Aquat Geochem (2009) 15:485–495
DOI 10.1007/s10498-009-9062-7

REVIEW

Distribution, Speciation, and Extractability of Cadmium in the Sedimentary Phosphorite of Hahotoé-Kpogamé (Southern Togo)

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Received: 23 September 2007 / Accepted: 27 February 2009 / Published online: 21 March 2009

Abstract The geochemistry and extractability of Cd in the phosphorite deposits of Hahotoé-Kpogamé (southern Togo) have been studied using various methodologies such as Cd distribution in profiles, grain-size dependence analysis of Cd content, Cd localization using scanning electron microscopy (SEM), sequential acid extraction, and a leaching experiment with artificial seawater. Results demonstrate that in the phosphorite deposits of Hahotoe-Kpogame, Cd is enriched by a factor of 157 compared to shale and by a factor of 3 compared to average world phosphorite composition. The main carrier of Cd appears to be apatite. This is evidenced by significant high positive correlations between the Cd content and P_2O_5 (in bulk sediment$r = 0.7$ and in the 1–0.2 mm fraction $r = 0.9$). The grain-size dependence of Cd contents (concentrations decreasing with decreasing grain size) and SEM analysis supports these conclusions. Secondary Cd carriers include calcite, goethite, and various bone fragments. Sequential extraction tests with acetic acid and EDTA show an extraction rate reaching up to 40%. Leaching experiments with artificial seawater show evidence of Cd release in seawater. This leads to the conclusion that the processing of phosphorite by wet sieving using seawater and dumping of phosphorite tailings into the coastal waters of Togo can be a major source of marine pollution with Cd.

Keywords Phosphorites · Extractability · Cadmium speciation · Sequential extraction

1 Introduction

The geochemistry of phosphorites and their main constituent mineral francolite (carbonate fluorapatite) have been widely studied, owing to their economic importance and the

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potential utility of their geochemistry, mainly estimating paleo-marine chemistry (Cathcart 1980). Due to the numerous isomorphic substitutions in the francolite, marine sedimentary phosphorites are enriched with trace elements (Cd, Cr, Cu, Ni, V, Ba, Sr, U, and Zn) as well as some rare earth elements (REE) (Gulbrandson 1966, Tooms et al. 1969; Altschuler 1980, Jarvis et al. 1994, Al-Hwaiti et al. 2005). Cd is one of the trace elements highly enriched in phosphorites. The average Cd concentration in phosphorites is 18 mg/kg, which is 60 times its average content in shale, 0.3 mg/kg (Altschuler 1980). Some phosphorite deposits contain significantly higher average Cd concentrations than the "World" average phosphorite, such as in Senegal 65 mg/kg (Lucas et al. 1979). In these phosphorites, discrete samples with Cd concentrations of hundreds of mg/kg are not uncommon. The main difficulty in the interpretation of the geochemistry of Cd is to identify carrier phases in phosphorite. Some authors report that Cd does not replace Ca in the apatite structure in some sedimentary phosphorites, because no correlation is found between P_20_5 and Cd (Prévôt 1990; Nathan et al. 1997). The prevalent opinion is that Cd in phosphorites is related to organic matter (Gulbrandsen 1966, Baturin and Oreskin 1985). However, Sery et al. (1996) indicate that the cadmium occurs in the apatite lattice of sediment phosphorite ores from "west Africa." Nounah et al. (2005) have synthesized apatite with a great deal of cadmium in the lattice.

Cd in the environment is known as a very toxic heavy metal (Nomiyama 1975). The use of phosphorite ore as a fertilizer is a major pathway for Cd pollution of soil and groundwater (Cook and Ferney 1988; Merry and Tiller 1991). According to the previous studies, Cd mean values of 80 mg/kg or 66 mg/kg (Johnson AKC 1987, unpublished; Kunkel H 1990, unpublished) have been encountered in the phosphorites of Hahotoé/Kpogamé; however, those studies explained neither the speciation nor the possible bioavailability of Cd in the phosphorite deposits of Togo.

