



Mechanisms of fluoride release in sediments of Argentina's central region

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HIGHLIGHTS

- Fluvial and loess sediments of Central Argentina release high fluoride concentrations.
- Fluoride release depends on pH and dominant cation in the solution.
- Dissolution of a Ca/F-bearing phase is the primary source of fluoride at acidic pH (<6).
- Desorption from Fe/Mn(hydr)oxides occurs under alkaline conditions.

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ABSTRACT

We analyze the sources and mechanisms that control the release of fluoride from sediments collected from two types of aquatic reservoirs in the central region of Argentina: 1) mountainous rivers draining crystalline rocks from the Sierras Pampeanas ranges, and 2) shallow aquifers in loessic sediments. The assessment was performed on the basis of experimental work and the study of chemical and mineralogical characteristics of sediments in contact with F-rich waters of the studied region. The chemical and mineralogical compositions of sediments were analyzed by ICP/OES, DRX, and SEM-EDS. Batch experiments were conducted to evaluate the kinetics of fluoride release under variable pH and ionic composition of the solution. The enhanced release of fluoride at more acidic pH, the inhibition of release in Ca-rich solutions and the positive significant linear trends between Ca^{2+} and fluoride concentrations suggest that the dissolution of a Ca/F-bearing phase (like fluorapatite) strongly controls the dynamics of fluoride in the early stages of water–sediment interaction, particularly under acidic conditions. Calculations revealed that the dissolution of an amount of FAp equivalent to that estimated in the studied sediments may widely account for the values measured in the leaching experiments at pH 6, whatever the dominant cation in the solution. Under such conditions, dissolution of FAp (present as coatings onto glass surfaces or as detritic grains) is likely the major primary source of fluorine in the studied sediments. Contribution from biotite may be also considered as a source in fluvial sediments. When adequate surfaces are present the released anions may partially be scavenged from the solution by adsorption at acidic pH. Increasing alkalinity in the aquatic reservoirs may then release the adsorbed fluoride through desorption or through competition with other anionic species. Comparing both mechanisms, dissolution predominates at lower pH while desorption is the main contribution under alkaline conditions.

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1. Introduction

High levels of naturally-occurring F^- are usually found in Argentinian groundwaters, specially in different parts of the Chacopampean plain (i.e., Kruse and Ainchil, 2003; Warren et al., 2005; Fiorentino et al., 2007; Francisca and Carro Perez, 2009; Gómez et al., 2009). It is estimated that about 1.2 million inhabitants drink groundwaters with fluoride contents that exceed Argentinian as well as international guideline values. Depending on the temperature, such standards vary between

0.8 and 1.7 mg L^{-1} for drinking water (CAA, 1994; WHO, 2004). The source of fluoride in Chacopampean shallow and deep groundwater has been generally attributed to volcanic shards present in loessic sediments (i.e. Nicolli et al., 2012 and references therein). Bearing in mind that there are no references on the occurrence of fluorine-bearing minerals in aquifers, it is clear that such conclusions were mostly based on water geochemistry.

The occurrence of F-rich waters in the Chacopampean region is not only associated with loess sediments. Recently, García et al., 2012 described F-rich groundwaters and river waters in the northern portion of the Sierras Chicas de Córdoba (central-western Argentina), where several cases of mild and severe dental fluorosis in children were detected. F-bearing minerals in the crystalline rocks of the

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region, such as biotite and fluorapatite (FAP), have been assigned as the main fluoride sources in water. The occurrence of F-rich waters associated with granitic terrains has been described worldwide (e.g. Chae et al., 2007; Reddy et al., 2010; Martinez et al., 2012). As fluorine is an incompatible lithophile element (Faure, 1991), it preferentially partitions into silicate melts as magmatic crystallization proceeds (Xiaolin and Zhenhua, 1998). For that reason, F-bearing minerals are generally associated to late-stage pegmatite granites, hydrothermal vein deposits and rocks that crystallize from highly evolved pristine magmas (Taylor and Fallick, 1997; Nagadu et al., 2003; Scaillet and Macdonald, 2004). Among primary minerals, biotite and muscovite may contain about 1 wt.% of F, while contents are higher in accessory minerals such as fluorapatite (~3.8 wt.%), topaz (~11.5 wt.%), and fluorite (~48 wt.%) (Speer, 1984).

Several factors may control the mobility of fluorine in natural waters. Many authors have described fluorite dissolution, enhanced by calcite precipitation, as one important mechanism of fluoride release to waters in equilibrium with calcite (i.e. Genxu and Guodong, 2001; Desbarats, 2009; Currel et al., 2011). The dissolution of fluorite may also be enhanced by other mechanisms that result in Ca^{2+} scavenging, such as cation exchange or apatite precipitation. The dynamics of F^- ions may also be controlled by adsorption/desorption onto different mineral surfaces, mainly Fe or Al (hydr)oxides but also calcite. In general F^- is preferentially adsorbed to mineral surfaces under neutral to acidic conditions (i.e., Omuetti and Jones, 1977; Sposito, 1989; Sparks, 1995; Arnesen and Krogstad, 1998; Hiemstra and Van Riemsdijk, 2000; Tang et al., 2009). This trend could be altered at acid pH (i.e. F^- is desorbed from mineral surfaces) by competing with some other anions such as HCO_3^- , phosphate, arsenate and silicate species usually present in natural waters.

In this work, we analyze the sources and mechanisms that control the release of fluorine from sediments collected from: 1) mountainous rivers draining crystalline rocks from the Sierras Pampeanas ranges, and 2) shallow aquifers in loessic sediments. The assessment was performed on the basis of experimental work and the study of chemical and mineralogical characteristics of sediments in contact with F-rich waters of the Chacopampean region.

2. Materials and methods

All solutions were prepared from analytical reagent grade chemicals and purified water (Milli-Q system).

2.1. Sampling, chemical and mineralogical analyses

The studied sediments were collected in two sites in the Chacopampean region, where F-rich waters were reported. Samples AR and AB correspond to river bed sediments collected from the upper and medium reaches of the Charbonier River in the Sierras Chicas de Córdoba, Central Argentina (30°46'S; 64°32'W and 30°46'S; 64°34'W respectively). Samples L1 and L10 correspond to loessic sediments collected from two different sections in the northern Chacopampean Plain. Sample L1 was taken from the bottom of a 9.3-m vertical section at Corralito (32°00'S; 64°09'W; 490 m a.s.l.) that is exposed along an abandoned road excavation, 35 km south of Córdoba city. Sample L10 was collected from a 5.0-m freaterimeter located in Lamadrid city (27°38'S; 65°14'W; 293 m a.s.l.), 90 km south of the city of San Miguel de Tucumán. At the moment of sampling, sediment samples were completely saturated. The location of samples is shown in the GoogleMaps file available in the online version.

After collection, samples were air-dried and separated into two portions. One was sieved through <63 μm mesh, while the remaining was ground in an agate mortar. Chemical analyses were carried out on the ground total fraction by ICP/OES after lithium metaborate/tetraborate fusion. Water, carbonate, and organic matter were determined gravimetrically in a previously weighted portion of the total

sample. X-ray diffraction (XRD) analysis was performed in the <63 μm size-fraction.

Clay mineralogy was determined in the <2 μm size-fraction. Separation of this fraction was performed following the USGS open file report 01-041 guideline. Briefly, a portion of the sediment was suspended in 1:4 acetic acid overnight in order to remove carbonates. The procedure was repeated until a foamless suspension was attained. In a second step, organic matter was eliminated with 3% hydrogen peroxide until the addition of hydrogen peroxide to the samples no longer caused bubbling. After each step, the suspensions were allowed to settle and then washed by centrifuging with distilled water.

