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An X-ray absorption fine structure spectroscopy study of germanium-organic ligand complexes in aqueous solution

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Abstract

The local environment around Ge(IV) in 0.002 to 0.023 m aqueous solutions at ambient temperature was characterised as a function of pH and in the presence of different organic ligands (citric and oxalic acids, and catechol) using high resolution X-ray absorption fine structure spectroscopy (XAFS). Results show that both in organic-free solutions at acid to basic pH and in carboxylic acid-bearing solutions at neutral to basic pH and catechol-bearing solutions at acid pH, Ge is coordinated with four oxygens with mean Ge–O distances of 1.75 ± 0.02 Å. This is consistent with the formation of the aqueous $Ge(OH)_4^\circ$ and $GeO(OH)_3^-$ complexes and confirms the results of previous studies based on solubility, potentiometry and Raman spectroscopy ([Pokrovski, G.S., Schott, J., 1998a. Thermodynamic properties of aqueous Ge(IV) hydroxide complexes from 25 to 350°C: implications for the behavior of germanium and the Ge/Si ratios in hydrothermal fluids. Geochim. Cosmochim. Acta 62, 1631–1642; Pokrovski, G.S., Schott, J., 1998b. Experimental study of the complexation of silicon and germanium with aqueous organic species: implications for Ge and Si transport and Ge/Si ratio in natural waters. Geochim. Cosmochim. Acta 62, 3413–3428]). By contrast, in carboxylic acid-bearing solutions at acid pH and in catechol-bearing solutions at pH > 4 Ge is coordinated by 6 oxygen atoms with Ge–O distances ranging from 1.85 to 1.94 Å. This implies the formation of chelate type complexes with the organic ligands. These results are in agreement with germanium speciation scheme in organic-bearing solutions proposed by Pokrovski and Schott (1998b), and explain a stronger affinity of germanium, compared with silicon, to chelating organic compounds. The formation of Ge–organic acid complexes can lead to a significant increase of Ge/Si ratios in organic-rich fluids and should be taken into account when using these ratios measured in surficial waters and biogenic opals to estimate chemical-weathering intensity and Ge and Si global fluxes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Germanium; Aqueous speciation; X-ray absorption fine structure (XAFS) spectroscopy; Organic ligands; Chelates; Dissolved organic carbon (DOC)

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1. Introduction

The most intriguing feature of germanium geochemistry is its capability of separating from silicon in certain terrestrial environments. Although in the earth's crust most germanium is dispersed through silicate minerals due to the isomorphic substitution of tetrahedral Ge(IV) for the chemically similar Si(IV), germanium is highly enriched relative to silicon in a variety of geological materials such as pegmatites, low temperature hydrothermal sulphides, iron oxi-hydroxides, and coals (Froelich and Andreae, 1981; Bernstein, 1985). In most natural waters, Ge is assumed to be present in the form of $Ge(OH)_4^{\circ}(aq)$, similar to aqueous silica $Si(OH)_4^{\circ}(aq)$, and to behave as a tracer for silicon, being incorporated into biogenic opal as if it were a heavy stable isotope of silicon (Froelich et al., 1985a,b; Mortlock and Froelich, 1987; Lewis et al., 1988; Froelich et al., 1992). The Ge/Si ratio in opals is thus believed to be a function of silica's biochemical cycle and to reflect the intensity of continental weathering and mid-ocean ridge hydrothermal circulation, the two main processes contributing to the flux of Si in the biosphere (Froelich and Andreae, 1981; Murnane and Stallard, 1990; Mortlock et al., 1993). However, unlike that of silicon, aqueous germanium speciation can be significantly affected by the presence of dissolved organic matter. Recent potentiometric and solubility measurements (Pokrovski and Schott, 1998b) demonstrated that Ge forms stable complexes with carboxylic, di-*ortho* phenolic and polyalcoholic functional groups typical of natural organic matter, whereas the corresponding complexes formed by silicon are very weak. To explain this difference, it is necessary to know the structure and geometry of the aqueous complexes formed by Ge with organic ligands. The purpose of this paper is to characterise the local environment around Ge in aqueous solutions of organic ligands using XAFS spectroscopy.

X-ray absorption fine structure (XAFS) spectroscopy is the only method which provides direct information on the local chemical environment (valence state, nature and number of neighbours, atomic distances) around a selected element (here Ge) in a multicomponent system. Few studies of Ge in solids and aqueous solutions of geochemical interest using XAFS technique have been reported in the literature.

Bernstein and Waychunas (1987) have shown that Ge substitutes for Fe(III) in the octahedral metal sites of natural Ge-bearing hematite and goethite, with average Ge–O distances of 1.88 Å. Martin et al. (1997) demonstrated that Ge is randomly distributed in the tetrahedral sheets of synthetic talcs where it substitutes for Si and exhibits Ge–O distances of 1.75 Å. An EXAFS spectrum of a 0.01 m germanic acid aqueous solution at neutral pH reported by Bernstein and Waychunas (1987) is consistent with the predominance of $Ge(OH)_4^{\circ}(aq)$ species with Ge–O distances of 1.74 Å.

Although many studies have been reported in the chemical literature on the stability of aqueous germanium complexes with carboxylic acids, polyalcohols, phenol and catechol derivatives (see Pokrovski, 1996), the stoichiometry and molecular structure of these complexes are poorly known. The present study complements our recent work on the stability of aqueous Ge(IV)-organic ligand complexes as a function of temperature (25–90°C) using solubility and potentiometric techniques (Pokrovski, 1996; Pokrovski and Schott, 1998b). The experimental conditions used in the present study were chosen to test the validity of previous assignments of the geometry of Ge complexes formed with carboxylic acids (citric and oxalic) and di-*ortho*-phenol (catechol) (Moeller and Nielsen, 1953; Everest, 1955; Vartapetian, 1957; Antikainen and Malkonen, 1959; Andrianov and Nazarenko, 1963; Evdokimov and Kogan, 1971; Pokrovski and Schott, 1998b) which were based on the interpretation of solubility, potentiometric or ion-exchange measurements.

Currently available synchrotron radiation sources allow XAFS analyses in the fluorescence mode of aqueous Ge at concentrations as low as 10^{-4} m. The experimental data obtained in this study provide quantitative information about both interatomic distances and the number and chemical identity of atoms within a 5 Å radius around Ge atom. The organic ligands used in this study represent the main functional groups of humic and fulvic acids found in aquatic systems (carboxylic and OH-phenolic) and thus can serve as models of Ge-binding sites in natural organic matter. The results obtained in this study should lead to an improved interpretation of the Ge/Si ratios and modelling of Ge transport in surficial waters. This information should also help to

elucidate the mechanisms of Ge uptake by mineral solid phases from aqueous solution (Bernstein and Waychunas, 1987; Martin, 1994; Martin et al., 1992; Martin et al., 1997).