The tailings from phosphorite mining are being dumped directly into the coastal waters of Togo after the processing of the ore in the factory of Kpémé located near to the Beach, 30 km far away from the mining area. These mining activities are the main source of trace metal pollution in the coast of Togo (Gnandi and Tobschall 1999).

The aim of this study is to identify the factors controlling Cd distribution, speciation, and bioavailability using acid extraction and leachability of Cd from the phosphorites of Togo geological setting and studied localities.

The phosphorite deposits of Togo occur in a paleogeographical coastal basin that extends from the southeastern corner of Ghana through Togo and Benin into Nigeria. The exploited phosphatic layer, C1, extends SW–NE between Avéta and Dagbati over a length of 30 km, whereas the width does not exceed 3 km. The thickness of the economically valuable layer varies between 1 and 10 m (Fig. 1). The layer overlies an attapulgite clay layer and a phosphatic limestone of layer C2-3. This layer is covered with red barren soil being 2–30-m thick (Kilinc and Cotillon 1977).

2 Material and Methods

Phosphorite profile sampling was carried out during the dry season in February 2006 at four locations from the exploited layer C1, underlying attapulgite, and phosphatic limestone C2-3. Samples for heavy metal extraction studies and Scanning Electron Microscopy (SEM) were named as Mb and Mm: Mb represents the raw material and Mm the purified and marketable ore. For Cd, speciation various methods were used including grain-size

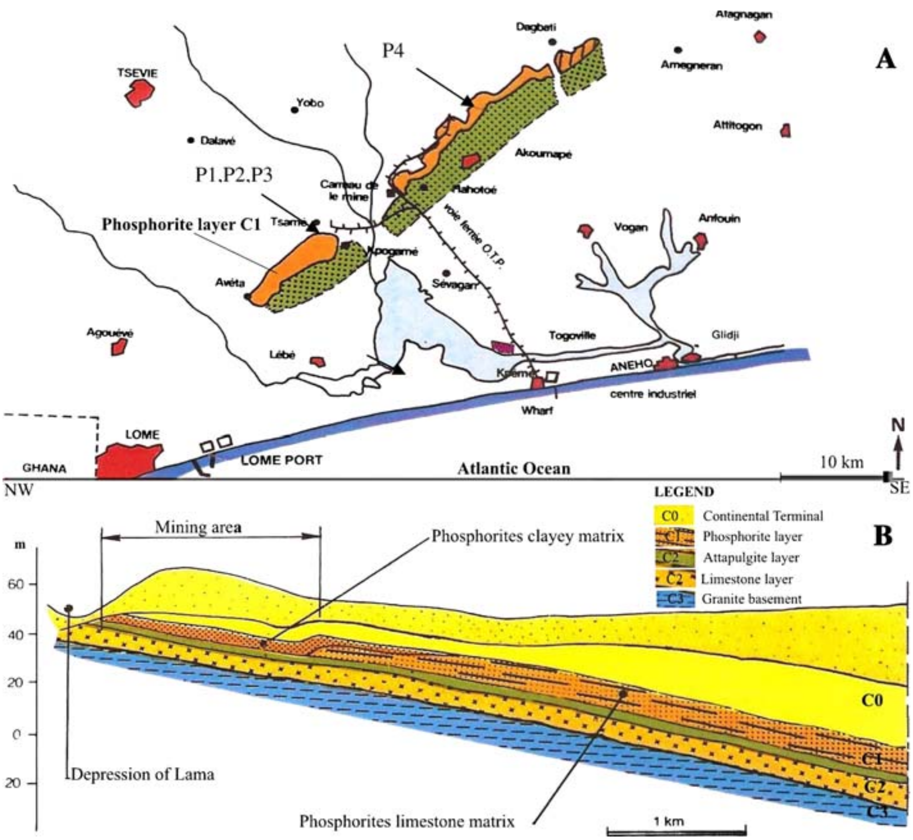

Fig. 1 Map showing the phosphorite deposits of Hahotoe-Kpogame with sampling profiles and a geological cross section

dependence of Cd concentrations, correlation coefficients between the contents of trace and major elements, and SEM.