The mineralogy of both fractions (<63 μm and <2 μm) was determined by XRD analysis performed with a Philips X'Pert PRO X-ray diffractometer operating at 30 kV and 15 mA and using Cu-K α radiation. Measurements were performed in both, random (<63 μm) and oriented (<2 μm clay-size fraction) samples. Oriented slides were tested in air-dried and ethylene glycol solvated preparations. XRD data was obtained in the 2θ range from 4 to 65° (step size: 0.004; 3.5 s/step) for random samples and from 2 to 30° (0.004/2 s) for oriented samples. The mineralogical interpretation was done using the software X'Pert HighScore, installed on the X-ray diffractometer.

2.2. Scanning Electron Microscopy (SEM) and microprobe analysis of sediments

SEM/EDS studies were performed with a JEOL 35 JXA-8230 electron probe microanalyzer coupled with an energy-dispersive X-ray (EDS) analyzer. The samples were prepared in graphite stubs and coated with carbon. In addition, SEM was coupled with focused energy dispersive X-ray analyses (EDAX DX4) in order to perform the elemental semi-quantification. The detection limit of microprobe analyses was about 0.5% for fluorine and the spatial resolution was about 1 μm .

2.3. Fluorine release experiments in sediment samples

Batch experiments were performed to study the kinetics of fluoride release and to investigate the influence of pH and ionic composition on the process. Reactions were carried out in cylindrical, water-jacketed and lidded reaction vessels, in order to keep the temperature constant at 25.0 ± 0.5 °C. The suspensions were prepared using 100 mL of a 0.1, 0.01 and 0.001 M NaNO_3 solutions aiming to reach the ionic strength values typically found in the studied environments. About 5 g of dry sediment (ground total fraction) was added to the corresponding NaNO_3 solution and the pH of the suspension was adjusted to 6.0 or 8.0 by the addition of either 0.1 M HNO_3 or NaOH . Suspensions were continuously stirred until the experimental end. Aliquots of the suspension were withdrawn after 1 h, and two, five and seven days from the moment of pH adjustment, and filtered through a 0.45 μm cellulose membrane filter. Fluoride was measured in the separated supernatant. During the experiment, pH was continuously checked and kept constant by adding either 0.1 M HNO_3 or NaOH . The same procedure was followed in experiments conducted with Ca^{2+} electrolyte solutions (CaCl_2).

The total fluoride concentration was measured using a specific fluoride combination electrode (ISE 25) connected to an Orion pH meter. A total ionic strength adjustment TISAB buffer (TISAB: 58 g NaCl + 57 mL acetic acid + 10 Na-citrate, adjusted to pH 5.2 with 5 M NaOH in a total volume of 1 L) was used to adjust pH before measurement, and to eliminate any interference from high levels of aluminum and iron that could be present in the solution (Shen et al., 2003). The calibration curve was constructed using NaF standard solutions, subjected to the same treatment previously described.

3. Results

3.1. Chemical and mineralogical characteristics of sediments

The bulk chemical composition of the studied sediments was similar, being the contents of organic matter and carbonate the most conspicuous differences among them (Table 1). The red mud (AR) collected in the upper stretch of the Charbonier River showed the highest concentration of organic matter. Carbonate concentrations were similar in all the studied sediments, but values were slightly higher in the fluvial white mud (AB) sample.

Dominant mineralogy in all studied sediments was homogeneous. Primary minerals determined by XRD were quartz, K-feldspar, and plagioclase (Fig. 1). Biotite and chlorite were present in fluvial samples only. Calcite was also present in all samples, while gypsum was detected only in fluvial sediments. Illite and kaolinite were predominant clay-size (<2 µm) fraction (Fig. 2).

The heavy mineral fraction, which was not visible in the XRD patterns due to its restricted proportion (<5%), were identified using SEM/EDS. Ti–Zr oxides, titanite, Fe and Mn(hydr)oxide coatings, and FAp were found in loess samples, as well as volcanic glass, authigenic barite, and pyrite. Very scarce and micrometric grains (~5 µm) of bastnäsite ((Ce,La)(CO₃)F) have been also identified in these samples. Detritic grains of FAp (~10 µm) were highly altered and associated with authigenic calcite (Fig. 3a).

Mineral weathering in fluvial sediments was less obvious than in loess samples (Fig. 3b). Granate, biotite, ilmenite, anatase, zircon, amphiboles, pyroxenes, calcite, FAp and coatings of Ti and Fe(hydr) oxides associated with altered biotite were observed. Microprobe analysis in FAp showed F contents of ~2.8%, which is typical for this mineral. In these sediments, detritic FAp was less altered and generally associated with clay minerals.

3.2. Batch kinetics experiments

Fig. 4 illustrates the results obtained at pHs 6.0 and 8.0 in the fluoride release kinetic experiments. In general, the kinetic process involved two stages: a first step, which occurs during the first hour, followed by a second much slower step that involves a gradual release of fluoride with time, until reaching equilibrium after 90 h.

The experiment results indicate that fluoride release is pH dependent. In general, lower pH leads to a higher release of fluoride (Fig. 4) and whatever the dominant cation in the solution. In the experiment carried out with the suspension of sample L10, a higher release at pH 8 was measured only in the first hour of reaction. The replacement of Na⁺ by Ca²⁺ as the dominant ion in the solution at constant pH was also studied. Changes in the cation composition lead to the inhibition of the fluoride release at both analyzed pH values. River bed sediments collected at the Sierras Pampeanas Ranges were more sensible to changes in pH and dominant cation whereas loess samples showed the lowest variations.

4. Discussion

4.1. Natural sources of fluorine

Several F-bearing phases have been detected in the analyzed sediments, FAp, biotites, volcanic glass, and Fe(hydr)oxides being the most relevant. From these sources, a distinction should be made between those considered as primary sources and those that clearly bind F[−] ions as a consequence of scavenging processes that occurred in the source or during transport of mineral particles to their final setting. Of all listed sources, FAp and biotite are primary sources, as fluorine was included into their lattices by substituting OH[−] ions during magmatic crystallization (Speer, 1984).

The kinetics of dissolution of biotite under different conditions of pH, ionic strength, and temperature has been extensively studied (e.g. Acker and Bricker, 1992; Kalinowski and Schweda, 1996; Malmström and Banwart, 1997; He et al., 2005) but none of such works deal with the release of fluorine during dissolution. In what was the only exception (Chae et al., 2006) constant fluoride concentrations in leaching experiments of biotite in pure water at pH 7 and 25 °C were achieved after 200 h of reaction. In their experiments, the concentration of Ca²⁺ decreased after a certain time of reaction which was interpreted as the result of fluoride precipitation or the occurrence of some other processes that result on the removal of Ca²⁺ ions, like adsorption and/or cation exchange.

Guidry and Mackenzie (2003) studied the dissolution kinetics of igneous and carbonate fluorapatite and they found that equilibrium was reached after 3 days, and that the concentration of fluoride, phosphate and calcium always increased as the dissolution took place. These authors also indicated that the fluoride concentration rapidly increased during the first day of reaction, and then dissolution became increasingly slower until equilibrium was reached. Furthermore, the dissolution of FAp was interpreted as a pH dependent process. Chaïrat et al. (2007) determined that FAp dissolution rates decreased for pH ≥ 3, remaining constant between 7 ≤ pH ≤ 10 and again decreasing for pH ≥ 10.

