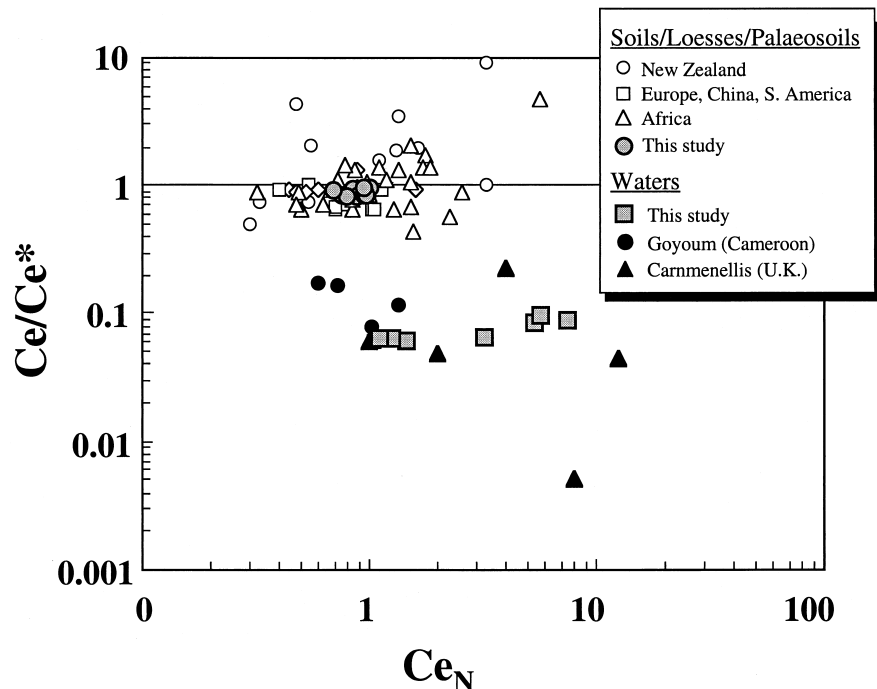


Fig. 7. Ce/Ce^* vs. Ce_N plot illustrating the extreme Ce depletion of Kervidy/Coët-Dan upland groundwater. Also shown for comparison (a) the results obtained by Smedley (1991) and Braun et al. (1998) for similar, strongly Ce-depleted groundwaters from the Cammenellis (South England) and Goyoum (Cameroon) areas, and (b) the published data for a large number of soil samples from different continents (Rankin and Child, 1976; Gallet et al., 1996; Gallet et al., 1998; this study). Note that none of the soil samples investigated so far has yielded REE profiles as Ce depleted as those characterizing these groundwaters. Would you please note that the Ce_N groundwater values are multiplied by 10^6 .

of dissolved organic ligands. As in the case of Th, REE seem to be strongly complexed by organic matter due to high stability constants (Byrne and Li, 1995). In the Kervidy wetland waters, REE concentrations are positively correlated with those in DOC (Fig. 11), and together with Th, REE contents increase in spring when DOC contents get higher (Table 1). Moreover, preliminary ultrafiltration experiences through decreasing pore-size membranes show that the DOC, REE, U, Th, Fe, Al and Mn contents decrease at each step of filtration (Table 2). The data show that most of the REE and Th, U and Al budget are controlled by the organic pool in the wetlands as previously suggested elsewhere (Thurman, 1985; Viers et al., 1997). However, since these elements may also be adsorbed to Fe and/or Al oxides, further investigation concerning the colloids separation has to be undertaken to really assess the role of the organic carriers in such a context.

Concerning the second point—lack of Ce anomaly—it is clear that this is a rather surprising feature given the redox sensitive chemistry of this element and the occurrence of seasonal redox variations in the Mercy wetland. From Figure 11, it can be seen that the organic-rich waters from this wetland indeed underwent changes in their redox conditions by the end of February (from oxic to anoxic) but that this change had no effects on the Ce/Ce^* ratio which remained close to one all other the course of the studied period. On the contrary, one can notice from Table 1 that this change corresponded to a marked build up of the dissolved Fe and Mn concentrations, which is likely to be due to the reductive dissolution of soil Fe and

Mn-oxyhydroxides. Thus, it appears that Ce, unlike Fe and Mn, behaves independently of the redox conditions in these wetland waters. We wish to consider that this is likely due to the fact that Ce and the other REE are not true dissolved species in these waters, but occur predominantly as organic complexes. Should the negative Ce anomaly often observed in oxic waters be due to CeO_2 (cerianite) precipitation (Braun et al., 1990; Koppi et al., 1996), one can propose two hypotheses to explain the lack of negative Ce anomaly in the Mercy wetland during the winter oxidizing period: (i) either precipitation becomes here impossible because of the complexation of Ce^{4+} (as other REE^{3+}) by organic matter, or (ii) cerianite precipitates, but is adsorbed onto colloids being then considered as part of the solution.