In a wet sieving procedure using de-ionized water and Atterberg tubes, samples were split into various size fractions. After sieving, samples were dried in an oven at about 70°C for several days. The selected, finely crushed samples were prepared for SEM as unpolished rough samples. These samples were placed on a coated carbon tape in the SEM, and then vacuum was applied. The SEM investigation was conducted at a magnification of 4,600× using a model LEO 1550VP SEM, at California Institute of Technology in Pasadena, CA, USA.

In addition, sequential extraction methods have been used on Cd-rich phosphorite samples to study the extractability of Cd. Acetic acid and hydrochloric acid were used to dissolve apatite and Cd from various sediment phases. The following solution phases (F1–F6) were made:

F1: Phosphorite + conc. acetic acid 1:1,000 (0.016 mol/l, pH 3.4)
F2: Residue of F1 + 5 ml conc. acetic acid 1:100 (0.16 mol/l, pH 2.9)
F3: Residue of F2 + 5 ml conc. acetic acid 1:10 (1.6 mol/l, pH 2.5)

F4: Residue of F3 + 5 ml conc. acetic acid (16 mol/l, pH < 1), only carbonate free phosphorite
F5: Residue of F4 + 5 ml 2 N hydrochloric acid (pH < 1)
F6: Residue of F5 + 5 ml conc. hydrochloric acid (pH < 1)

The selective release of Cd adsorbed on clay minerals was investigated using the EDTA (0.2 M Titriplex III°)- method. The method is fairly aggressive and will attack apatite (Farrah and Pickerling 1978). The selective release of Cd absorbed on organic material, Mn-oxide, and hydroxides was conducted using 1 M ammonium-acetate at pH 7 (Salomons and Forstner 1980).

The leachability of Cd in phosphorite was studied using saline water. With increasing salt concentration, the effect of the salinity on the dissolution of apatite and heavy metals were studied. These agitation experiments were carried out using raw phosphorite material and various concentrations of salt (ratio 1/10) in different time intervals (4, 12, 18 and 24 h).

The concentrations of trace and major elements in solutions were measured using an ICP-AES (ICP-AES Type Spectroflame from Spectro). Phosphorus was determined by colorimetric method after Morphy and Riley (1962) using molybdenum blue. The mineralogical compositions have been determined using thin section and X-ray diffractometry (Fig. 2).

3 Results

3.1 The Distribution of Cd in Phosphorites

The distribution of Cd in the ore is heterogeneous and the concentrations of the studied samples vary between 2 and 116 mg/kg with an average of 47 mg/kg (Table 1). In profile 1, Cd is significantly depleted in the upper part of the layer C1 compared to the other profiles 2, 3, and 4, where a small or minor depletion is observed. Cd enrichments are observable in specific horizons of the profiles, e.g., in the bottom of P1, P3 (transition zone between phosphorites and limestone) as well as in the middle of P4, a dark brown oxidized zone (ground water fluctuation zone). Maximum Cd concentrations were found in phosphorites in P4 oxidized zone (109 mg/kg) and in limestone under C1 with a concentration