Volcanic glass has been traditionally considered as the main source of several trace elements such as As, F, V, Mo, and U found in toxic concentrations in shallow groundwater from the Chacopampean plain (i.e., Nicolli et al., 2012 and references therein). Chemical analyses performed on volcanic glass grains separated from loess samples collected in Tucumán province revealed a rhyolitic composition and showed contents of fluorine that were lower than in the total sediment fraction (Nicolli et al., 2010). The occurrence of high levels of fluorine associated with volcanic ashes has been extensively reported worldwide (e.g., Oskarsson, 1980; Cronin et al., 2003; Wolff-Boenisch and Gislason, 2004; Witham et al., 2005; Delmelle et al., 2007; Jones and Gislason, 2008; Ruggieri et al., 2010; Ruggieri et al., 2011; Ruggieri et al., 2012). This association is related to the scavenging in the volcanic plumes of volatiles, including sulfur, halogens and metal species. Adsorption onto the ash surfaces may occur by gas-to-particle interactions or liquid-to-particle interactions. SEM images and profiling of deposited ash show the presence of salts on the ash surfaces (Rose, 1977; Rose et al., 1980). Ca²⁺, Na⁺, Mg²⁺, SO₄^{2−} and Cl[−] are the predominant species released on first exposure of volcanic ash to water (Delmelle et al., 2007; Smith et al., 1983). High concentrations of fluorine associated with volcanic ash are mostly due to fluorine compounds adsorbed onto the ash surface (Oskarsson, 1980). Delmelle et al. (2007) demonstrated using atomic force microscopy (AFM) imaging coupled with XPS and ash-leachate studies, that extremely thin coatings (<10 nm) formed at the ash surfaces probably throughout in-plume processes. This material is composed of relatively soluble sulfate and halide salts mixed with sparingly soluble fluorine compounds (likely, CaF₂, AlF₃ and Ca₅(PO₄)₃F). Regarding these observations, we may think that volcanic ash present in loess sediments from the Chacopampean plain is just a carrier of F-bearing salts that are in the form of thin coats onto the tephra surfaces.

Desorption from Fe, Al and Mn (oxy)hydroxides has also been mentioned as a secondary source of fluoride in groundwaters in contact with loess sediments (e.g., Smedley et al., 2005) as well as in some other parts of the world with similar geochemical characteristics, such as in the alkaline, Na-rich groundwater from the Yuncheng Basin, China (Currel et al., 2011). The adsorption of fluoride onto Fe (oxy)hydroxides is produced when fluoride replaces surface hydroxyls according to the reaction: FeOH^{−1/2} + F[−] = FeF^{−1/2} + OH[−] (Hiemstra and Van Riemsdijk, 2000), which shows that the reaction preferentially occurs under neutral to acidic conditions (i.e., Omuetti and Jones, 1977; Hao and Huang, 1986; Sposito, 1989; Sparks, 1995; Arnesen and Krogstad, 1998; Hiemstra and Van Riemsdijk, 2000; Tang et al., 2009).

Table 1

Chemical composition of the studied sediments. OM: organic matter.

Sample	SiO ₂ (%)	Al ₂ O ₃	Fe ₂ O _{3(T)}	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Total	H ₂ O	Carbonate	OM
AR	52.33	12.62	4.51	0.10	2.04	4.86	2.58	2.67	0.63	0.21	82.55	2.4	1.9	9.4
AB	62.82	12.84	4.81	0.10	2.09	4.84	2.42	2.95	0.65	0.14	93.66	0.6	2.3	2.6
L1	58.60	15.01	4.90	0.10	1.65	4.51	2.23	2.76	0.71	0.23	90.69	1.9	1.8	3.2
L10	61.24	15.94	5.41	0.09	2.35	2.57	2.49	3.39	0.79	0.14	94.40	0.9	2.0	2.6

4.2. Assessment of sources and mechanisms of fluoride release in the studied sediments

SEM/EDS observations in both, fluvial and loessic samples revealed the occurrence of accessory detritic FAp and abundant altered biotite. The equilibrium dissolution of FAp, represented in Eq. (1), indicates that F[−] and Ca²⁺ ions are released during dissolution preferentially under acidic pH:



Fig. 5a shows the relationship between Ca²⁺ and F[−] measured in the leachates of fluvial sediments with different dominant cation and pH conditions. In all cases, a positive linear trend between these two ions is observed, suggesting that they are released by the same source.

The slope remains constant at either different pH or dominant cation, but differs in different samples. The addition of Ca²⁺ to the solution leads to higher initial concentrations of Ca²⁺ and a slight decrease in the F[−] concentrations, moving to the right the correlation lines, but with no changes in the slope. This behavior suggests that: 1) at both analyzed pH values the mechanism of fluorine release that predominates in the two fluvial samples is the same; 2) the fluoride source is not exactly the same in the two studied samples; and 3) the higher amounts of fluoride released from sample AB and the weaker influence of Ca²⁺ in the release, suggest that in this sample, an additional source (e.g., F-bearing biotite) is contributing to the measured fluoride. Colombo et al. (2010) described F-rich micas in pegmatites and host A-type carboniferous granites from the northern Sierras Pampeanas region, that were considered to be one of the main fluoride sources in rivers and groundwater that are in contact with these rocks (García et al.,