2. Experimental

2.1. Material and methods

Germanic acid aqueous solutions used in the present study where prepared by dissolution at ambient temperature of a powder of commercial GeO_2(hex) (Aldrich, 99.999%) in deionized water. Aqueous Ge concentrations were determined by the colorimetric molybdate-blue method (Pokrovski, 1996). Solutions containing organic ligands were prepared by dissolving weighted amounts of normapur citric and oxalic acids or catechol in aqueous solutions of germanic acid. The solutions were filtered through a 0.45 μm Millipore filter. pH was adjusted with NaOH or HCl solutions and monitored with a combination pH glass electrode (Schott 61) calibrated on the activity scale using the phthalate, phosphate and borate NBS buffers ($pH_{25°C} = 4.01$, 6.86 and 9.18, respectively).

(a)   **(b)**
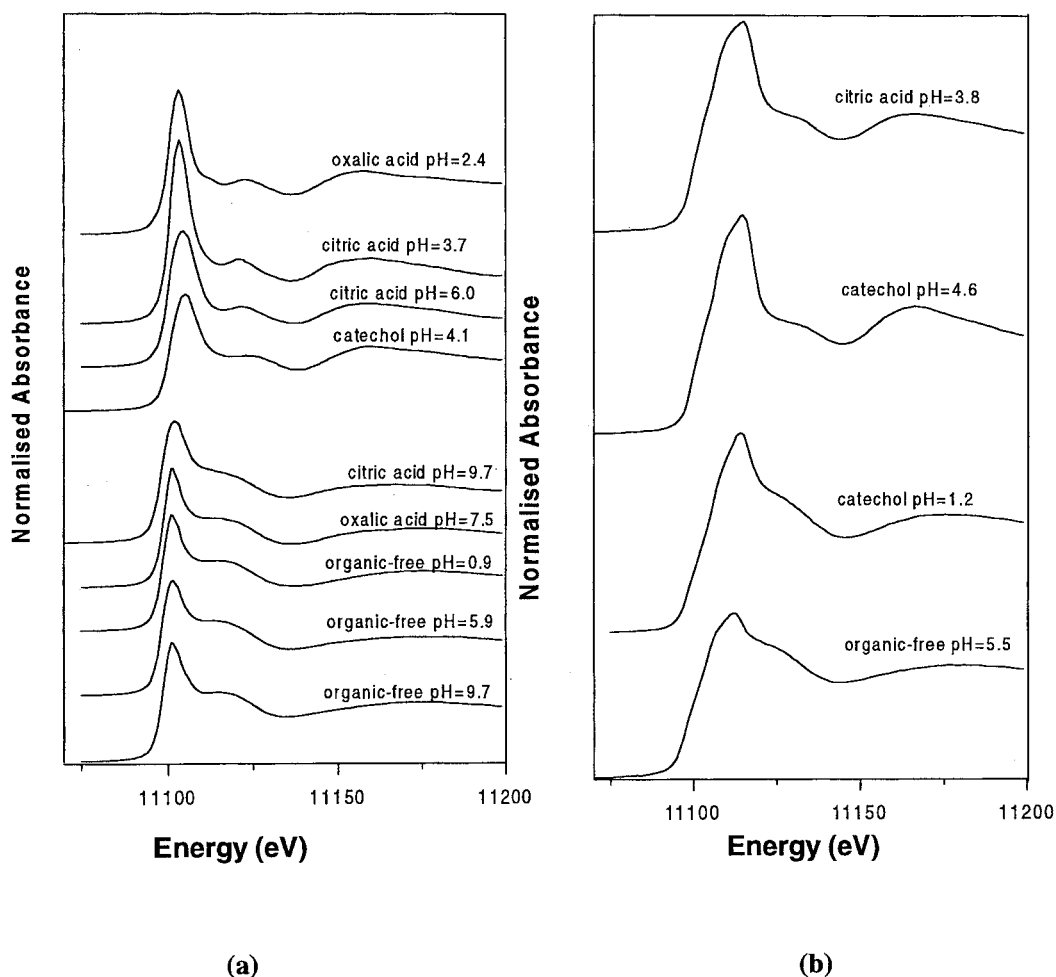
Fig. 1. X-ray absorption near-edge spectroscopy (XANES) normalised spectra at Ge K-edge for concentrated ($0.015 \leq m_{Ge} \leq 0.023$) (a), and diluted ($0.002 \leq m_{Ge} \leq 0.0027$) (b) Ge-bearing aqueous solutions.

XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) spectra were collected at the Ge K-edge ($\sim$ 11 103 eV) over the energy range 10 900–11 850 eV at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on the collaborative research group IF BM32 beam line. The storage ring was operated at 6 GeV with 200 mA electron current. The spectra were collected using a Si (111) double-crystal monochromator allowing energy resolution of 2 eV at the Ge K-edge. Energy calibration was accomplished by assigning to a value of 11103
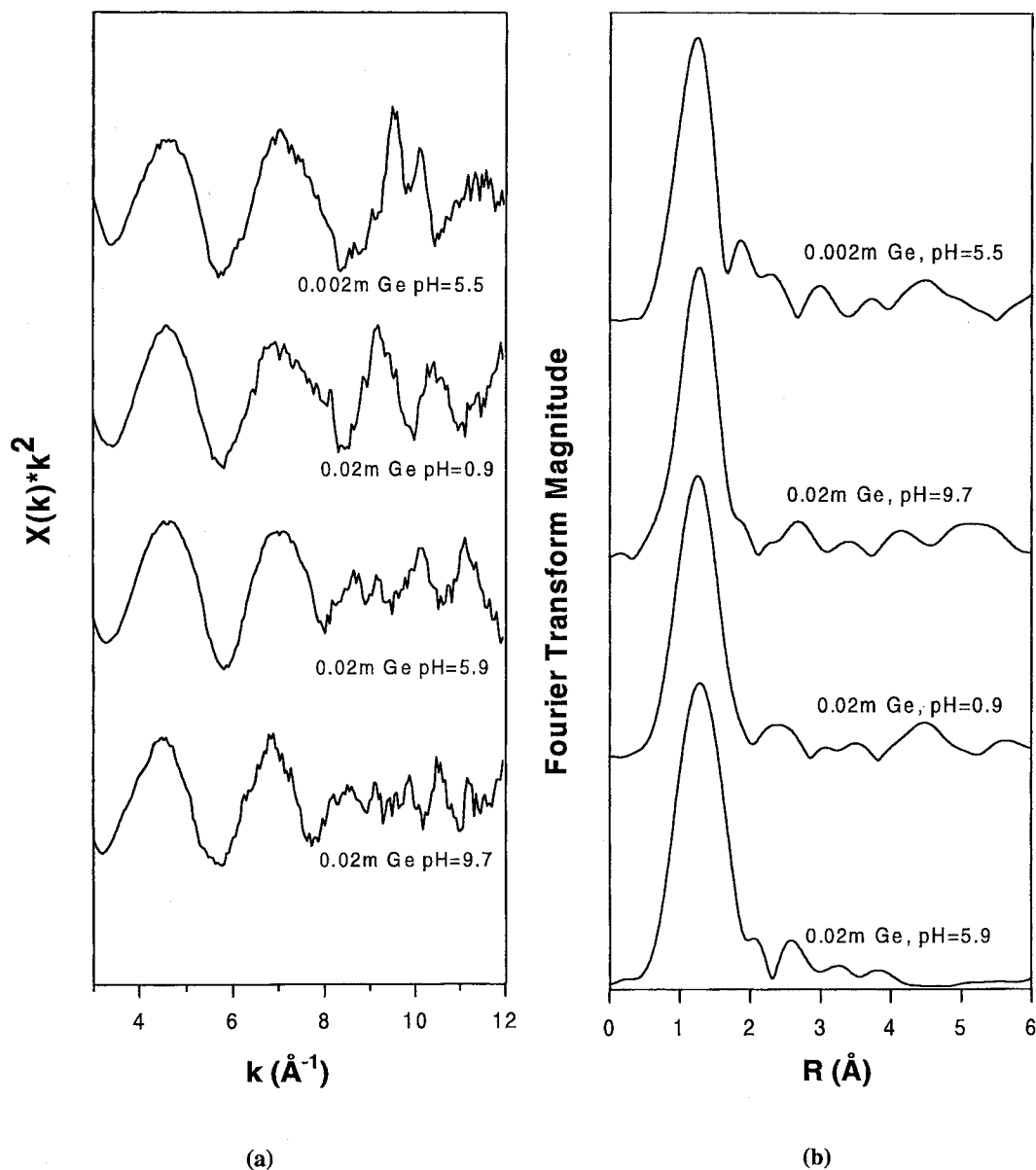