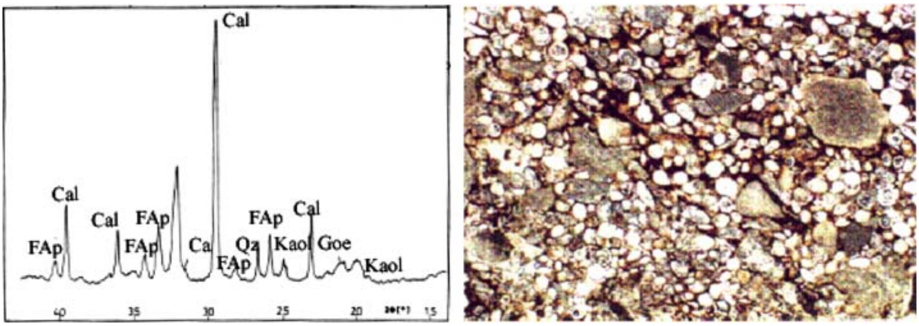

Fig. 2 X-ray diffractometry picks (left) and thin section picture (right) of phosphorite of Togo showing ovoid apatite mineral, calcite intraclasts, and bone fragments cemented by clay: FAp = Carbonate fluorapatite, Cal = Calcite, Qz = Quartz, Kaol = Kaolinite, Goe = Goethite

Table 1 Cd and major element contents of the phosphorites of Hahotoé/Kpogamé. Average World phosphorites (Altschuler 1980). F1 and F2 enrichment factors compared to shale and world phosphorites

Profile #	Depth (m)	Sample (#)	Cd (mg/kg)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)	Na_2O (%)	P_2O_5 (%)
P1	−0.10	1	2	0.19	30.86	1.06	0.1	6.89	0.39	4.96
	−0.30	2	23	0.42	8.71	16.04	0.17	30.20	0.29	22.66
	−1.00	3	34	0.11	3.11	2.12	0.09	48.32	0.24	31.74
	−2.00	4	25	0.21	4.21	0.98	0.18	45.48	0.2	28.54
P2	−0.10	5	50	0.16	3.36	9.06	0.12	45.05	0.23	23.88
	−0.30	6	41	0.32	1.65	7.78	0.40	21.24	0.38	28.76
	−1.00	7	53	0.13	2.51	1.51	0.12	40.28	0.19	36.01
	−2.00	8	36	0.36	7.77	2.69	0.57	27.76	0.28	25.59
P3	−0.20	9	48	0.17	3.92	3.32	0.16	40.67	0.25	31.50
	−0.40	10	43	0.14	2.97	1.59	0.11	35.90	0.21	30.65
	−1.20	11	30	0.26	5.50	4.85	0.24	36.04	0.21	30.10
	−2.20	12	55	0.18	3.57	2.00	0.21	37.78	0.35	27.30
P4	−0.30	13	41	0.12	2.16	0.81	0.31	28.07	0.25	31.76
	−1.40	14	109	0.06	1.26	5.76	0.20	21.14	0.26	27.88
	−2.30	15	48	0.18	3.30	0.56	0.52	36.80	0.52	30.18
	−2.90	16	116	0.15	2.56	1.26	0.55	42.95	0.27	29.75
		Min	2	0.06	1.26	0.56	0.09	21.14	0.19	22.66
		Max	116	0.42	8.71	16.04	0.57	48.32	0.52	36.01
		Mean	47	0.20	3.77	4.02	0.26	35.85	0.28	29.09
Shale (Wedepohl 1991)			0.3	0.46	15.12	6.75	2.49	3.09	1.29	0.16
World Phosphorite (Altschuler 1980)			18	0.1	1.8	2.3	1.3	40.4	–	23.0
		F1	157.08	0.43	0.25	0.60	0.11	11.60	0.21	181.79
		F2	2.62	3.09	2.09	1.73	0.20	0.89	–	1.26

of 116 mg/kg. Earlier investigations by Kunkel H. 1990 (unpublished) report an average concentration of Cd of 66 mg/kg with a maximum of 267 mg/kg (Kunkel H 1990, unpublished) report high Cd concentrations in the transition zone between the phosphorite and limestone layers, and attribute this enrichment to the precipitation, in the buffer zone, of Cd leached by the tropical weathering from the upper parts of the layer C1. In the iron oxide fraction of the phosphorites, Cd concentrations range from 6 to 48 mg/kg with an average of 25 mg/kg. The analysis of various phosphatised fossil bone fractions and shark teeth indicated a Cd average concentration of 145 mg/kg (Kunkel H 1990, unpublished).