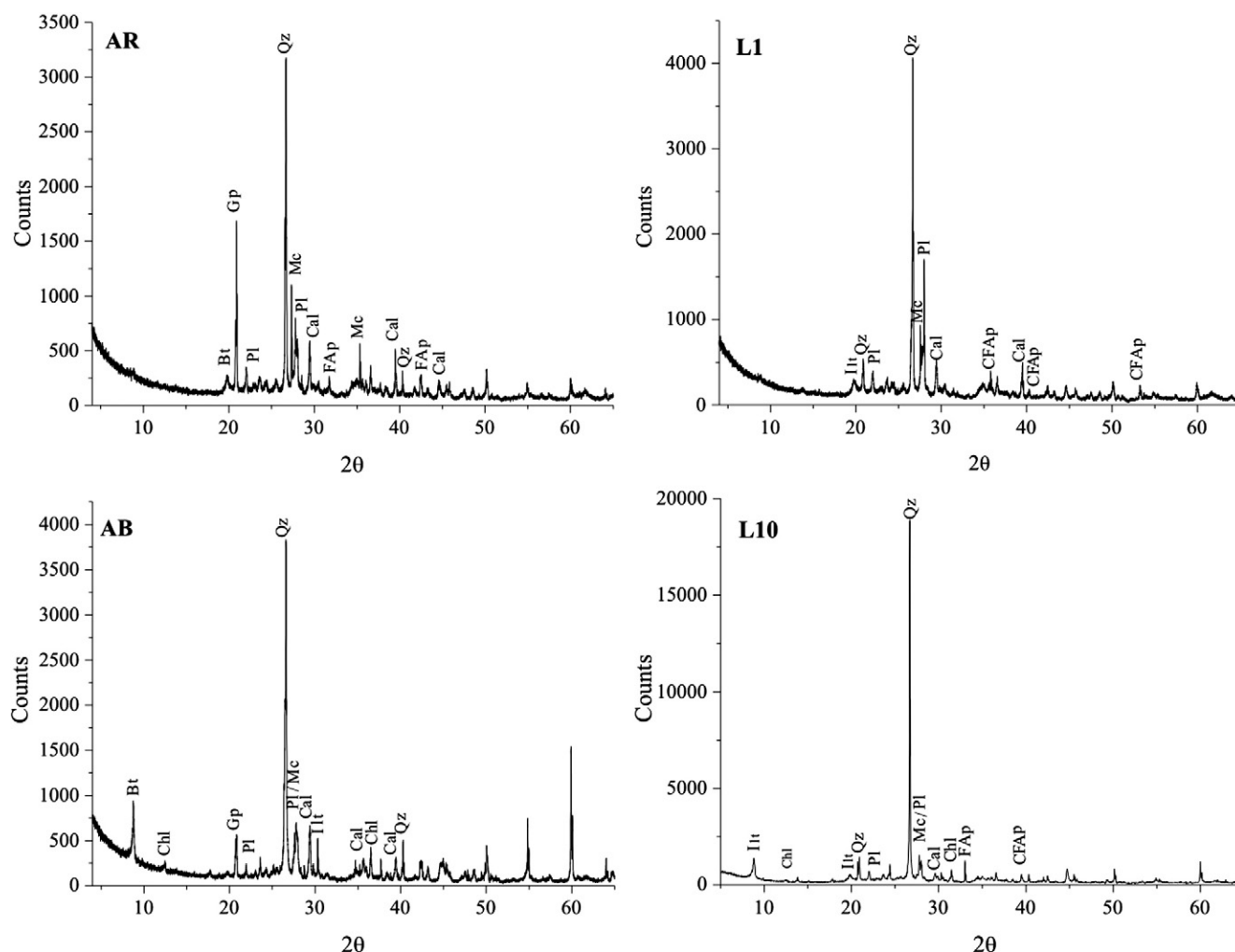


Fig. 1. XRD diagrams of fluvial (AB and AR) and loess (L1 and L10) sediments. QZ: quartz; Bt: biotite; Pl: plagioclase; Gp: gypsum; Mc: microcline; Cal: calcite; FAp: fluorapatite; Ill: illite; Chl: chlorite; CFAP: carbonate fluorapatite.

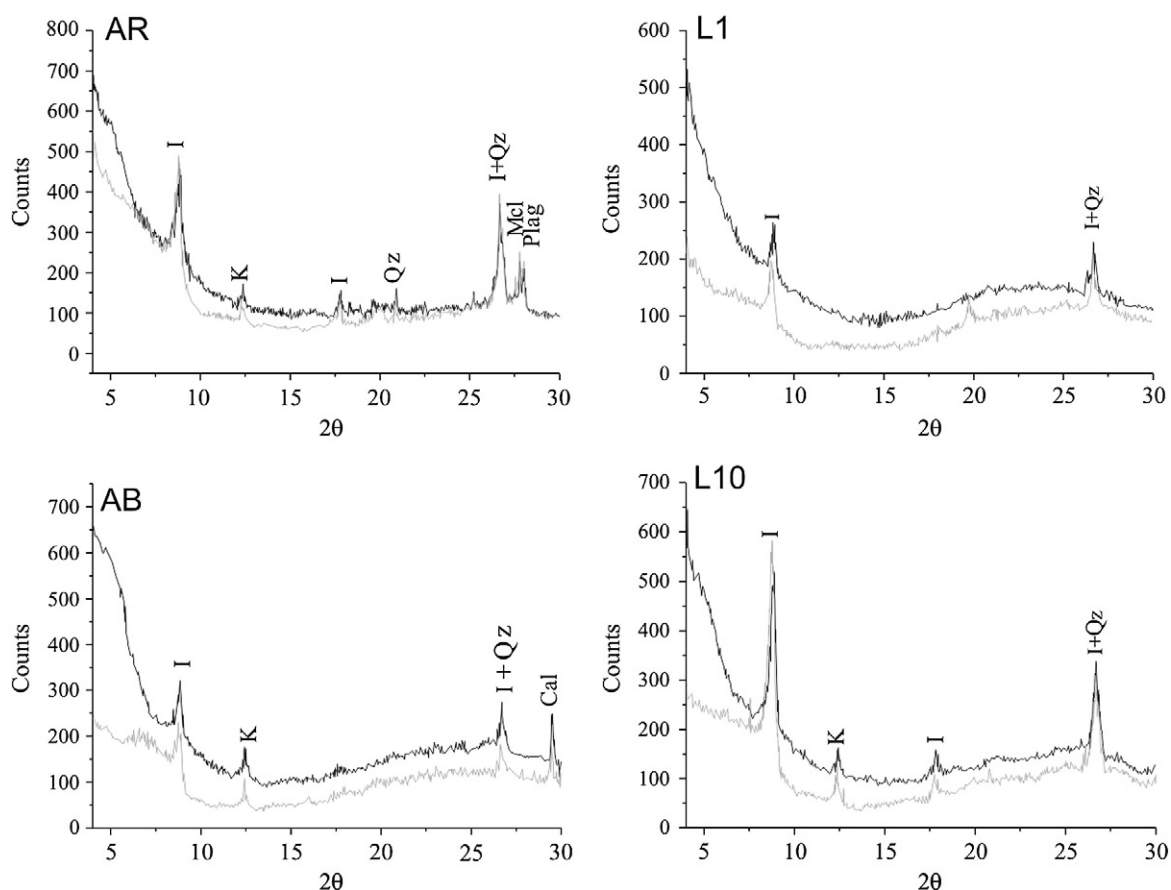


Fig. 2. XRD diagrams showing the clay mineralogy (<2 μm) of fluvial (AB and AR) and loess (L1 and L10) sediments. Black lines correspond to air dried samples; red lines correspond to ethylene glycol solvated samples. QZ: quartz; Ill: illite; Pl: plagioclase; Mc: microcline; Cal: calcite; Kln: kaolinite.

2012). Some other accessory minerals such as primary FAp (Fig. 3b) are also considered as important fluoride sources.

Positive linear correlation between Ca^{2+} and fluoride concentrations was also observed in experiments carried out with L10 suspensions (Fig. 5b), and unlike fluvial sediments, changes in pH led to different trends in the release of Ca^{2+} and fluoride ions. At pH 6 the behavior is similar to that described for fluvial sediments, but at pH 8 increasing fluoride concentrations are observed at almost constant Ca^{2+} concentrations. Therefore, for this sediment sample, two processes seem to be responsible for fluoride release: 1) dissolution of a Ca/F-bearing phase, likely detritic grains, coatings of FAp or secondary F-bearing calcite, at pH 6, and 2) desorption from Fe/Mn(hydr)oxide surfaces at pH 8. The latter is mostly produced in the first hour of reaction, as indicated in Fig. 4d. Ca^{2+} concentrations could not be measured in all extracts obtained from L1 suspensions, but from the analysis of the kinetic curves obtained for L1 suspensions in Fig. 4c, it is clear that these two processes can also be inferred for this sample. According with the observed trend, higher release of fluoride is always obtained at pH 6 in Na-dominant suspensions, suggesting that the dissolution of a F-bearing phase predominates at pH 6 during the time evaluated in the experiment. At pH 8, the inhibition of the release in Ca-dominated suspensions is lower, which indicates that desorption could be more important than dissolution in the final stages of the reaction.