As regards the third question—which is the role of temporary reductive processes?—it is to be noted that the build up of trace-element contents occurs in phase with DOC and Eh variations (Fig. 11). This strongly suggests that the redox and colloidal organic matter seasonal variability, which is characteristic of many wetland waters world-wide, is likely to control the REE budget of these waters. As pointed out earlier, the Eh drop that occurred at the end of February was accompanied by an increase of the Fe and Mn content of the water, which is interpreted as due to the dissolution of soil-forming Fe and Mn oxyhydroxides (Lakind and Stone, 1989; Fergusson, 1990; Deng and Stumm, 1994; Chuan et al., 1996; Carroll et al., 1998). Fe and Mn oxyhydroxides are known to be very effective scavengers of REE and of other trace elements (Trolard et al.,

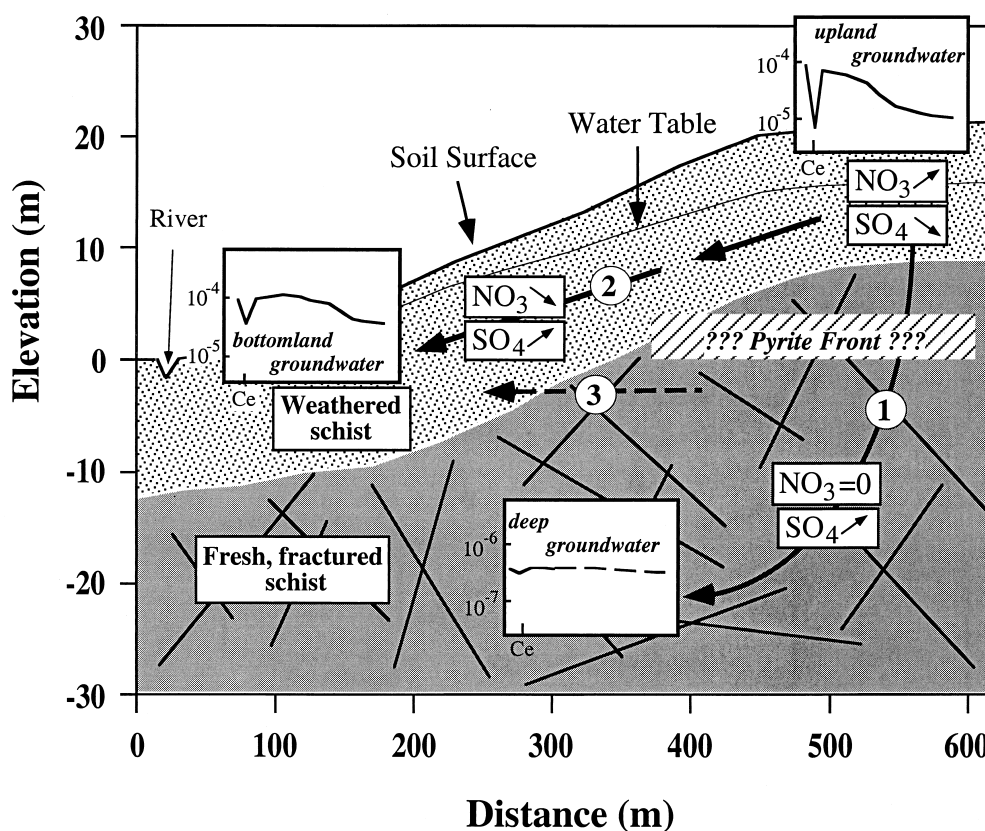


Fig. 8. Sketch diagram illustrating the presence of three groundwater flow paths in the organic-poor part of the Kervidy/Coët-Dan aquifer. Flow path N° 1 corresponds to recently recharged, nitrate-rich waters moving downwards into the lower, fresh schist compartment of the aquifer, while flow path N° 2 represents sub-horizontal water movement in the highly permeable upper compartment of the aquifer (weathered schist and loess units). Flow path N° 3 (represented as a dashed line) is assumed to correspond to return flow of deep, denitrified groundwater. The small black arrows on nitrate and sulfate white boxes correspond to increasing or decreasing contents. Note that the exact geometry of the pyrite front which is thought to trigger autotrophic reduction of the nitrate has still to be determined. See text for further details. Adapted from Molénat (1999) and Molénat et al. (2000a).