3.2 Grain-Size Dependence of Cd Concentration in Phosphorite

The Cd concentrations decreased with decreasing grain size (from sand to clay fraction) and this decrease is parallel to that of P_2O_5 and CaO, which confirms that all these elements belong to apatite lattice. This behavior of P, Ca, and Cd can be explained by the fact that these elements together belong to the apatite lattice. The highest Cd concentrations are found in the fractions between 1–0.2 mm and 0.2–0.1 mm with 132 mg/kg and 142 mg/kg, respectively (Table 2), where the largest values of P_2O_5 are also found. The smallest concentrations are found in the clay fraction (Fig. 3).

Table 2 Grain-size dependence of the distribution of Cd (mg/kg), CaO, P_2O_5 and Fe_2O_3 (in %) for some selected phosphorite samples

Fraction (mm)	Cd	Fe_2O_3	CaO	P_2O_5	Cd	Fe_2O_3	CaO	P_2O_5
	Sample 2				Sample 9			
0.2–1	13	7.03	23,89	18,8	82	0.38	54.8	46.8
0.1–0.2	35	3	48.5	32.5	52	0.96	42.7	40
0.06–0.1	29	6.17	47.4	30.6	50	1.38	43.9	35.6
0.002–0.06	23	7.89	29.4	24.8	25	8.21	21.1	16.6
<0.002	18	19.69	24.6	21.5	10	11.07	9.65	7.09
	Sample 4				Sample 10			
0.2–1	32	0.49	52.16	25.4	44	0.64	46.45	35.1
0.1–0.2	28	0.3	60.4	33.4	52	0.53	48.2	39.6
0.06–0.1	32	0.33	52.4	31.8	48	1.2	44.8	39.1
0.002–0.06	20	2.45	34.9	23.6	28	6.71	24.5	18.3
<0.002	9	4.15	16.5	9.47	10	11.77	8.74	7.37

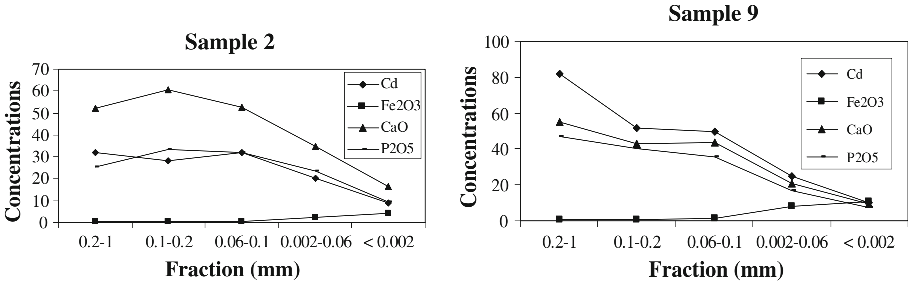

Fig. 3 Grain size dependence of the concentrations of Cd, P_2O_5, CaO and Fe_2O_3 in 2 phosphorite samples (Cd in mg/kg), Al_2O_3, Fe_2O_3, CaO and P_2O_5 in (%)

3.3 Correlation Coefficients

In studied Togo phosphorite, Cd exhibits a significant positive correlation with phosphorus in the bulk sediment of phosphorites ($r = 0.7$, $n = 15$), and the correlation is higher in the "pure phosphate" fractions 1–0.2 mm ($r = 0.90$), where maximum P_2O_5 concentrations are found. However, other phases such as calcite, Iron, and manganese oxides are potential carriers of Cd in phosphorites as well. There are moderate correlations between Fe and Mn oxides contents and that of Cd (Table 3). Kunkel H 1990 (unpublished) found significantly higher correlation coefficients (r up to 0.98) between Cd and P_2O_5 in apatite-rich fresh facies of Togo phosphorites.