Fig. 2. Normalised k^2-weighted EXAFS spectra (a) of organic-free Ge-bearing aqueous solutions and their corresponding Fourier transforms (b).

eV the energy of the maximum of the spectrum derivative of Ge metal. XAFS data for the solutions were collected at ambient temperature in the fluorescence-yield mode using a cell with kapton-film windows. The cell was oriented at 45° to the X-ray beam. To maintain a constant orientation of the cell while changing samples, that insures the reproducibility of spectra and facilitates absorbance adjustment, the solutions were introduced into the cell via a hole in its upper part using a syringe, without moving the cell. The Kα-fluorescence intensity was measured using a solid-state Canberra five-element detector whose ion chamber was cooled with liquid nitrogen. Fluorescence intensity–energy spectra were obtained by averaging two individual scans for each solution in order to improve the signal-to-noise ratio.

The counting time varied from 3 s per step in the pre-edge region to 30 s at 14 $\mathring{A}^{-1}$ for a total integration time of 1.5 h.

2.2. Data reduction

XAFS data extraction and analysis were performed using SEDEM (Aberdam, 1998) and XAFS2.6 (Winterer, 1996) packages. Both programmes have given the same results in the limit of the uncertainties when extracting structural information for the first coordination shell around Ge (see below). The near-edge (XANES) data (from 50 eV below to 100 eV above the edge) were normalised and superposed to compare the edge positions and the shape of peaks for different solutions (Fig. 1a,b). EXAFS spectra
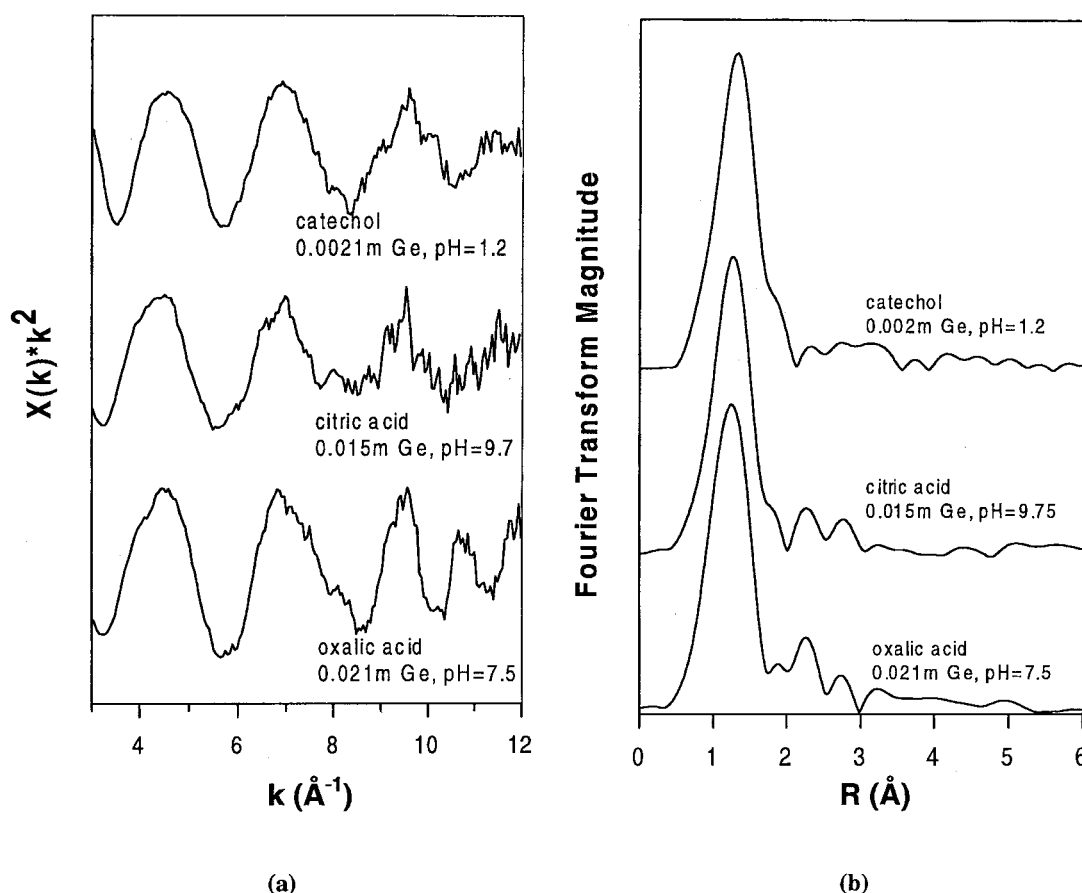

(a)   **(b)**

Fig. 3. Normalised k^2-weighted EXAFS spectra (a) of organic-bearing aqueous solutions in which Ge is not complexed with the organic ligands and their corresponding Fourier transforms (b).