1995; Bau, 1999). Therefore, it is expected that the seasonal reductive dissolution of Fe and Mn oxyhydroxides should lead to an increase of the trace-element concentrations of wetland waters. As recently established (Olivie-Lauquet et al., 2000), DOC and Eh variations may be controlled by microbial activity when temperature increases in these waterlogged soils. Then, the microbial activity enhance the chemical weathering leading to release of REE and other trace elements in solution.

5. CONCLUDING REMARKS

Several conclusions regarding the nature of the processes that control the hydrochemistry of REE in shallow groundwater can be derived from this study, some having local implications other having a much broader significance. Firstly, on a *local scale* the data have shown the following:

1. The previously determined hydrological domains do correspond to “hydrochemical” end-members which are: (i) the shallow groundwaters from the hillslope domain; (ii) the deepest groundwater domain; and (iii) the wetland domain.
2. Within the groundwater table itself, the different REE signatures between the upper levels and the deepest part of the

water table are due to the combining of several processes, namely: (i) the occurrence of water circulating in the weathered zone characterized by a large negative Ce anomaly related to oxidizing conditions, which prevents mobilisation of Ce and other REE. (ii) At depth, this Ce anomaly tends to disappear in response to both reducing conditions in the fresh schists by stabilizing Ce(III) in solution, and removal of other REE from the solution. This removal of REE may occur, either during secondary sulfate minerals precipitation, or by colloids-borne REE trapping through the soil pores when water is circulating.

3. The nature of the involved colloids seems to be different along the hillslope (mainly mineral) and in the wetlands (organic).

On a *global scale*, this study put constraints on the role of the source-rock composition, the redox changes as well as the colloidal pool on the distribution of REE in groundwaters as established by the following concluding remarks:

1. One of the most striking result is probably the dominant control of the colloidal organic matter on REE and other trace-element budgets in the wetlands, which is comparable

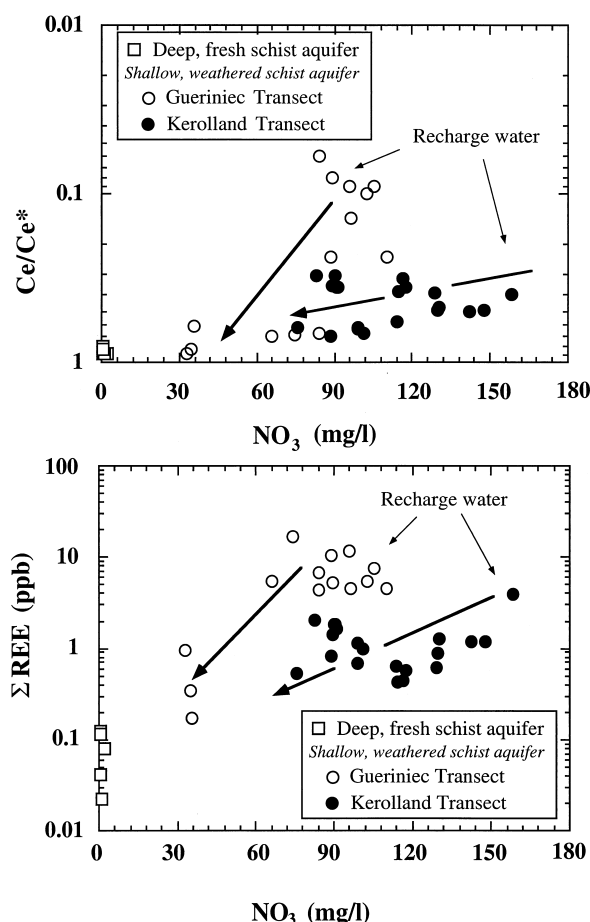


Fig. 9. Diagrams showing rough positive correlations between (a) Ce/Ce* ratios and (b) REE contents, and NO_3^- concentrations for Kervidy/Coët-Dan groundwaters. The arrows indicate chemical evolution along shallow groundwater flow paths N° 1 (see Fig. 8) for Kerolland and Guériniac transects.

to the situation observed in wetlands from tropical zone (Viers et al., 1997; Braun et al., 1998). This result is of broad significance as it demonstrates that the REE distribution in catchments is more likely controlled by hydrological and ensuing redox conditions constraints than by climatic conditions.

