Control of the mobilization of arsenic and other natural pollutants in groundwater by calcium carbonate concretions in the Pampean Aquifer, southeast of the Buenos Aires province, Argentina

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*Title Page

Control of the mobilization of arsenic and other natural pollutants in groundwater by calcium carbonate concretions in the Pampean Aquifer, southeast of the Buenos Aires province, Argentina.

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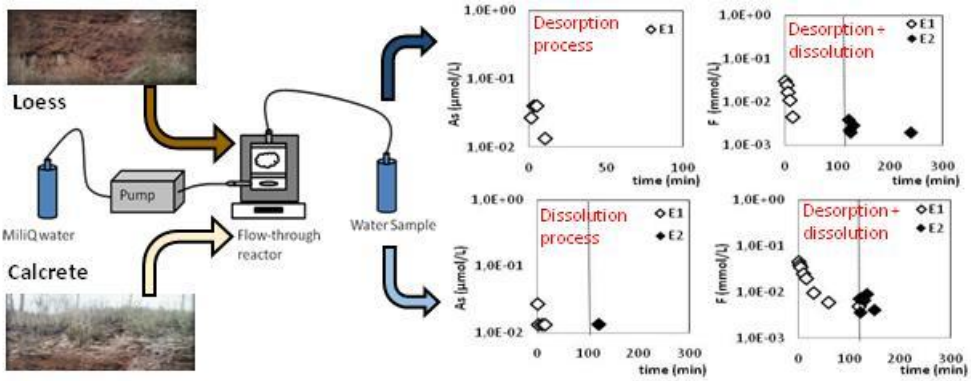
*Graphical Abstract

GRAPHICAL ABSTRACT



HIGHLIGHTS

- The origin of As, F and other pollutants in groundwater is still misunderstood.
- Consumption of water with high content of As is a major threat for human health.
- Time-resolved experiments were used to study elemental release in water.
- As, V, Ba, Sr are probably coprecipitated with calcite and F adsorbed on calcite.
- The mobility of pollutants in the Pampean Aquifer is controlled by calcrete.

ABSTRACT

The water supply for human consumption in the Chaco-Pampean region in Argentina is restricted by the low quality of groundwater due to elevated concentrations of arsenic and other trace elements. Previous studies indicated a complex concurrence of factors and processes that are believed responsible to control the distribution of arsenic in groundwater. For a better understanding of the origin of trace elements in the Pampean aquifer, flow-through experiments with loess and calcrete samples representative of the sediments that constitute the aquifer were carried out in continuous flow reactors. The aqueous solutions were collected and the concentrations of $SiO_2(aq)$, Ca^{2+}, SO_4^{2-}, Na^+, Cl^-, F^- and trace elements (Ba, Sr, V, and As) were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), high performance liquid chromatography (HPLC) and capillary electrophoresis. The experiments showed differences in the release rate of elements to the solution according to the type of sediment. The highest concentrations of V, Ba, and As were measured in experiments conducted with loess, and these elements were released quickly to the solution in the first minute of the test. In the case of loess, V and As are suggested to be adsorbed on the solid particles surface. Conversely, the experiments conducted with calcrete showed a lower but continuous release of those elements. This last result may indicate that the trace elements were coprecipitated in the calcite. In addition, it was demonstrated that F did not come from the dissolution of minerals such as fluorapatite, but both desorption from solid surface and dissolution from calcite minerals account for the release of F. This study support that both dissolution and adsorption-desorption processes can control the mobility of trace elements, with an emphasis on the role of calcrete in the retention and the mobilization of trace elements in the Pampean aquifer.

Keywords: Arsenic - carbonate concretions - loess - groundwater contamination –kinetic modeling – Pampean aquifer

INTRODUCTION

Arsenic dissolved in water is one of the most important concerns regarding drinking uses in many areas of the world. Naturally-occurring high arsenic (As) groundwater concentrations are widely distributed in some large regions of different countries, including the USA (Scanlon et al., 2009; Chappells et al., 2014), Mexico (Wurl et al., 2014), Argentina (Nicolli et al., 1989; Gomez et al., 2009), China (Guo et al., 2015), Chile (Sancha and O'Ryan, 2008), Vietnam (Erban et al., 2013), India (Chakraborti et al., 2016) and Bangladesh (Fendorf et al., 2010). The consumption of water with high concentration of As is related to arsenicosis, being an important threat for human health (Agusa et al., 2014; Joseph et al., 2015). About 140 million people in the world are exposed to As contaminated drinking waters. Other trace elements such as fluoride and vanadium are also of concern for human health. High fluoride concentrations in waters are associated with dental fluorosis and sometimes bone fluorosis (Sota de la et al., 1997), while vanadium can cause aneugenic effects and irritation of the respiratory tract (M. Costigan, 2001).Because of their important impact on human health, it is necessary to improve the understanding of the processes responsible for trace elements release and mobilization.