As mentioned before, detritic grains of FAp were detected by SEM/EDS analysis of the loess samples. Fig. 3a shows the occurrence of scarce and highly altered grains of this mineral, generally associated with secondary calcite. Precipitation of authigenic calcite is favored by high alkalinity and the pH conditions of natural waters. This process promotes further FAp dissolution, explaining the opposite trends between fluoride and Ca^{2+} ions described in field observations of the

Chacopampean plain (i.e., García et al., 2009; Gómez et al., 2009). FAp coatings onto volcanic glass surfaces were not directly determined through SEM/EDS observations, but the occurrence of small peaks of P (Fig. 6), associated with elemental abundances of Si, O, Ca, Na, Fe and Al, that match those found in rhyolitic glasses (Hanson et al., 1996) may be indicating the presence of F-bearing coatings already described in volcanic particles (Delmelle et al., 2007). Due to low concentrations, (i.e., likely below the method detection limit), F-bearing coatings were not detected.

4.3. Estimation of fluoride release from pure phases

The results shown above, suggest that FAp dissolution and desorption from mineral surfaces are the main mechanisms of fluoride release in the studied samples. However, these phases are not abundant in sediments. In consequence, to what extent they may account for the levels of fluoride measured in the leaching experiments? In order to answer this question, we have performed some calculations of a pure FAp dissolution by using the geochemical code PHREEQC 2.16 (Parkhurst and Appelo, 1999) coupled with the Wateq4f database, in which some assumptions were made as indicated below. Desorption was calculated on the basis of parameters available in the literature for a pure goethite.

Dissolution simulations of a number of moles equivalent to the amount of pure FAp estimated in sediments revealed that dissolution may completely explain the levels of fluoride measured in leaching experiments. For simulation, the 50% of the concentration of P_2O_5 in the sediments was assigned to FAp (Table 2), considering that P may be included into the feldspar lattice as an impurity or may occur as a major constituent in other accessory minerals such as monazite. Ruggieri et al. (2010) estimated that about 50% of P measured in sequential extractions performed in volcanic ashes is associated with the silicate network. This

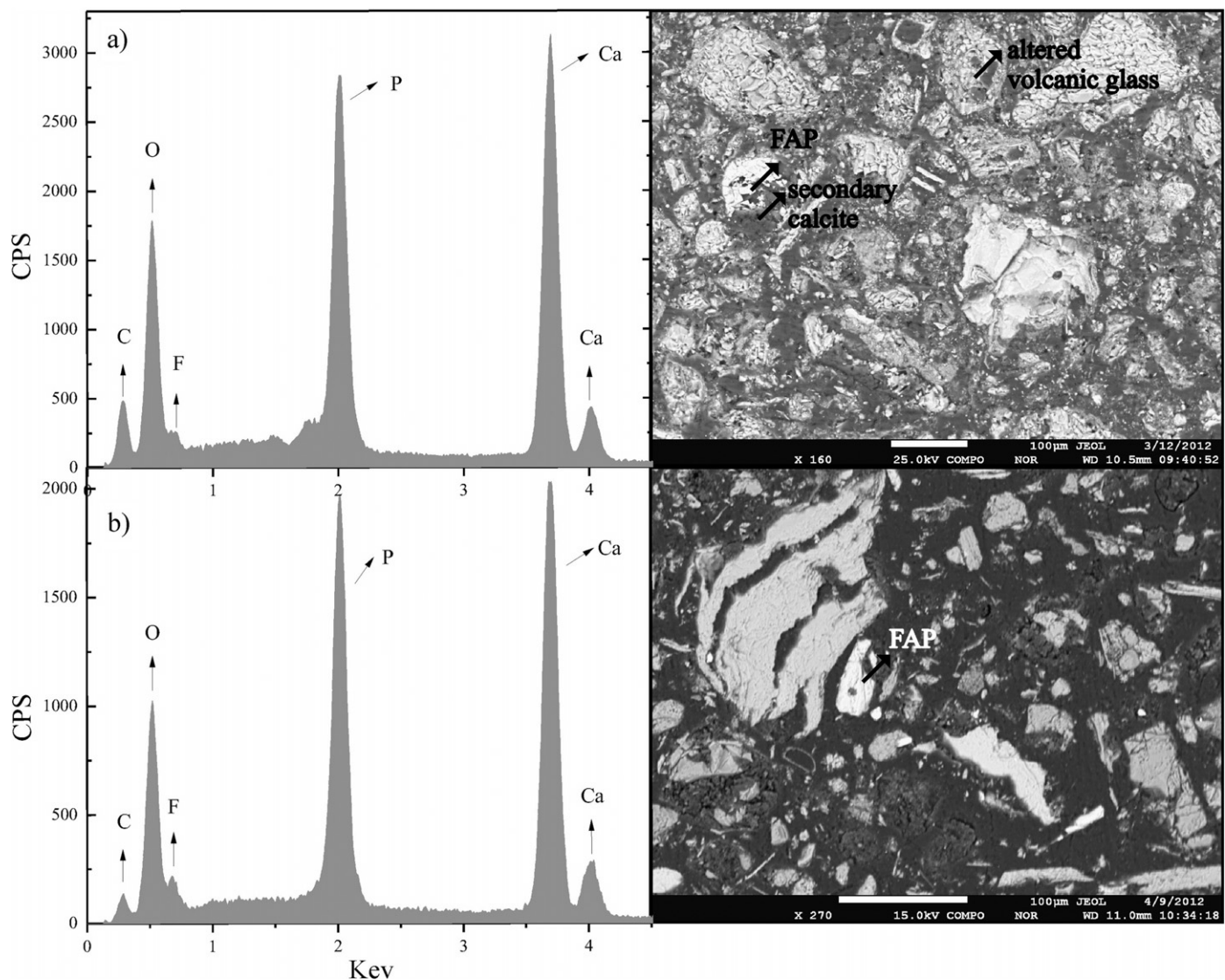


Fig. 3. SEM images of fluvial and loess sediment samples (a and b). The right-hand column shows the EDS diagrams obtained for FAP grains.

percentage was considered to be a rather conservative estimation for our sediments. Because the dissolution of FAp is linked with calcite precipitation, both phases (calcite + FAp) were considered in the model. The composition of the initial solution was NaCl or CaCl_2 0.001 M and 0.01 M for fluvial and loess samples, respectively. Calculations were run until equilibrium conditions were reached for both, FAp and calcite.

In agreement with experimental results, calculations show that the most favorable conditions for FAp dissolution correspond to Na-dominated and slightly acidic solutions (pH 6). Under such conditions, the amount of fluoride recovered experimentally fluctuates between 16 and 71% of the fluoride that could potentially be released from the FAp moles used in the calculations and in the presence of an excess of calcite. Lower efficiencies of FAp dissolution (16–26%) were obtained in experiments carried out with loess and the AR fluvial samples. Higher dissolution rates were achieved with experiments carried out with the AB fluvial sample (75%). Calculations performed with suspensions at pH 6 and Ca^{2+} as dominant cation also revealed the inhibition of FAp dissolution, although the theoretical concentrations of fluoride were enough to completely explain the amounts obtained experimentally (Fig. 7a).