were analysed following the classical procedure (Teo, 1986; Sayers and Bunker, 1988). The first operation consisted of subtracting background absorption by fitting a victoreen to the before-edge region, extrapolating it over the EXAFS region and then subtracting it from the raw X-ray absorption spectrum. Then, the atomic absorption (after-edge base line) was determined using cubic splines and subtracted from the

data. Energies were recalculated into k-space ($\mathring{A}^{-1}$) with E_o (i.e., the energy where k is zero) arbitrarily chosen at zero of the edge first derivative. The k^n-weighted ($0 \leq n \leq 3$) EXAFS spectra were Fourier transformed over the k range 2 to 12 $\mathring{A}^{-1}$ using a Kaiser–Bessel window function (Bonnin et al., 1985) with τ values of 4 in order to reduce termination effects in the Fourier transform (FT). It was found
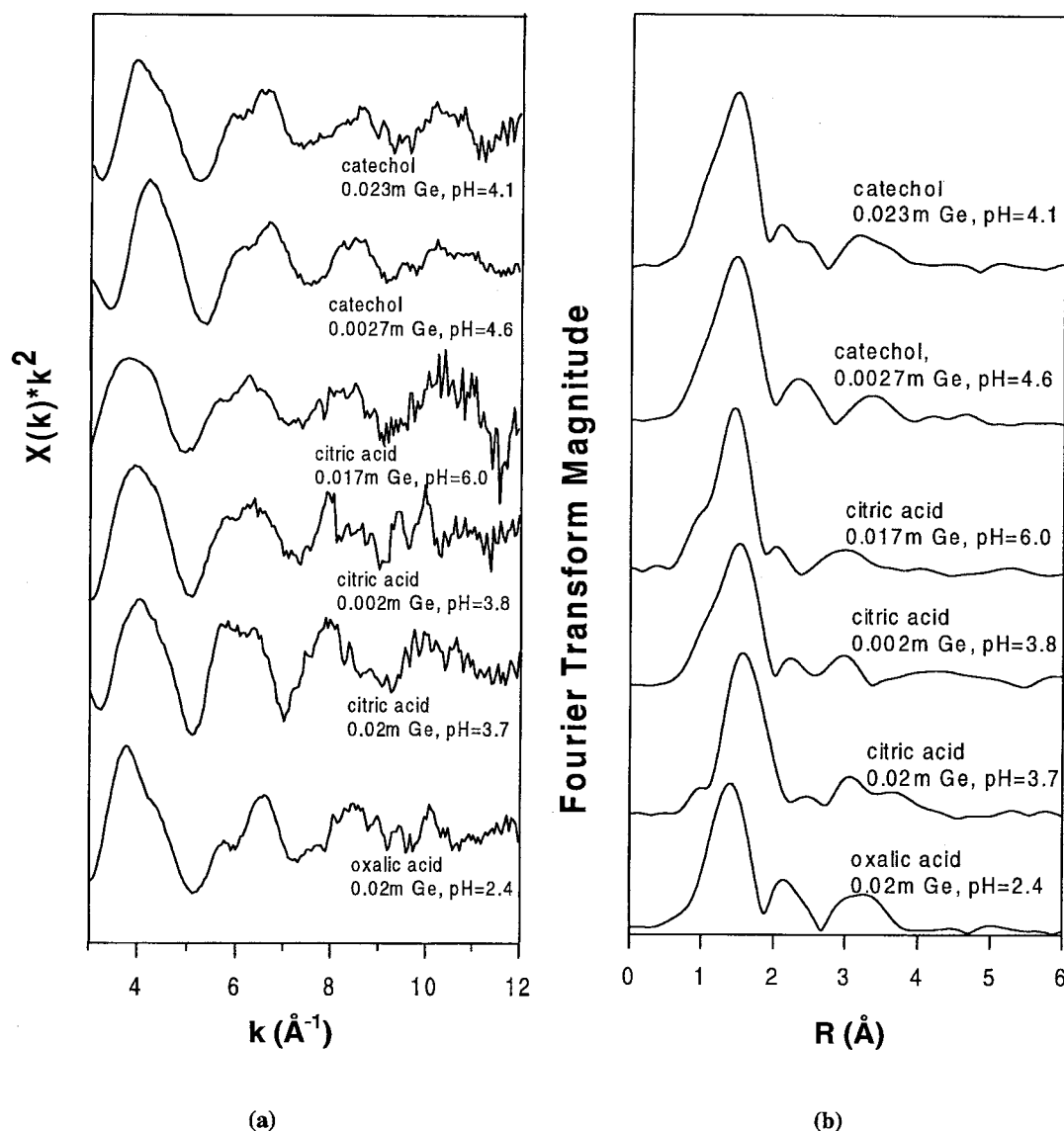

Fig. 4. Normalised k^2-weighted EXAFS spectra (a) of organic-bearing aqueous solutions in which Ge is complexed with the organic ligands and their corresponding Fourier transforms (b).

that the k^2-weighted spectra (Figs. 2a, 3a and 4a) provide the best peak resolution and the highest signal-to-noise ratio when doing FT (Figs. 2b, 3b and 4b). The resulting modulus of the FT is a curve similar to a radial distribution function (RDF) but uncorrected for phase shifts caused by absorbing and neighbouring atoms. Each RDF peak corresponds to one or several atomic shells. To extract structural information, one or several RDF peaks were back transformed into momentum space (inverse Fourier Transform, IFT) (Fig. 5). Modelling of these EXAFS oscillations (IFT) by least-squares fitting gives average structural parameters for the Ge environment (identity of first and second (if present) neighbour atoms, distances between Ge and their neighbours (R), average coordination numbers (N), and Debye–Waller factors (σ^2) which are a measure of
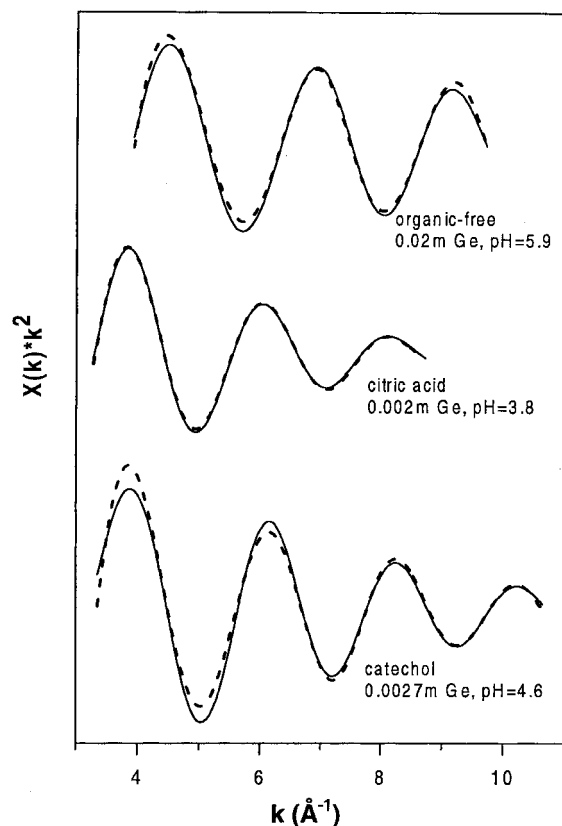