3.4 Scanning Electron Microscope (SEM) Analysis

The analysis of individual grains using SEM records high Cd values within individual pellets (Fig. 4), indicating that Cd belongs to apatite structure where it substitutes for Ca in the studied phosphorites.

Table 3 Correlation coefficients between the contents of Cd and major elements (as oxides) in various grain-size fractions of the phosphorites of Hahotoé-Kpogamé. Togo

Fraction (mm)	Cd–P	Cd–Ca	Cd–Fe	Cd–Mn	Cd–Mg	Cd–Cr	Cd–Ni	Cd–V	Cd–Zn	Cd–Zr
Bulk sed (15)	**0.70**	0.23	−0.37	0.10	−0.13	−0.31	0.09	−0.51	0.27	−0.63
1–0.2 (16)	**0.90**	**0.59**	−0.54	−0.16	−0.07	−0.6	0.42	−0.54	−0.16	−0.62
0.2–0.125 (16)	0.16	−0.16	**0.73**	**0.59**	**0.58**	0.40	0.42	**0.88**	0.31	**0.75**
0.125–0.063 (16)	−0.12	−0.55	**0.68**	**0.61**	**0.83**	**0.59**	**0.63**	0.28	0.11	**0.79**
0.063–0.002 (12)	0.20	0.32	−0.13	0.14	−0.08	−0.03	0.17	−0.33	0.39	−0.62
<0.002 (12)	**0.61**	**0.58**	0.31	0.32	0.2	0.41	0.45	−0.51	0.1	−0.01

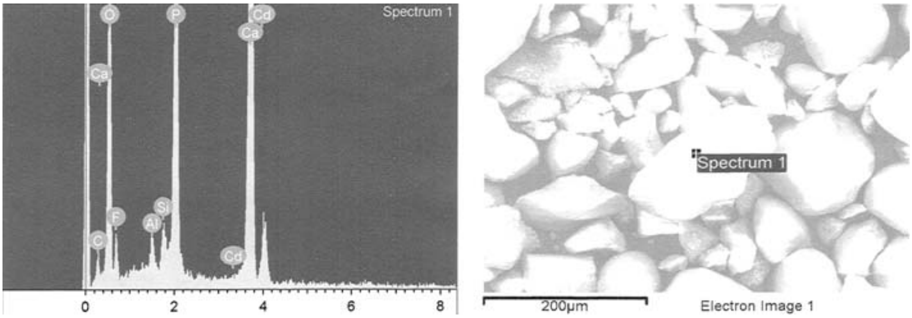

Fig. 4 Scanning electron microscopy (SEM) analysis of individual apatite grain from studied phosphorite (raw material) showing high Cd content (Cd = 0.52 weight %) in the mineral lattice

4 Extractability of Cadmium from Phosphorite

4.1 Sequential Extraction

The acid sequential extraction of Cd-rich phosphorites shows that the dissolution behavior of Cd correlates with the increase of apatite solubility with acid concentration. There was a significant positive correlation between the dissolved amounts of Cd, CaO, and P_2O_5. Using of weak acid up to 3% of CaO and P_2O_5 leads to 2% Cd extraction. Using of strong acid results in 40% of Cd, CaO, and P_2O_5. The trend for CaO, Cd, and P_2O_5 curves is the same, which is attributed to the dissolution of the francolite (Fig. 5).

Extraction with EDTA also shows that the amount of Cd extracted correlates well with CaO and P_2O_5 (Fig. 6). Extraction with ammonium acetate gives a very low CaO dissolution as well as a high amount of Cd release.