At pH 8, theoretical FAp dissolution cannot explain the levels of fluoride recovered experimentally, whatever the cation that

dominates in the solution. In consequence, another process is controlling the release of fluoride under alkaline conditions, more likely desorption from adequate surfaces. Some calculations were performed in order to evaluate if this contribution may account for the levels of fluoride measured experimentally. Firstly, the amount of Fe(hydr)oxide coatings was considered to be 2% of the total Fe content determined in the sediments by ICP/OES. This proportion was determined on the basis of oxalate-extractions performed with loessic sediments from La Pampa province (Smedley et al., 2005). Secondly, to set the concentration of adsorption sites, some references from the literature were taken into account, especially the values reported by Hiemstra and Van Riemsdijk (2000) for fluoride adsorption onto goethite. Finally, stoichiometric calculations of fluoride release from desorption were performed based on the above mentioned conditions and the results reported by Tang et al. (2009), who estimated that the amount of fluoride desorbed from goethite was about 60% at pH 8. All data considered in desorption calculations are shown in Table 2. The obtained results show that all the studied sediments may release similar amounts of fluoride by desorption from Fe(hydr)oxide coatings at pH 8 (Fig. 7b) independently of the dominant cation in the solution. Indeed, this is true due to the similar concentrations of FeO measured in sediments (Table 1). As seen in Fig. 7b, desorption can only explain

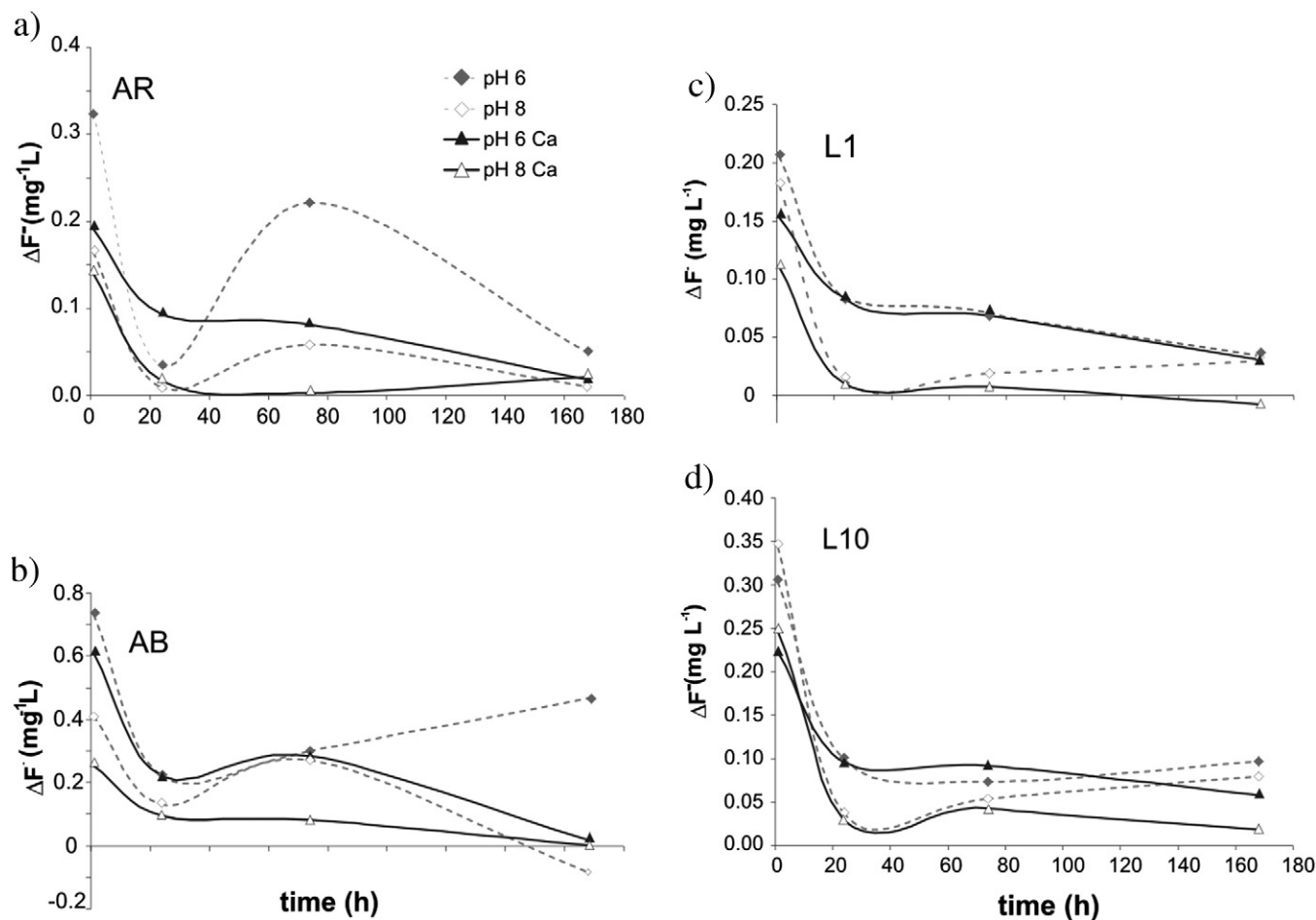


Fig. 4. Kinetics curves showing the release of fluoride with time. Full symbols: pH 6; open symbols: pH 8; circles: Na^+ -dominant suspensions; triangles: Ca^{2+} -dominant suspensions.

all the fluoride released from sediments AR and L1 in NaCl solutions, while in the remaining samples, another source of fluorine needs to be considered. Fap dissolution occurs in some minor proportion at pH 8 (Fig. 7a), so it can be considered along with desorption as a complementary source of fluorine at pH 8. The dashed black line in Fig. 7b shows the theoretical amount of fluoride that could potentially be released at pH 8 from both, desorption and Fap dissolution in the studied sediments. The change of dominant cation in the solution at pH 8 clearly inhibits Fap dissolution, and hence, the amount of fluoride released by this process becomes negligible. Under such condition, desorption completely account for the levels of fluoride determined experimentally in all the studied suspensions, with the exception of AB sample, where another source different to desorption and Fap dissolution must be considered, likely alteration of F-rich biotite as indicated above.

Competition was not considered in the previous discussion, but this process may frequently occur in heterogeneous systems such as in natural waters. In HCO_3^- rich waters such as those in contact with the studied sediments, the dominant anion usually competes with fluoride for surface sites. Although dissolution seems to be the main mechanism of fluoride release at pH 6, competition with HCO_3^- should also be considered as an important contribution. In the analyzed experiments, the dissolution of calcite is the main source of HCO_3^- to the dissolved pool. This mechanism predominates at acidic pH, as well as the adsorption of HCO_3^- onto Fe(hydr)oxide surfaces. As a consequence, calcite dissolution and subsequent HCO_3^- adsorption may lead to the release of fluoride by competitive desorption,

even under acidic pH. In order to evaluate the extent of competition in the studied systems, the dissolution of calcite at pHs 6.0 and 0.01 and 0.001 M ionic strengths was simulated, using PHREEQC 2.13 (Parkhurst and Appelo, 1999). In the calculations, it was considered that 1 mol of HCO_3^- may replace 1 mol of fluoride in the corresponding surface site. Comparing the simulated concentration of HCO_3^- with the concentrations of fluoride measured in the leachates at the end of the experiments it was found that F^- concentrations are significantly higher (89, 31, 21, and 29 μM for AB, AR, L1 and L10 samples respectively) than the values calculated for HCO_3^- (5 μM). Therefore, the amount of fluoride that may be released by competition with HCO_3^- at pH 6 is not significant, and in consequence, the contribution of fluoride through competitive desorption with bicarbonate ions is considered rather secondary in the studied sediments.

4.4. Implications in natural waters

The experimental pH range evaluated in this work is slightly wider than what is observed in natural waters from the Chacopampean region and Pampean ranges, which is typically circumneutral to alkaline. Besides, the effect of Ca-dominated waters was analyzed, in spite that natural conditions mostly correspond to Na-rich waters. These chemical characteristics were selected in order to identify the primary sources of fluorine and as aids to characterize the mechanisms of release under conditions different to those observed in the natural environments.

