



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., Omueti 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 2 θ 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.

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