- The Ce behaviour in the organic waters from wetlands may not be completely controlled by redox processes. The surface properties of the organic colloids are probably able to complex Ce and/or interfere or partially mask the redox processes by inhibiting the development of Ce anomaly in oxidizing waters. This has a strong implication because, as with Fe, Ce cannot be then considered as a good tracer of redox conditions in organic-rich waters. Indeed, this may complicate the use of Ce content as a redox proxy in organic-rich paleosols, and restoration of redox conditions at the time of deposition or pedogenesis.

To conclude the results stemming out of this study suggest that REE can be used as an efficient 'hydrological tool.' Although being potentially affected by chemical (redox, adsorption, complexation...) processes and therefore being consid-

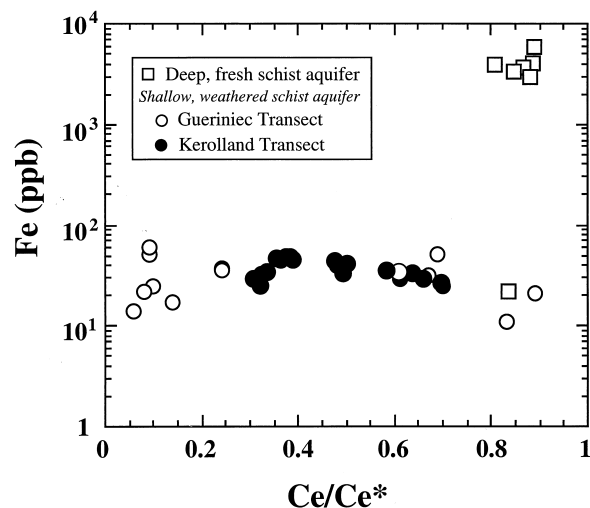


Fig. 10. Fe vs. Ce/Ce* plot illustrating contrasted Ce anomaly-Fe relationship between deep and shallow, organic-poor groundwaters.

ered as a non-conservative tracer, the different REE patterns display fingerprints typing each hydrological domain through space and time. Furthermore, their sensitivity to redox variation, complexation or uptake onto sorptive surfaces strongly suggest that the REE can be also useful tracers of groundwater-rock interaction elsewhere.

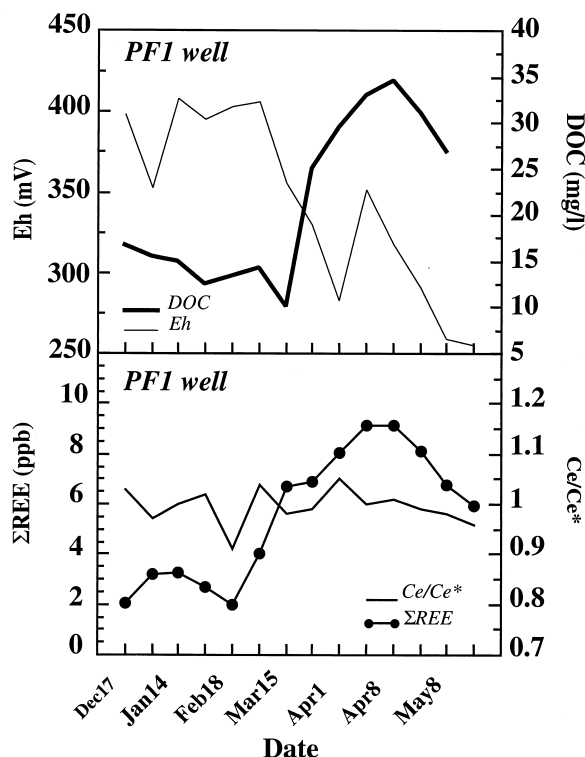


Fig. 11. Time series results for PF1 wetland well waters. Note that while Eh, DOC and REE contents show marked seasonal variations the Ce/Ce* ratio remains nearly constant throughout the entire studied period.