Fig. 5. First-shell Fourier-filtered EXAFS spectra (dashed lines) and least-squares fits (solid lines) of Ge for selected aqueous solutions.

disorder and represent the mean square deviation of the interatomic distance from its average length). Theoretical backscattering amplitude and phase-shift functions for Ge–O and Ge–Ge pairs were computed using the FEFF 7 ab initio code (Ankudinov and Rehr, 1996; Zabinski et al., 1995), assuming the local structure around Ge in GeO_2 (hex, quartz-like; Jorgensen, 1978) and GeO_2 (tetr, rutile-like; Wyckoff, 1963). As standard values, the amplitude reduction factor S_o^2 and Debye–Waller factor were set to 1 and 0, respectively, in the calculations of these functions. The minimum uncertainties of first-shell distances and coordination numbers for O-nearest neighbours when using these functions are estimated to be ± 0.02 Å and ± 1 atom, respectively. The high noise and weak intensities of the second RDF peaks did not permit to adequately model the second shell around Ge atoms (see below).

Self-absorption and disorder (thermal and static) may present a problem in determining accurate structural parameters (Brown et al., 1988; Farges et al., 1993). Self-absorption usually results in erroneously low coordination numbers, but it is unlikely to be a problem for elements at the low concentration of the experimental solutions used in this study ($m_{Ge} <$ 0.025 mol/kg). A quantitative approach to consider disorder is to add in the expression of the partial radial distribution function (i.e., pair-correlation function of the neighbouring distances around the absorbing element) three- (C_3) and four-order (C_4) cumulants accounting for the anharmonicity (Crozier et al., 1988; Farges et al., 1996; Farges, 1996). The typical values of C_3 and C_4 found when fitting our IFT spectra were of the order of 10^{-4}, and did not change significantly R and N values derived from least-square fits without cumulants. As a result, in order to reduce the number of variables and thus the uncertainties on the derived parameters, we decided do not use the anharmonic cumulants when extracting R, N and σ values.

3. Results

3.1. Results from XANES analysis

The normalised Ge K-edge XANES spectra of the investigated solutions are shown in Fig. 1a,b. Solu-

tion compositions are given in Table 1. The spectra of the 'relatively more concentrated' Ge solutions ($0.015 < m_{Ge} < 0.023$) without organic compounds and those in the presence of citric and oxalic acids at high pH (pH > 7) have edge-crests at 11 101–11 102 eV. In the organic-free aqueous solutions germanium is present as the neutral tetrahydroxide $Ge(OH)_4^\circ$ at acid and neutral pH or its negative counterpart $H_3GeO_4^-$ at pH > ~9 (Baes and Mesmer, 1976; Pokrovski and Schott, 1998a). As germanium was shown to be not complexed with neither citrate nor oxalate at pH > 7–8 (Pokrovski and Schott, 1998b), the hydroxide Ge species $Ge(OH)_4^\circ$ and $GeO(OH)_3^-$ are also dominant in the carboxylic acid-bearing solutions investigated. Thus, all these solutions are likely to contain Ge in tetrahedral coordination with oxygen. By contrast, solutions of citric and oxalic acids at acid pH (pH < 6) and of catechol at pH ~ 4 exhibit a significantly higher edge-crest energy (11 104–11 105 eV). It has been shown recently by Pokrovski and Schott (1998b) from potentiometric and solubility measurements that Ge(IV) is likely to form hexacoordinated complexes with carboxylic

acids and *ortho*-phenols in these solutions. Similar differences (2–3 eV) between the edge-crest energies of the quartz-like GeO_2(hex), the rutile-like GeO_2(tetr) and amorphous GeO_2 were also measured by Bernstein and Waychunas (1987) and Farges et al. (1995), respectively. GeO_2(hex) and GeO_2(tetr) contain Ge in tetrahedral and octahedral coordination with oxygen, respectively (Martin, 1994; Wyckoff, 1963). As a result, the higher edge-crest energies measured in the solutions in which Ge is complexed with organic ligands represent a direct evidence of a different (likely octahedral) coordination of Ge in its organic complexes in comparison with the inorganic hydroxide complexes (tetrahedral coordination). Moreover, it can be seen on Fig. 1a that the XANES spectra of the solutions where Ge is complexed with organic ligands are different in the after-edge shape from those of non-complexed Ge, exhibiting a feature at ~ 11 120 eV and a deeper minimum at ~ 11 130–11 140 eV. This also supports the conclusion about the different Ge environment in Ge–organic complexes compared to that in germanic acid.

Table 1
Parameters derived from EXAFS data at Ge–K edge of aqueous germanium-bearing solutions

Solution	pH (20°C)	CN	R (Å)	σ^2 (Å)	q fit quality
Organic-free					
Ge 0.002 m	5.5	4.2	1.73	0.0063	0.093
Ge 0.020 m	5.9	4.0	1.77	0.0010	0.010
Ge 0.020 m	0.9	3.9	1.76	0.0014	0.019
Ge 0.020 m	9.7	3.8	1.74	0.0010	0.037
Catechol					
Ge 0.0027 m + catechol 0.10 m	4.6	6.5	1.91	0.0050	0.011
Ge 0.023 m + catechol 0.10 m	4.1	5.7	1.90	0.0057	0.036
Ge 0.0021 m + catechol 0.10 m	1.2	4.2	1.76	0.0053	0.030
Citric acid					
Ge 0.002 m + citric acid 0.02 m	3.8	6.3	1.94	0.012	0.002
Ge 0.02 m + citric acid 0.10 m	3.7	5.9	1.90	0.0046	0.027
Ge 0.017 m + citric acid 0.10 m	6.0	6.5	1.88	0.006	0.012
Ge 0.015 m + citric acid 0.11 m	9.7	4.2	1.78	0.0053	0.032
Oxalic acid					
Ge 0.022 m + oxalic acid 0.10 m	2.4	6.6	1.85	0.0067	0.034
Ge 0.020 m + oxalic acid 0.10 m	7.5	4.3	1.76	0.0006	0.13

CN = Ge coordination number, R = Ge–O mean distance, σ^2 = squared Debye–Waller factor, $q = \Sigma(y_{exp} - y_{fit})^2 / s_i^2 / \Sigma X(k)^2$, where $y_{exp} - y_{fit}$ = difference between experimental and calculated EXAFS absorption coefficient ($X * k^2$) of the filtered signal for each point, and s_i^2 = standard deviation of each experimental point.