The mobility of arsenic in sedimentary environments has been studied in previous investigations, because high As concentration in drinking water is particularly common in arid or semi-arid regions (Robertson, 1989; Wyatt et al., 1998; Levy et al., 1999; Mahlknecht et al., 2004, Farooqi et al., 2007; Currell et al., 2011, Wang et al., 2018; Yang et al., 2018). The desorption from Fe-(hydr)oxides was identified as the main process for As release in these areas under oxidizing environments. In the Pampean aquifer, the origin of As, F, Ba, Sr, and V, has been widely studied. Many authors attributed the high concentration of these elements with the presence of volcanic glasses (Nicolli et al., 1989; Smedley et al., 2002; Kruse and Ainchil, 2003; García et al., 2012; Auge, 2014). Other studies attributed the elevated

concentration of trace elements to the process of desorption from Al/Fe/Mn oxides (Smedley and Kinniburgh, 2002; Bhattacharya et al., 2006; Gomez et al., 2009). Nevertheless, volcanic glass shards are generally present in a homogeneous proportion in the Pampean sediments, whereas the concentrations of As, F and other trace elements show high variability throughout the territory (Blanco et al., 2012). For this reason, it is believed that other mechanisms could control the mobility of those elements in the groundwater.

The ability of calcite ($CaCO_3$) to retain inorganic contaminants has been described by many authors (Comans and Middelburg, 1987; Reeder, 1996; Tesoriero and Pankow, 1996; Cheng et al., 1999; Pokrovsky and Schott, 2002; Roman-Ross et al., 2003; Stipp et al., 2003; Renard et al., 2015). The uptake of contaminants in calcium carbonates can occur via adsorption on solid surface or coprecipitation reactions. Calcite has been shown to be capable of retaining such trace elements, retarding their transport, and thus plays an important role in the migration of contaminants in natural environments (Zachara et al., 1991; Stipp et al., 1992; Paquette and Reeder, 1995; Elzinga et al., 2002; Rouff et al., 2004). As banks of calcrete are extensively present in the Pampean sediments, adsorption or coprecipitation with calcite could explain most, or part, of the variability of As, F, V, Sr and Ba in the Pampean aquifer.

In the Chaco-Pampean plain of Argentina, the shallowest groundwater is contained in a sedimentary deposit of aeolian origin, which is one the most important sources of water supply for water to the population, agriculture and industry, and contributes to more than 60% of the country's gross national product (Schulz and Castro, 2003). The quality of the water from this reservoir depends on the hydrological balance and the interaction with the materials that constitute this aquifer. The quality of groundwater for drinking purposes varies greatly due to the presence of inorganic contaminants such as arsenic, fluoride, and other trace elements such as vanadium, strontium, and barium (Nicolli et al., 1989; Smedley et al., 2002). The negative effect of the consumption of water with high content of arsenic in this region is

well known (Hopenhayn-Rich et al., 1996; Bardach et al., 2015). In the province of Buenos Aires, arsenic concentration ranges from 23 to 289 $\mu g.l^{-1}$ (Al Rawahi et al., 2015) and the fluoride concentration is approximately 1.0 $mg.l^{-1}$ (Kruse and Ainchil, 2003; Martínez et al., 2012; Calvi et al., 2016). In the central arid area of the country, the concentrations of arsenic and fluoride can be as high as 4.8 $mg.l^{-1}$(Bundschuh et al., 2004), and 28 $mg.l^{-1}$ respectively (Smedley et al., 2002). In this area, the barium and vanadium concentrations are approximately 45 $\mu g.l^{-1}$ and 50 $\mu g.l^{-1}$, respectively (Smedley et al., 2002). The concentrations of these elements exceed the WHO guidelines values in many places (As: 10 $\mu g.l^{-1}$; F: 1.5$\mu g.l^{-1}$), presenting risks for human health and limiting the use of groundwater resources (Nicolli et al., 1989; Bundschuh et al., 2000; Smedley et al., 2000; Fiorentino et al., 2007; Smedley et al., 2008; Nicolli et al., 2012a; Nicolli et al., 2012b). Whereas barium and strontium are present in solution as Ba^{2+} and Sr^{2+} cations, vanadium is generally found in solution as vanadate anions (HVO_4^{2-}, $H_2VO_4^-$), (Al Rawahi, 2016). Arsenic can be present in four oxidation states (-III, 0, + III, + V) but in the studied hydrological system, it is most commonly found as As (III) ($H3AsO_3$ or $H_2AsO_3^-$) and As (V), ($H_2AsO_4^-$ o $HAsO_4^{2-}$).The As (V) form is predominant at neutral and alkaline pH (Smedley et al., 2001). Those inorganic forms of arsenic (As(III) and As(V)) are highly toxic and mobile in the environment (Smedley and Kinniburgh, 2001; Jang et al., 2016).