4.2 Leachability with Saline Water

The extraction, under agitation in saline water, showed that the amounts of Cd and P_2O_5 dissolved in seawater increased with salinity. For example, the dissolved amounts of P_2O_5 increased from 14.4 to 32.4 mg/l and of Cd increased from $4.4.10^{-3}$ to $9.2.10^{-3}$ mg/l, when the salinity was increased from 9 mg/l to 33 mg/l over 24 h. There is a good correlation between the dissolution of apatite and Cd as well (Fig. 7). Generally, the dissolution rate with saline water is smaller (0.09–0.2%) than that with acid or EDTA but

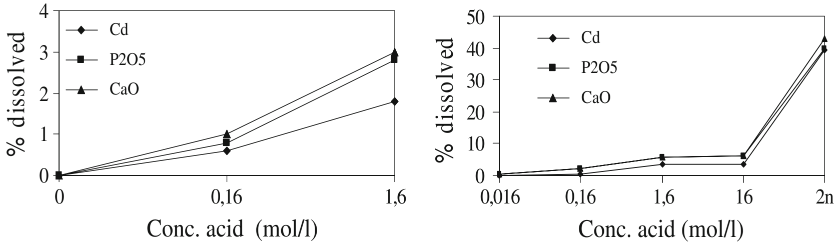

Fig. 5 Extractability of Cd, CaO, and P_2O_5 of Togo phosphorite during sequential extraction using increasing concentration of acetic acid

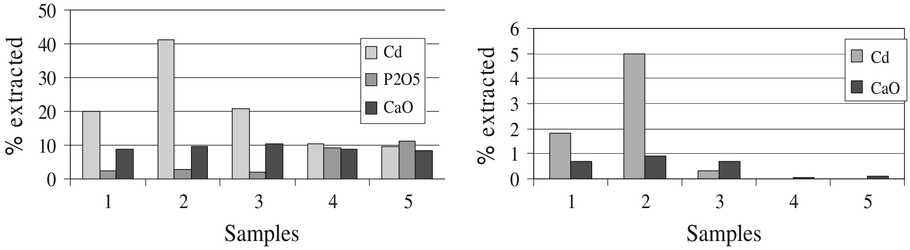

Fig. 6 Diagrams showing the extraction rate of Cd, CaO, and P_2O_5 (in mg/kg) of phosphorites of Togo using EDTA (left) and ammonium acetate (right)

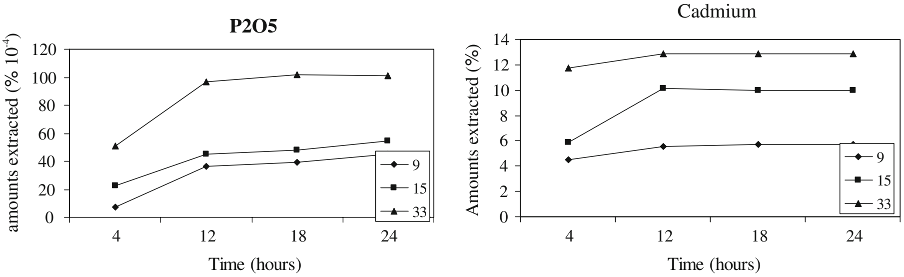

Fig. 7 Extraction of phosphate and Cd using raw phosphorite material and various concentrated saline water (9 mg/l, 15 mg/l, and 33 mg/l NaCl) with agitation, over 4, 12, 18, and 24 h (ratio phosphorite/seawater 1/10)

these amounts are significant in the context of the toxicity of Cd in the marine environment. Indeed, the WHO and European Union norms for cadmium are very strict and are settled by 0.01–1 mg/kg for fish and 0.003–0.005 mg/l for drinking water (European Union 1998; Corvi et al. 2005).