Similar to their 'concentrated' analogs, the spectra of the 'relatively more diluted' ($0.002 < m_{Ge} < 0.0027$) organic-free Ge solutions and those where germanium is not complexed with organic ligands (catechol at pH = 1.2) where Ge is coordinated with 4 oxygens, exhibit edge-crests of 2–3 eV lower than their counterparts where Ge–organic complexes are dominant (catechol at pH = 4.6 and citric acid at pH = 3.8). As for the 'concentrated' solutions, this difference in edge-crest position provides evidence for an increase of Ge coordination from four-fold in non-complexing media to six-fold in the presence of organic matter. The after-edge shape of the spectra is distinctly different for the solutions of 'complexed' and 'free' germanium, exhibiting the same features as those observed for their concentrated analogs. The analysis of EXAFS spectra which provides more quantitative information on atomic distances and co-ordination numbers (see below) is consistent with the XANES results.

3.2. Results from EXAFS analysis

The normalised k^2-weighted EXAFS spectra of the Ge solutions investigated together with their corresponding Fourier Transforms (uncorrected for phase shift) are presented in Figs. 2–4a–b. All FT spectra exhibit first RDF peaks located between 1.2 and 1.4 Å. These peaks correspond to the Ge–O pairs. The backtransformed into k-space Fourier Ge–O filtered contribution of the first atomic shell for all solutions was fitted with four parameters: N = coordination number, R = Ge–O mean distance, σ = Debye Waller factor; and ΔE = difference of energy threshold between theoretical phase function and spectrum of the sample studied. The fitting results together with a fit quality parameter (q) are reported in Table 1. Three characteristic examples of least-square fits of the EXAFS spectra obtained in this study (organic-free solution at pH = 5.9, cate-chol-bearing solution at pH = 4.6, and citrate-bearing solution at pH = 3.8) are shown in Fig. 5.

Data analysis confirms that for all solutions only oxygen (or OH) is present as first neighbour around Ge. In organic-free solutions at acid and neutral pH Ge exhibits a coordination number 4 ± 0.2, with average Ge–O distance of 1.75 ± 0.02 Å. This is in agreement with the Ge–O distance for tetrahedrally

coordinated Ge in the quartz-like GeO$_2$ (1.74 Å, Smith and Isaacs, 1964). These coordination numbers and atomic distances are thus consistent with
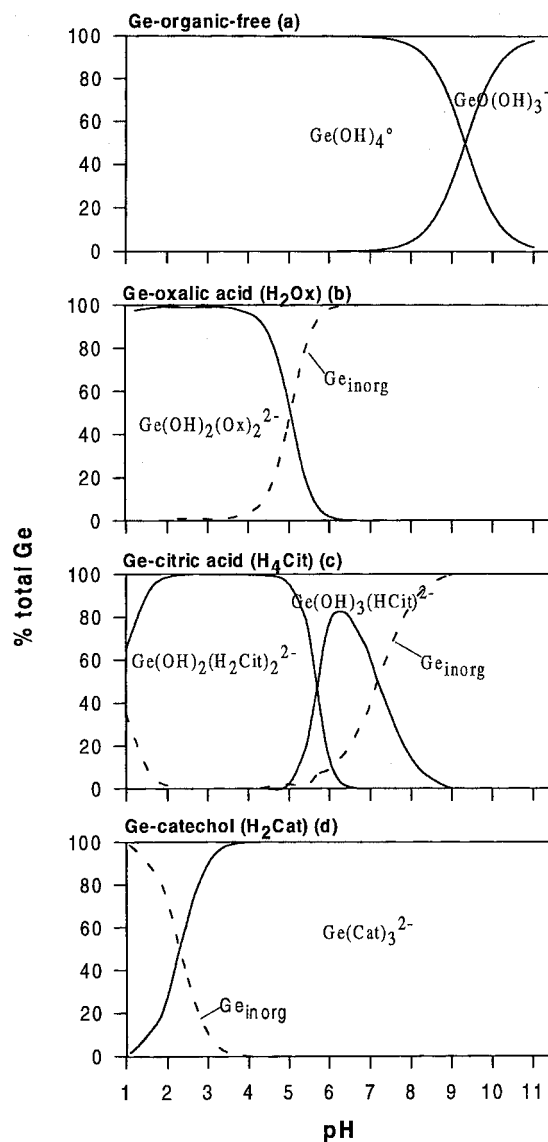

Fig. 6. Distribution curves of Ge hydroxide complexes (a) and Ge complexes with oxalic acid (b), citric acid (c) and catechol (d) as a function of pH at 25°C in aqueous solutions containing 0.02 m of Ge and 0.1 m of corresponding organic compound. The dashed lines represent the percentage of the free inorganic germanium, $Ge_{inorg} = Ge(OH)_4^\circ + GeO(OH)_3^-$, in the presence of the organic ligands. All curves were generated using the stability constants for Ge species reported by Pokrovski and Schott (1998b).

tetrahedral $Ge(OH)_4$ groups in aqueous solution at acid and neutral pH (Fig. 6). Our results are in agreement with previous EXAFS data of Bernstein and Waychunas (1987) and our solubility and Raman spectroscopic measurements (Pokrovski, 1996; Pokrovski and Schott, 1998a). In a basic solution (pH = 9.7), Ge shows a similar coordination number (3.8) and Ge-O average distance (1.74 Å). Since the EXAFS technique cannot make difference between Ge–O and Ge–OH pairs (hydrogen is too light scat-

terer to be seen by EXAFS), this result is in agreement with the dissociation of germanic acid in alkaline solutions with the formation of $GeO(OH)_3^-$ (Baes and Mesmer, 1976).