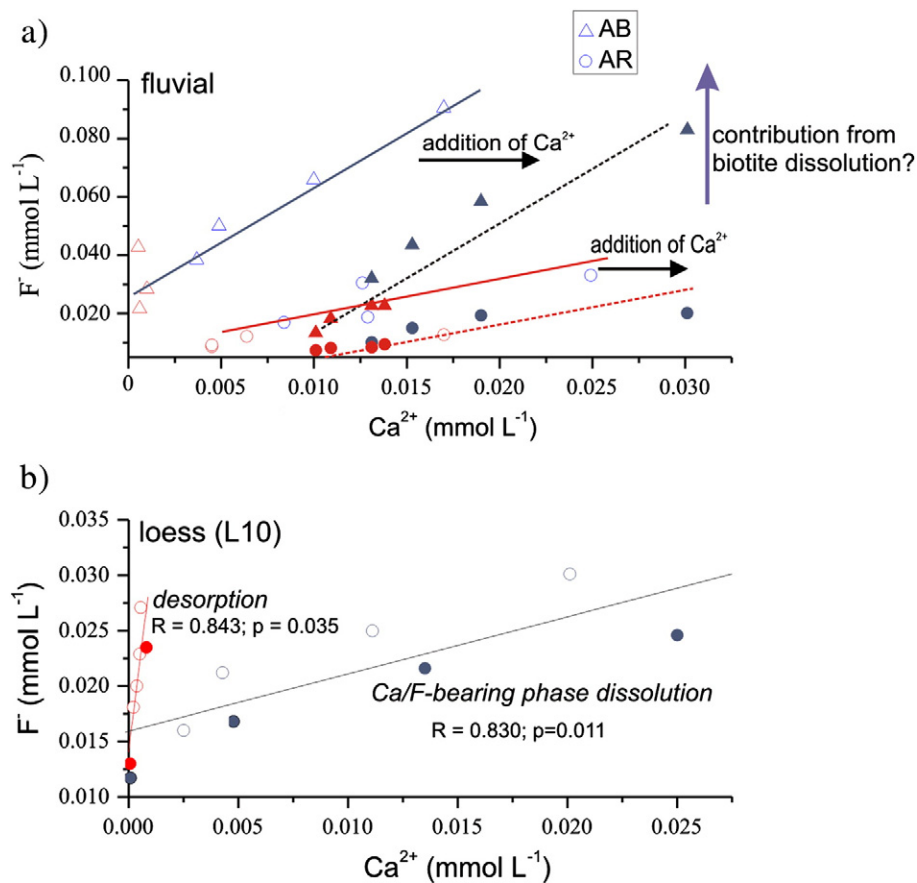


Fig. 5. Scatter diagrams' showing the relationship between Ca^{2+} and F^- concentrations in experiments carried out with a) fluvial sediment suspensions and b) loess suspensions. Full symbols: Ca^{2+} -dominant suspensions; open symbols: Na^+ -dominant suspensions. Black symbols: pH 6; Gray symbols: pH 8. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

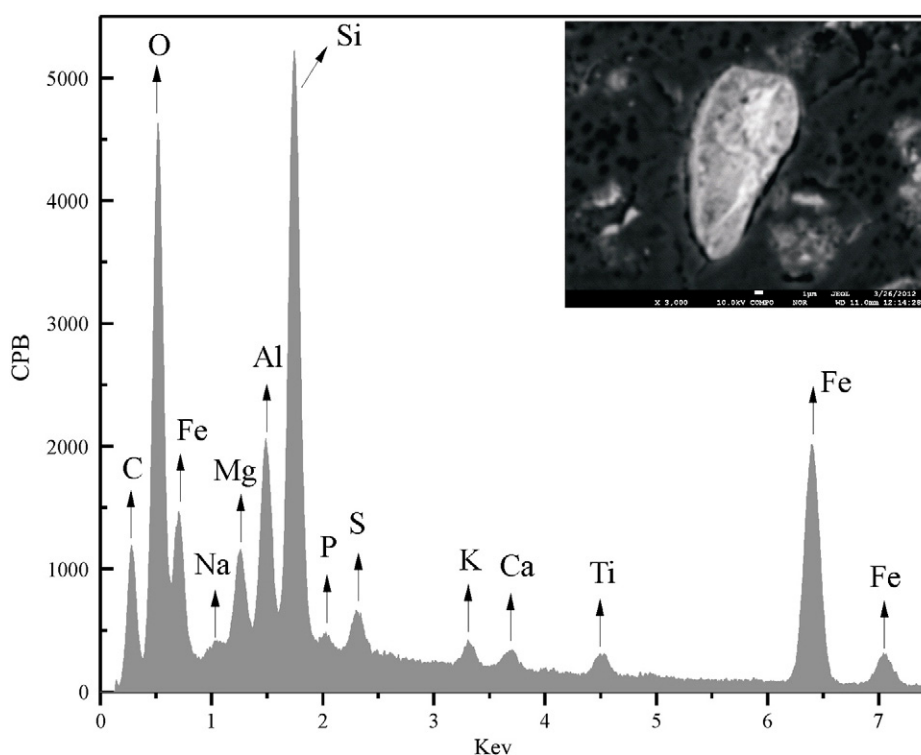


Fig. 6. EDS analysis and SEM image of a volcanic glass grain in loess sample (L10).

Table 2

Parameters used in calculations of pure FAp dissolution and fluoride desorption from pure goethite.

Samples	FAP content (mol g ⁻¹)	Measured (mg L ⁻¹)		Calculated (mg L ⁻¹)			
Na ⁺ -dominant suspensions							
		pH 6	pH 8	Dissolution		Desorption ^a	
				pH 6	pH 8	pH 6	pH 8
						20% desorption ^b	80% desorption ^b
AR	9.87E ⁻⁶	0.0126	0.0049	0.0486	0.0044	0.0021	0.0062
AB	6.57E ⁻⁶	0.0344	0.0145	0.0486	0.0045	0.0022	0.0066
L1	1.08E ⁻⁵	0.0078	0.0048	0.0499	0.0054	0.0022	0.0067
L10	6.57E ⁻⁶	0.0114	0.0103	0.0499	0.0054	0.0025	0.0074
Ca ²⁺ -dominant suspensions							
AR	9.87E ⁻⁶	0.0077	0.0036	0.0383	0.0009	0.0020	0.0062
AB	6.57E ⁻⁶	0.0255	0.0090	0.0412	0.0009	0.0022	0.0066
L1	1.08E ⁻⁵	0.0063	0.0024	0.0287	0.0012	0.0022	0.0067
L10	6.57E ⁻⁶	0.0093	0.0074	0.0308	0.0009	0.0025	0.0074

^a For a goethite with a SSA of 300 m² g⁻¹, $\Gamma_{\text{max}} = 603.8 \mu\text{mol g}^{-1}$.^b Tang et al. (2009).

According to experimental results, both types of sediments show a similar general behavior regarding the release of fluoride, but some slight differences may be distinguished. Mineralogical composition, the extent of alteration of sediments and water geochemistry are the most conspicuous factors affecting fluoride release.