Acknowledgments—We thank the technical staff in Rennes, both at Géosciences Rennes and at INRA Science du Sol for their kind assistance in part of as well the sampling as the analytical work. DOC measurements were done in ECOBIO (CNRS UMR 6553-Rennes I University, France). M. Valladon and B. Reynier are gratefully acknowledged for their help during ICP-MS measurements in Toulouse (OMP-CNRS UMR 5563) (France). P. Smedley and anonymous reviewers are thanked for thorough and constructive comments as well as E. Oelkers and F. Podosek for editorial handling. This research was supported by the INSU-CNRS through Programmes PRH, PNRH and GDR CAREN.

Associate editor: E. H. Oelkers

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APPENDIX A

Table A. Major and trace-element composition of Kervidy soils and bedrock.^(a)

Sampling Locality	Mercy Wetland					Kerolland transect (PJ3 Well)						Deep, fresh schist (BRGM Well)
Sampling depth (cm)	0–17	17–27	27–43	117–143	230–253	0–25	25–38	38–51	73–88	210–225	390–417	1,700–4,000
SiO ₂ (%)	59.17	74.79	70.78	72.02	80.23	74.36	73.69	63.29	70.55	60.92	58.77	85.31
Al ₂ O ₃	13.57	12.43	16.17	13.41	7.04	9.59	9.57	14.52	12.47	18.2	19.02	6.92
Fe ₂ O ₃	4.71	1.60	2.17	5.09	6.54	3.89	4.16	9.87	6.2	7.13	7.77	1.79
MnO	0.01	0.01	0.01	0.02	0.01	0.03	0.03	0.08	0.02	0.1	0.07	—
MgO	0.48	0.35	0.56	0.51	0.51	0.52	0.52	1.43	1.05	2.23	2.5	0.04
CaO	0.14	0.05	0.04	0.02	0.03	0.25	0.28	0.14	0.14	0.08	0.14	0.01
Na ₂ O	0.14	0.13	0.09	0.01	—	0.54	0.68	0.42	0.64	0.76	0.66	—
K ₂ O	2.27	2.30	3.11	2.70	1.26	1.79	1.76	2.38	2.19	3.21	3.41	1.57
TiO ₂	0.80	0.85	0.89	0.71	0.45	1.07	1.07	0.98	1.03	0.93	0.96	0.46
P ₂ O ₅	0.10	0.03	0.03	0.04	0.06	0.12	0.13	0.09	0.06	0.11	0.14	0.03
L.O.I.	16.77	5.24	4.44	3.88	2.74	6.24	6.24	5.89	4.16	4.7	4.81	2.19
Total	98.2	97.8	98.3	98.4	98.9	98.4	98.1	99.1	98.5	98.4	98.3	98.3
Rb (ppm)	95	91	119	103	47	73	73	95	88	118	127	58
Sr	51	56	71	63	39	54	54	45	52	47	49	56
Ba	642	572	714	577	286	434	430	562	506	725	759	356
Th	4	2	4	7	4	6	4	7	9	9	9	3
U	3	3	2	2	2	3	3	1	3	4	3	2
La (ppm)	31.4	24.9	24.04	24.31	21.43	30.68	30.85	30.03	32.27	32.38	29.73	26.99
Ce	61.5	50.2	50.0	52.3	41.65	64.51	64.64	63.97	68.65	67.03	62.31	59.86
Pr	7.58	6.03	5.96	5.95	5.13	7.46	7.47	7.52	7.95	8.37	7.76	7.29
Nd	29.7	23.3	23.1	23.38	20.07	28.16	28.40	28.74	30.46	33.09	30.66	29.11
Sm	5.82	4.86	4.92	4.95	4.29	5.58	5.64	5.84	6.22	6.98	6.45	5.6
Eu	1.27	1.11	1.18	1.14	0.93	1.22	1.21	1.31	1.34	1.58	1.49	1.14
Gd	5.25	4.77	4.75	4.74	4.24	5.26	5.19	5.54	5.81	6.80	6.23	4.25
Tb	0.76	0.74	0.75	0.74	0.62	0.81	0.81	0.80	0.83	0.95	0.94	0.59
Dy	4.65	4.78	4.83	4.48	3.63	5.19	5.14	5.28	5.53	6.21	5.95	3.34
Ho	0.92	0.96	0.98	0.92	0.71	1.05	1.04	0.99	1.04	1.18	1.18	0.63
Er	2.80	2.90	2.96	2.71	2.01	3.21	3.17	3.16	3.31	3.69	3.54	1.8
Tm	0.40	0.42	0.44	0.41	0.29	0.46	0.46	0.45	0.46	0.51	0.52	0.27
Yb	2.64	2.73	2.84	2.61	1.83	3.03	2.94	2.99	3.12	3.39	3.30	1.52
Lu	0.41	0.41	0.44	0.41	0.27	0.46	0.46	0.45	0.47	0.51	0.53	0.25
Ce/Ce*	0.91	0.93	0.95	0.99	0.91	0.97	0.97	0.97	0.98	0.93	0.94	0.97

^(a) Samples recovered from drill cuttings corresponding to the wells monitored during this study. Sampling localities are given in Fig. 1.