In the catechol-bearing solution at pH = 1.2 and in oxalate and citrate-bearing solutions at pH > 7, Ge has a coordination number of 4 and Ge–O distances ranging from 1.76 to 1.78 Å, values which are close to those obtained in organic-free solutions. These data suggest that Ge is present as $Ge(OH)_4^\circ$ (pH <
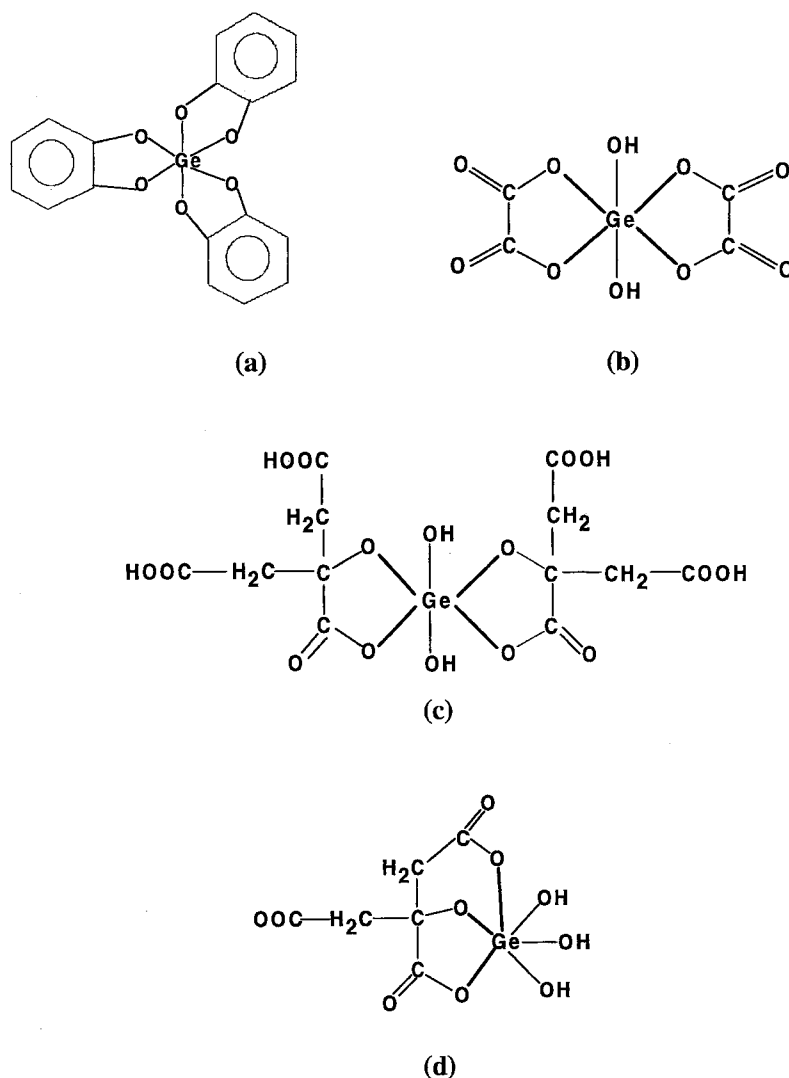

Fig. 7. Schematic representation of Ge–catechol (a), Ge–oxalic acid (b) and Ge–citric acid (c and d) complexes. Two different Ge–citric acid complexes were found from the potentiometric and solubility measurements of Pokrovski and Schott (1998b) (see also Fig. 6).

$\sim$ 9) or GeO(OH)$_3^-$ (pH > 9) in these solutions. This result is in agreement with our potentiometric and solubility measurements (Pokrovski and Schott, 1998b) which showed that Ge is not complexed by catechol and carboxylic acids at low and high pH, respectively (Fig. 6).

In the catechol-bearing solutions at pH $\sim$ 4, oxalate-bearing solution at pH = 2.4, and citrate-bearing solutions at pH = 3.7, 3.8 and 6, Ge coordination is close to 6 and the corresponding Ge–O distances range from 1.85 to 1.94 Å (Table 1). These values are typical for an octahedral Ge–O distance (1.88 Å in the GeO$_2$(tetr) rutile-like structure, Hazen and Finger, 1981). Ge octahedral coordination in these solutions implies the formation of chemical bonds between Ge and the oxygens of carboxylic and diphenolic groups. This is in agreement with our potentiometric and solubility measurements (Pokrovski and Schott, 1998b) which demonstrated that Ge aqueous speciation is dominated by complexes with catechol at neutral and basic pH and with carboxylic acids at acid pH (Fig. 6). The results obtained from this EXAFS study together with the Ge:ligand ratio in the complexes and their charge derived from our potentiometric measurements permit us to propose structures for Ge aqueous complexes (Fig. 7). With catechol Ge forms a 1:3 complex in which it uses its d-orbitals to increase its coordination number from 4 to 6. Results for Ge complexation with oxalic and citric acids imply the formation of bidentate chelates constituted of pentagonal rings with two functional groups (carboxyl and/or hydroxyl) in the *cis*-position. The required formation of a chelate ring for the complex stability is also supported by the absence of complexation between Ge and mono-functional carboxylic groups (e.g., acetic acid, Pokrovski and Schott, 1998b), and by the general rule that metal polydentate (chelate) complexes are much more stable that their monodentate analogs (Martell and Hancock, 1996).

Low signal-to-noise ratio did not allow accurate separation and analysis of the second atomic shell around Ge atoms. This can be explained by use of dilute solutions and the weak signal from the light back-scattering carbon and/or oxygen atoms. Although the FT for some solutions show a weak second contribution at $\sim$ 2.2–2.5 Å, this feature was not reproducible for all solutions in which Ge specia-

tion is the same. Moreover, the relative intensity and position of this second peak depended strongly on both the power of k (n) used to compute $X(k)^* k^n$, and the k-range of the apodization window in the Fourier Transform. It should be noted also that the R value for this peak is too short to be attributed to the distances between Ge and the oxygens from the second hydration sphere of Ge(OH)$_4$ species ($R_{\text{Ge}-\text{OH}_2} > 4$ Å, Rustad and Hay, 1995) or to Ge–Ge pairs in polymerised germanates ($R_{\text{Ge}-\text{Ge}} > 3$ Å, Martin et al., 1997). As a result, this feature is likely to arise from the high noise in our dilute solutions and the short k-range which could be analysed ($k < 12$ Å^{-1}).

4. Discussion

The results obtained in this study show that germanium forms hexacoordinated complexes with organic ligands having hydroxyl–alcoholic, hydroxyl–phenolic and carboxylic functional groups. The key for the formation of such complexes is the establishment of bidentate covalent bonds (of ester type) leading to the formation of polygonal rings containing a Ge atom and two groups such as C–OH, O=C–OH or C=O. The eagerness of Ge to enlarge its coordination number from 4 to 6 explains the high stability of its organic complexes (Pokrovski and Schott, 1998b).

Unlike germanium, silicon was not observed to form ester-type complexes with carboxylic acids nor polyalcohols (Öhman et al., 1991; Poulson et al., 1997; Pokrovski and Schott, 1998b). Although silica forms, like germanium, hexacoordinated complexes with catechol and its derivatives (Flynn and Boer, 1969; Öhman et al., 1991; Sedeh et al., 1992, 1993; Sjöberg et al., 1985), their stability constants are about 10 (!) orders of magnitude lower than those for their germanium analogs (Pokrovski and Schott, 1998b). In view of the results obtained in this study, the weak affinity of silica for aqueous organic ligands can result both from steric strains affecting the complexes in which Si is tetracoordinated, and the reluctance of Si, unlike Ge, to enlarge its coordination sphere to form hexacoordinated complexes.