5 Discussion

The distribution of Cd is heterogeneous and some horizons in the layer C1 show particularly elevated concentrations, e.g., iron oxide-rich (109 mg/kg) and phosphatic limestone horizons (116 mg/kg). Due to tropical weathering, Cd is depleted at the top of the profiles and it is fixed preferentially either onto calcite and iron oxide minerals or onto new re-crystallized apatite mineral at the bottom in the transition zone between phosphorite and limestone (McArthur 1980, 1985). Highest Cd concentrations, up to 116 mg/kg, are found in this zone, where the adsorption of Cd onto calcite minerals will be enhanced by the alkaline pH which is provided by the calcite-H_2O buffer system (MacBridge 1980). The concentration of P_2O_5, CaO, and Cd decreases linearly with decreasing grain size. This suggests that these compounds belong to the same francolite phase. Maximum values of Cd were found in the sandy sediment fraction, where the highest contents of P_2O_5 were also found. We also found significant positive correlations between Cd and P_2O_5 in bulk sediment ($r = 0.7$) as well as in the sand grain fractions rich in apatite ($r = 0.9$). The evidence that Cd belongs to apatite structure is a characteristic of the Togo phosphorites. Some authors report that, in some sedimentary phosphorites, Cd does not replace Ca in the apatite structure because no correlation is found between Ca and P_2O_5 (Prévôt 1990; Nathan et al. 1997; Al-Hwaiti et al. 2004). Cd is introduced in the sediment environment by organic matter but the carrier phase obviously changes during sediment digenesis, where Cd is incorporated into apatite lattice by isomorphic substitution with calcium (Modified after Samuel et al. 1999).

$$Ca_5(PO_4)_3OH + 7H \leftrightarrow 5Ca^{2+} + 3H_2PO^{4-} + H_2O$$

$$5Cd^{2+} + 3H_2PO^{4-} + H_2O \leftrightarrow Cd_5(PO_4)_3OH + 7H^+$$

Where the $Cd_5(PO_4)_3OH$ is the mineral cadmium hydroxyapatite.The overall reaction is:

$$Ca_5(PO_4)OH + 5Cd^{\ 2+} \leftrightarrow Cd_5(PO_4)_3OH + 5Ca^{2+}$$

$$\underset{\text{[Carbonate Francolite]}}{Ca_5[(PO_4)_{3-x}(CO_3)_x](F \cdot OH)} \leftrightarrow \underset{\text{[Francolite]}}{Ca_5(PO_4)_3(F \cdot OH)} + CaO + CO_2$$

The linear correlation between the amounts of Cd and P_2O_5 released during the extraction test and the study of individual apatite grains using SEM method confirms this statement. However, during the post-genetic alteration, some Cd is released from apatite.

The amounts of Cd extracted during acid extractability test used as a proxy of bioavailability varied linearly with the amounts of P_2O_5 extracted. This supports the hypothesis that Cd, P_2O_5, and CaO belong to the same phase. Up to 40% of Cd can be extracted using acetic acid (2 N) or 0.2 M EDTA, suggesting adsorption onto clay minerals. Extraction with saline water is attributed to Cd adsorbed weakly onto calcite, apatite, and goethite minerals. Some authors observed similar results in estuarine waters where brackish water mixes with seawater (Salomons and Förstner 1984; Bopp and Biggs 1981).

6 Conclusions

The phosporite deposits of Hahotoé Kpogamé (Southern Togo) are highly enriched with Cd when compared to the world average of phosphorite deposits. The main Cd carrier phase in studied phosphorite is apatite. Secondary carrier phases are calcite and iron and manganese minerals.

The extraction tests with acetic acid and EDTA show that Cd in the studied phosphorite is partially bioavailable, which suggests that the exploitation of phosphorite ores as fertilizer could be the source of soil and groundwater Cd pollution. Leaching experiments with artificial seawater show relatively high amounts of Cd are released into seawater. This leads to the conclusion that the processing of phosphorite by wet sieving using seawater or the dumping of phosphorite tailings into the coastal waters of Togo can be a major source of marine pollution with Cd in the coast of Togo. Detailed studies on Cd distribution on soils and groundwater around mining and processing sites are necessary for risk assessment. Bioaccumulation analyses are also necessary.

Acknowledgments We thank the members of host laboratories at the Scripps Institution of Oceanography, University of California San Diego and Cal-Tech Laboratory in Pasadena for permitting the use of their facilities.

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