Concentrations of major and trace (Rb, Sr, Ba, Ni, Cr, Cu, Zn, Th, Pb and U) elements were determined by XRF spectrometry at the Rennes I University (France) using a Philips PW 1404 sequential spectrometer. Analytical uncertainties are estimated at 3% for major elements, except for MnO and P₂O₅ whose concentrations are precise to only 10 and 5%, respectively. Analytical errors are estimated at about 3% for Rb, Sr, Ba, Ni, Cr, Zn, Zr and Pb, 10% for Th and 25% for U. REE were analyzed by ICP-MS (HP 4500, Hewlett Packard) at the Rennes I University. An international standard (BHVO basalt) was used to check the validity of the dataset. Analytical uncertainties, including chemical preparation, blank effect and mass spectrometry analysis are estimated at about 3% for each REE.

L.O.I. corresponds to Loss On Ignition.

— indicates concentration below the detection limit.

APPENDIX B

ANALYTICAL PROCEDURE

1. Sample Collection and Filtration

Samples of hillslope groundwater were collected from one spring (Boquetteu, see Fig. 1) and nine wells located along two transects (the Kerolland and Guériniec transects in Fig. 1) perpendicular to the topographic slope (i.e. along a direction parallel to the expected groundwater flow path). These wells (PJ1–4; PG2–6) are between 3- to 6-m-deep. Deep groundwater samples were collected from two 10-m-deep wells set up in the bottomland part of the Kerolland (PJ6; Fig. 1)

and Guériniec (PG1; Fig. 1) transects, and from a 40-m-deep well dug by BRGM close to the outlet of the Kervidy/Coët-Dan catchment (see Fig. 1). Finally, samples of organic-rich groundwater were collected from two shallow wells (PF1, 0.5-m-deep, and PF3, 1.5-m-deep) located in the Mercy wetland (Fig. 1).

Water samples were regularly collected from December 1997 to May 1998, except those recovered from PG1 and the deep BRGM well which were sampled only once, in February and January 1998, respectively. The frequency of sampling was about one sample every one or two months for the hillslope groundwaters, while for the wetland waters this frequency was reduced to one sample twice a month, or even less (i.e. one sample every three or five days during the onset of reduced conditions in March 1998). The Boquetteu spring was moni-

Table B. Comparison of the analytical accuracy of the instruments used during this study against certified and published values of the SLRS-3 water geostandard.