The tetrahedral coordination induces an angular distortion in the formed chelate which gives rise to

strain energy (Bennett, 1991; Martell and Hancock, 1996). Molecular orbital calculations for bidentate Si–organic complexes indicate that the 5-membered ring structure is the most stable configuration when Si is hexa- or pentacoordinated with Si–O–Si bond angle of 90°C (Bennett and Casey, 1994). This result is confirmed by X-ray diffraction studies of Si-catechol complexes, which show that Si is located at the centre of a slightly deformed bi-pyramid with 6 oxygen atoms at its apices. The O–Si–O angles and Si–O distances in this bi-pyramid which range from 86 to 94°, and from 1.77 to 1.81 Å, respectively (Flynn and Boer, 1969), differ significantly from those in the $Si(OH)_4$ tetrahedron which are equal to 104° and 1.65 Å, respectively (Kubicki et al., 1993). However, it is well known that, unlike germanium, which has a bigger ionic radius (0.39 Å for Ge^{4+} vs. 0.26 Å for Si^{4+}), silicon usually exhibits a coordination four in its compounds with oxygen (oxides, silicates), in conformity with the Pauling's rule. Thus, the Si reluctance to be octahedrally coordinated by oxygen atoms explains the weak stability of its complexes with aqueous organic species.

5. Geochemical implications

The results obtained in this study and that of Pokrovski and Schott (1998b) strongly suggest that the complexation of Ge with aqueous humic and fulvic acids, which have the same functional groups as the simple organic ligands, could be important in natural waters. The extent of Ge complexation with an aqueous humic acid can be roughly estimated by assuming that the stability constants of Ge complexes formed with the humic acid different functional groups are the same as those with simple organic compounds having the same groups. Such calculations show that in a solution containing 20 mg/l of DOC and 10^{-9} m of Ge, typical concentrations in tropical watersheds (Thurman, 1985; Viers et al., 1997), complexes with aromatic hydroxyl groups (catechol type) can account for more than 95% of the total dissolved Ge at pH $\geq 6-7$. The carboxylic groups of humic acids can also contribute to Ge complexation ($\sim$ 10% of total Ge) in acidic waters (pH $\leq 5-6$). Similar calculations carried out for silicon in the same solution containing 20 mg/l of DOC and 10^{-4} m of Si, and assuming that the stability constant of the complexes formed by Si with the phenolic OH-sites of the humic acid is equal to that of Si–catechol complexes (Pokrovski and Schott, 1998b), suggest that Si-humic acid complexation is negligible ($< 0.1\%$ of total Si).

Our predictions of Ge and Si complexation with humic substances are supported by the results of ultrafiltrations on tropical waters from Zsimi–Zoetele watershed in Cameroon (Viers et al., 1997). Moreover, strong complexation of Ge by organic matter leads to the increase of Ge/Si ratio in organic-rich river waters. For example, Ge/Si was found to be about 4×10^{-6} in tropical waters with > 10 mg/l of DOC (Viers et al., 1997) against 0.6×10^{-6} in organic-poor, ($< 1-2$ mg/l of DOC) river waters and $\sim 10^{-6}$ in the earth's crust (Mortlock and Froelich, 1987).

The high stability of Ge–organic complexes indicates that dissolved organic matter can differently affect the biogeochemical cycles of Ge and Si which are generally considered as chemical analogs following the same geochemical pathways (Froelich and Andreae, 1981; Froelich et al., 1985b). It has been hypothesised that temporal variations in the relative intensity of continental weathering and ocean hydrothermal activity might be estimated from the Ge/Si ratio of opals in marine sediments, because inorganic germanium is incorporated into biogenic opal as if it were a heavy isotope of silicon (Froelich and Andreae, 1981; Froelich et al., 1992). More recently, it has been suggested that chemical weathering intensity on the continent can be related to river Ge/Si ratios (Murnane and Stallard, 1990). The results obtained in this study imply that the Ge/Si ratios measured in organic-rich rivers should be used with caution to estimate chemical-weathering intensity because they can be significantly increased due to Ge complexation with organic matter. Moreover, the complexation of Ge with organic ligands could affect germanium biological uptake compared to silicon. As a result, the Ge/Si ratios measured in marine opal sediments formed in organic-rich waters are not likely to reflect the Ge/Si ratio in seawater environment. More data about the amount and nature of dissolved organic matter are necessary to interpret measured Ge/Si ratios in different environments and to unambiguously use germanium as a tracer for geochemical processes.

6. Conclusion

(1) The local environment around Ge(IV) in 0.002 to ~ 0.02 m aqueous germanium solutions at ambient temperature was characterised as a function of pH and in the presence of different organic ligands (citric and oxalic acids, and catechol) using XAFS spectroscopy. Results show that in organic-free solutions Ge is coordinated with four oxygens with mean Ge–O distances of 1.75 ± 0.02 Å. This is consistent with the formation of $Ge(OH)_4^\circ$ complex at acid to neutral pH and of $GeO(OH)_3^-$ in alkaline solution. In the presence of carboxylic acids at neutral and basic pH and of catechol at acid pH, Ge also exhibits a four-fold coordination, suggesting the absence of organic complexes and the dominance of $Ge(OH)_4^\circ$ or $GeO(OH)_3^-$ species. In contrast, in carboxylic acid-bearing solutions at acid pH and in catechol-bearing solutions at pH > 4, Ge is coordinated by 6 oxygen atoms with Ge–O distances ranging from 1.85 to 1.94 Å. This implies the formation of chelate type complexes with the organic ligands. These data strongly support the speciation scheme for germanium in organic-bearing solutions derived from the recent potentiometric and solubility measurements reported by Pokrovski and Schott (1998b).

(2) The readiness of germanium to enlarge its coordination from 4 to 6 can explain the high stability of its complexes with di- and polyfunctional carboxylic acids, polyalcohols and *ortho*-diphenols. Unlike germanium, silica forms very weak complexes with these organic ligands. The absence of stable Si complexes with aqueous organic compounds can be explained both by steric constraints affecting the complexes in which Si is tetracoordinated, and by the reluctance of Si to enlarge its coordination sphere to form hexacoordinated Si–O structures.

(3) The results obtained in this study together with those of Pokrovski and Schott (1998b) suggest that the presence of humic acids which have carboxylic and phenolic functional groups can considerably affect aqueous Ge speciation. By contrast, Si-humic acid complexes are likely to be negligible in most natural waters. The formation of Ge-humic acid complexes leads to a significant increase of Ge/Si ratios in organic-rich fluids and should be taken into account when using the Ge/Si ratios measured in surficial waters and biogenic opals to estimate chemical-weathering intensity and Ge and Si global fluxes.

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