Thus in fluvial sediments, mostly made up by slightly altered minerals originated from the weathering of F-rich igneous and metamorphic rocks, the release of fluoride to the water seems to be controlled by the dissolution/alteration of primary fluorine bearing minerals, more likely FAp and biotite. As the release of fluoride occurs rapidly during the FAP dissolution, we might expect that most is liberated in the first reaction stages between this mineral and the more acidic rainwater. Lower pH is usually found in the upper

catchments and, therefore, dissolution of FAP may be more favored in smaller streams where CO₂ is supersaturated in the outcropping water; in such situations when water comes in touch with the atmosphere, pH rapidly equilibrates (i.e., becomes neutral or alkaline) and the mechanism of fluoride release may switch to desorption.

In the analyzed loess samples, the extent of mineral alteration is higher than in fluvial sediments. Highly alkaline pH (≥ 8) and dominant Na–HCO₃ composition are typical features in groundwaters in contact with such sediments (Nicolli et al., 2012 and references therein). Primary sources of fluorine such as detritic FAP and biotite are less frequent and the release of fluoride from such primary sources could occur under more acidic conditions developed locally as a consequence of anthropic alterations (i.e. Garcia et al., 2007). However,

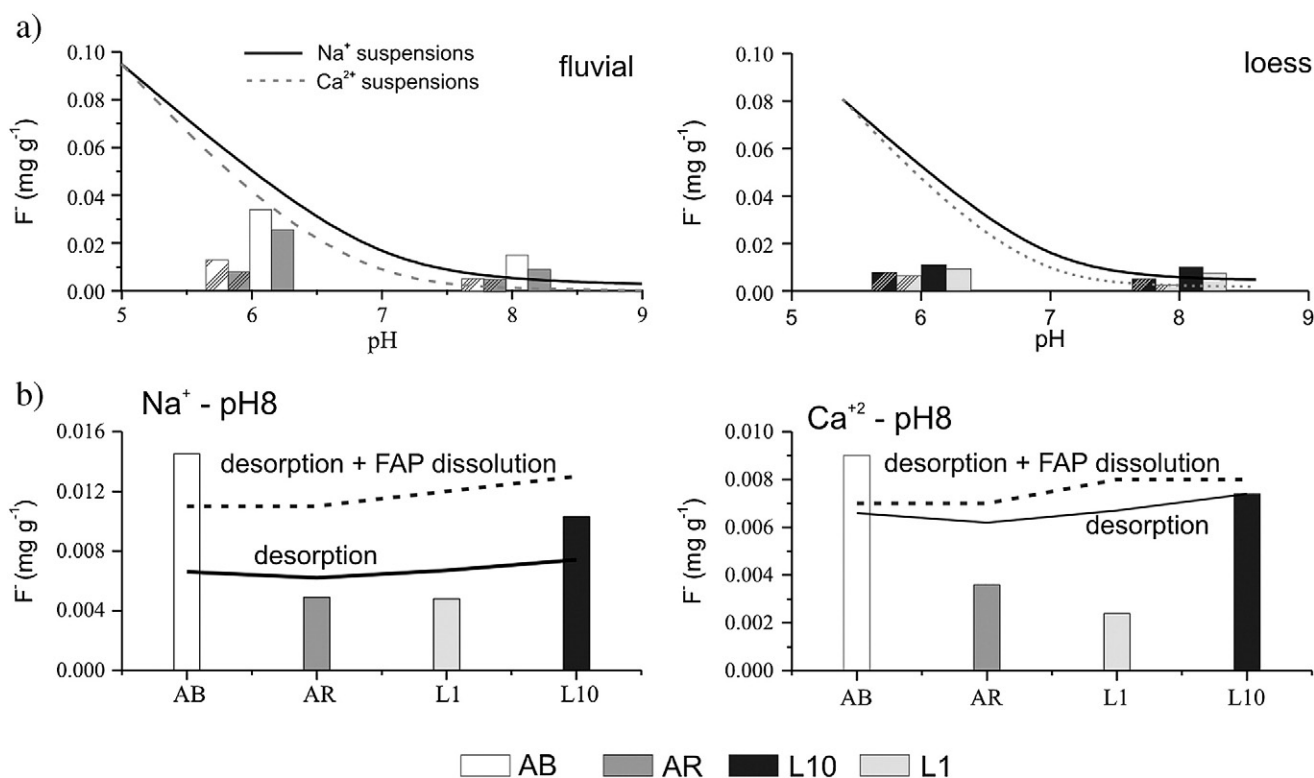


Fig. 7. Graphs showing the theoretical (bars) and experimental (lines) amounts of fluoride released from the studied sediments by a) FAP dissolution; solid line corresponds to Na⁺-dominant solution; dashed line corresponds to Ca²⁺-dominant solution and b) desorption.

as mentioned above, thin coats of fluorine salts associated with volcanic ash particles are rapidly leached in pure water (i.e. Delmelle et al., 2007; Ruggieri et al., 2012). As volcanic glass is a major constituent in the Chacopampean loess (Nicolli et al., 1989; Nicolli et al., 2010) we may expect an important contribution of fluoride from this source at neutral to slightly alkaline pH. Once fluoride is released by these primary sources, it could be partially adsorbed onto Fe/Mn(hydr) oxide coatings or it could co-precipitate along with calcite when supersaturation conditions predominate.

5. Conclusions

The sediments collected from rivers and shallow aquifers at some selected parts of the central region of Argentina, have shown fluoride release in leaching experiments carried out under variable conditions of pH and dominant cation in the solution matrix.

Experimental results indicate that the dynamics of fluoride release is mostly controlled by two factors: pH and the concentration of Ca^{2+} in the solution. The enhanced release of fluoride at more acidic pH, the inhibition of release in Ca-rich solutions and the positive linear trends between Ca^{2+} and fluoride concentrations suggest that the dissolution of a Ca/F-bearing phase (like FAp) strongly controls the dynamics of fluoride in the earlier stages of water–sediment interaction (i.e., 7–10 days), particularly under acidic conditions (pH 6). Theoretical calculations revealed that FAp dissolution in an amount equivalent to that estimated in the studied sediments may widely account for the values measured in the leaching experiments at pH 6, regardless of the dominant cation in the solution. Under such conditions, dissolution of FAp (present as coatings onto glass surfaces or as detritic grains) is likely the major primary source of fluorine in the studied sediments. Contribution from biotite may be also considered as an important primary source in fluvial sediments from the Pampean ranges. When adequate surfaces are present (Fe/Mn oxides), as it occurs in the studied sediments, the released anions at acidic pH may be partially scavenged from the solution by adsorption; increasing alkalinity in the aquatic reservoirs may then release the adsorbed fluoride through desorption or competition with other anions such as carbonate, phosphate and arsenate species.

The results obtained here indicate that dissolution of FAp enhanced by calcite precipitation and Ca^{2+} scavenging by cation exchange as well as desorption from Fe-oxides are the main mechanisms that control fluoride concentration in natural waters. Comparing both mechanisms, the dissolution predominates at lower pH (primary source) while desorption is the main contribution under alkaline conditions (secondary source). Regarding the analyzed samples, dissolution of less altered fluvial sediments (with FAp and biotite) are major sources of fluoride release, whereas loess sediments contribute mostly through desorption from Fe-oxides. The latter may also explain the correlation already described in the Chacopampean region between fluoride and other anionic species such as AsO_4^{3-} and VO_4^{3-} that are also adsorbed onto Fe-oxides and in consequence are desorbed along with fluoride when suitable chemical conditions occur.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi: <http://dx.doi.org/10.1016/j.scitotenv.2012.10.093>.

2012.10.093. These data include Google maps of the most important areas described in this article.

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