	Certified values ($\pm\sigma$)	This study ¹ ($\pm\sigma$)	This study ² ($\pm\sigma$)	Louvat (1997) ($\pm\sigma$)	Viers et al. (1997) ($\pm\sigma$)	Olivié-Lauquet et al. (in prep.) ($\pm\sigma$)
ICP-MS Type		Perkin Elmer Elan 5000	Perkin Elmer Elan 6000	V.G. Plasma Quad II	Perkin Elmer Elan 5000	Hewlett-Packard HP 4500
Al (ppb)	31 $\pm$ 3	31.9 $\pm$ 1.3	30.7 $\pm$ 0.6	30.3 $\pm$ 6.1	31.1 $\pm$ 1.2	31.1 $\pm$ 0.7
Mn	3.9 $\pm$ 0.3	3.9 $\pm$ 0.2	3.9 $\pm$ 0.1	3.5 $\pm$ 0.5	3.8 $\pm$ 1.5	3.8 $\pm$ 0.1
Fe	100 $\pm$ 2	110 $\pm$ 7	111 $\pm$ 6	106 $\pm$ 14	107 $\pm$ 11	109 $\pm$ 1
Sr	n.c.	31.3 $\pm$ 0.9	31.6 $\pm$ 0.9	30 $\pm$ 4	30.8 $\pm$ 6.2	32.7 $\pm$ 0.4
Ba	13.4 $\pm$ 0.5	13.4 $\pm$ 0.5	13.5 $\pm$ 0.3	12.6 $\pm$ 1.6	13.0 $\pm$ 0.4	13.5 $\pm$ 0.1
La	n.c.	0.228 $\pm$ 0.009	0.236 $\pm$ 0.007	0.24 $\pm$ 0.03	0.24 $\pm$ 0.01	0.234 $\pm$ 0.002
Ce	n.c.	0.27 $\pm$ 0.01	0.279 $\pm$ 0.008	0.30 $\pm$ 0.07	0.28 $\pm$ 0.01	0.278 $\pm$ 0.003
Pr	n.c.	0.057 $\pm$ 0.003	0.057 $\pm$ 0.001	0.059 $\pm$ 0.007	0.059 $\pm$ 0.001	0.0589 $\pm$ 0.0004
Nd	n.c.	0.22 $\pm$ 0.02	0.223 $\pm$ 0.007	0.23 $\pm$ 0.02	0.26 $\pm$ 0.01	0.225 $\pm$ 0.003
Sm	n.c.	0.041 $\pm$ 0.006	0.043 $\pm$ 0.002	0.050 $\pm$ 0.008	0.047 $\pm$ 0.008	0.046 $\pm$ 0.001
Eu	n.c.	n.m.	0.0057 $\pm$ 0.0008	0.011 $\pm$ 0.004	n.m.	0.0089 $\pm$ 0.0003
Gd	n.c.	0.027 $\pm$ 0.006	0.0294 $\pm$ 0.0001	0.038 $\pm$ 0.007	n.m.	0.033 $\pm$ 0.001
Dy	n.c.	0.022 $\pm$ 0.005	0.020 $\pm$ 0.001	0.023 $\pm$ 0.004	n.m.	0.0227 $\pm$ 0.0009
Er	n.c.	0.012 $\pm$ 0.003	0.0123 $\pm$ 0.006	0.012 $\pm$ 0.002	n.m.	0.0141 $\pm$ 0.0005
Yb	n.c.	0.011 $\pm$ 0.003	0.0108 $\pm$ 0.0004	0.011 $\pm$ 0.002	n.m.	0.0115 $\pm$ 0.0004
Th	n.c.	0.012 $\pm$ 0.004	0.011 $\pm$ 0.004	n.m.	0.046 $\pm$ 0.007	0.027 $\pm$ 0.002
U	n.c.	0.041 $\pm$ 0.006	0.051 $\pm$ 0.008	0.041 $\pm$ 0.008	0.042 $\pm$ 0.005	0.045 $\pm$ 0.001

⁽¹⁾ Mean of 18 separate measurements.⁽²⁾ Mean of 12 separate measurements.

n.c.: no certified value available.

n.m.: not measured.

Trace-element and dissolved organic concentrations in the 0.2 μ m filtrates of the Kervidy catchment groundwaters.

tored earlier, from September 1996 to January 1997, as part of an unpublished preliminary work. Several physico-chemical parameters were measured directly in the field: pH, temperature and redox potential (Eh). The pH was measured with a combined Sentix 50 electrode after a calibration performed with WTW standard solutions (pH = 4.01 and 7.00 at 25°C). The accuracy of the pH measurement is ± 0.05 . Eh was measured using a platinum combination electrode (Mettler Pt 4805). Electrodes are inserted into a cell constructed to minimize diffusion of atmospheric oxygen into the sample during measurement. Eh values are presented in millivolts (mV) relative to the standard electrode Ag/AgCl₂, and are corrected for temperature and pH drift using the equation of Bohn (1970):

$$\text{Eh cor. (mV)} = \text{Eh meas. (mV)} + 230 - 0.76 (T-25) + 60 \cdot (\text{pH}-7)$$

where Eh meas. is the Eh measured relative to the standard electrode Ag/AgCl₂; T and pH are the temperature (expressed as Celsius degree) and pH of the water, respectively. In this study, redox measurements are interpreted with justifiable caution, with the understanding that the electrode was responding to unidentified electroactive species that may not be in equilibrium with the chemical species of interest (Bohn, 1970). However, Eh measurements appear to be reliable indicators of redox state, particularly in soil solution where oxygen may be absent and dissolved iron concentration high.

Samples used for determination of dissolved (<0.22 μ m) trace-element and DOC concentrations were pumped using a Teflon tubing connected to a polyethylene syringe. The collected waters (about 50 ml) were immediately filtered on site using 0.22 μ m cellulose acetate

Table C. Detection limits and blank concentrations.⁽¹⁾

	Detection limit ⁽²⁾	Blank <0.22 μ m	Blank <100,000 D	Blank <30,000 D	Blank <5,000 D
Al (ppb)	0.054	0.6 $\pm$ 0.2	0.16 $\pm$ 0.03	0.12 $\pm$ 0.01	0.2 $\pm$ 0.1
Mn	0.01	0.06 $\pm$ 0.03	0.032 $\pm$ 0.003	0.008 $\pm$ 0.004	0.051 $\pm$ 0.004
Fe	1.12	21 $\pm$ 6	22 $\pm$ 2	2.6 $\pm$ 0.5	2.9 $\pm$ 0.4
Sr	0.070	0.02 $\pm$ 0.02	0.005 $\pm$ 0.003	—	—
Ba	0.016	0.04 $\pm$ 0.3	0.03 $\pm$ 0.01	—	0.054 $\pm$ 0.006
La	0.001	0.002 $\pm$ 0.002	—	—	—
Ce	0.001	0.003 $\pm$ 0.003	—	—	—
Pr	0.001	0.002 $\pm$ 0.002	—	—	—
Nd	0.011	0.01 $\pm$ 0.01	—	—	—
Sm	0.011	0.01 $\pm$ 0.01	—	—	—
Th	0.002	0.005 $\pm$ 0.004	—	—	—
U	0.002	0.005 $\pm$ 0.004	—	—	—

⁽¹⁾ The hereabove reported data were obtained using an ELAN 5000 Perkin Elmer ICP-MS.

— Indicates concentrations below detection limit.

⁽²⁾ Data from Viers et al. (1997).

Trace-element concentrations (in ppb, ppt or mg/l) in the different filtrates obtained by sequential (tangential) ultrafiltration for groundwater samples from the hillslopes (non-saturated zone: weathered schists) and from the wetland of the Kervidy catchment.

filter capsule (polyether sulfone membrane), and divided into two aliquots. Aliquots used for trace-element analyses (about 30 ml) were immediately acidified with ultrapure distilled 7M HNO₃ and stored in pre-cleaned, acid-washed polyethylene bottles. Those used for DOC analyses were not acidified and stored at 4°C in the dark. DOC measurements were performed within less than 36 h. after sampling.

A few larger (5 l) samples were also collected and successively filtered through membrane of smaller pore sizes (0.22 µm, 100,000 Daltons (D), 30,000 D – 1 D = 1 g mol⁻¹ and 1,000 D = 1 kD to carry out ultrafiltration experiments in order to allow separation of colloids from ‘true dissolved’ forms. Ultrafiltration experiments were performed using a Sartorius tangential filtration unit (Ultrasart). Two samples were filtered to 5 kD. Each membrane was cleaned in a bath of citrate tetraborate 0.2M, then rinsed successively with HNO₃ 0.1M, NaOH 0.1M and finally with 15 l of ultrapure water.

2. Chemical Analyses

Dissolved organic carbon content was analysed on a Shimadzu TOC 5000 carbon analyzer at the Laboratoire Ecobio (Rennes University). REE concentrations as well as concentrations of a few other trace elements (Ba, Sr, Fe, Mn, Al, Th, U) were determined by ICP-MS

(Elan 5000 and Elan 6000, Perkin Elmer) at the Toulouse University (France). Indium and Rhenium were used as internal standards. The isobaric interferences due to Ba and LREE oxides or hydroxides on the MREE and HREE were checked and corrected following the method developed by Valladon et al. (1995). The validity of the results presented here for Al, Mn, Fe, Sr, Ba, Th and U can be checked from Table 3 where concentrations measured during the course of this work for the international geostandard SLRS-3 (Riverine Reference Materials for Trace Metals certified by the National Research Council of Canada) are reported along with certified values and several published datasets. As can be seen in Table B, no certified REE content is given for SLRS-3. However, regular analyses of SLRS-3 performed along the course of this work yielded reproducible REE results (see Table B) which are in good agreement with previously published data (e.g. Viers et al., 1997; Louvat, 1997).

All procedures (sampling, filtration and storing) were carried out in order to minimize contamination. Blank results are reported in Table C for both 0.22 µm routine filtration procedure and ultrafiltration experiments, and compared in the same table to the detection limits determined on the ICP-MS based at Toulouse University (France). As can be seen, blanks were generally negligible, those for the REE being close to, or even lower than the detection limits.