Since the groundwater resources of the Pampean aquifer are threatened by the high toxicity of trace elements, it is important to improve the knowledge of their mobilization in this hydrologic system. In the present study, the putatively important role played by calcrete for the mobility of trace elements is investigated. Though the chemical composition of the water of the Pampean aquifer is commonly considered based on a thermodynamic equilibrium approach (Garrels and Christ, 1965; Glok Galli et al., 2014), it has been demonstrated in a previous paper that this assumption is questionable for some specific solid phases (Vital et al., 2018). To go beyond the thermodynamic equilibrium approach, flow-through experiments of interactions of loess and calcrete with water have been performed and coupled to reactive

transport simulations to identify the processes involved in the release of trace elements into the solution. In addition, while our previous study focused on the release of major elements, the present study aims at unraveling the source of trace elements released during the flow-through experiment with calcrete and loess samples.

DESCRIPTION OF THE STUDY SITE

The association of sediments occupying a surface area of more than one million square kilometers is known as the Pampean aquifer (Auge et al., 2002; Auge, 2008). The term "Pampean sediments" is an informal term and includes the Quaternary aeolian deposits of the Pampean region, consisting mainly of sand, silt, clay (Frenguelli and Teruggi, 1955). The sediments of the Pampean aquifer are considered as a formation of loess type. Unlike the "typical" loess, loess in Argentina has high contents of aluminosilicates and volcanic glass (Tricart, 1973; Pye, 1995; Zárate, 2003). In general, its composition is homogeneous, and most of its components originate from volcanic eruptions (Teruggi, 1957; Tricart, 1973). Calcareous formations occur as concretions and / or banks. Where the calcification is intense, banks of calcium carbonates result in sedimentary structures of the type of calcrete, locally denominated "tosca" (Sayago et al., 2001). The Pampean loess composition reveals 2 to 4% of calcium carbonate as calcite (Teruggi, 1993), mostly located in the upper part of the aquifer. Calcretes are widely abundant and common in the Pampean sediments, being well distributed superficially and at different depths. Calcrete is typical of the study site, forming continuous layers that have been related to paleo-surfaces (Teruggi et al., 1973), occupying the top of the hills. The calcretes may have formed over periods of several thousand years and are an indicator of semi-arid conditions (Zárate and Fasano, 1989). Calcrete layers are particularly abundant in the East of the Buenos Aires province, typically at a depth of around 1 m below ground level. This has resulted in the development of a largely flat-lying plain. This has been well described by Zárate and Folguera (2009) quoting original observations done by Charles

Darwin (Darwin, 1846). The hydrological conditions in the region are characterized by average annual precipitations around 900 mm, and a groundwater recharge estimated at 15% of total precipitation (Quiroz Londoño et al., 2012). The mean pH of the Pampean groundwater in the studied area is 7.15 (Quiroz-Londoño et al., 2008).

MATERIALS AND METHODS

1. Sample collection and mineralogical characterization

Samples of loess and calcrete were collected at an outcrop in the area of Mar del Plata, in the province of Buenos Aires, Argentina (38°05'12.7"S 57°38'57.1"W), (Figure 1).The area of sampling was chosen as being a representative area of the mineralogical composition of the Pampean aquifer in this sector of the Pampa plain. The outcrop includes both loess-like and calcrete sediments which were collected from a non-saturated zone with the same sedimentary composition as the Pampean aquifer. The samples were characterized in previous studies (Vital et al., 2016 ; Vital et al., 2018) using X-ray diffraction (XRD) coupled to Rietveld refinement and scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM/EDS). The analysis of the particle size distribution (PSD) by sieving revealed that loess is composed of 23 % of medium sand (0.25–0.5 mm), 15 % of fine sand (125–250 µm), 25% of very fine sand (62.5–125 µm) and 37 % of pelites (silt and clay, 0.997–62.5 µm).Calcrete samples were also collected in other areas of the province of Buenos Aires (Otamendi, Tandil and Tres Arroyos) in order to check the representativeness of the results obtained for As.

2. Flow-through experiments

The experiments were designed to monitor and measure the release of major and trace elements in the outflowing solution, as a function of reaction time with the solid samples of loess and calcrete (Figure 2). Continuous flow-through reactors simulate the conditions of an open geochemical system. The experiments were carried out using the set-up designed by

151 Cama et al. (2000). The Teflon-based continuous flow reactor of known volume of 21.2 $cm^3$was
152 placed on a magnetic stir plate at room temperature. The solid samples of either loess or
153 calcrete powders were introduced in the reactor. Through this reactor, deionized miliQ water
154 (pH = 5.7) was continuously injected at a determined flow rate of 5 $ml.min^{-1}$. In this study, the
155 objective of the experiment was to monitor the total release of the trace elements by the
156 calcrete and the loess samples. Thus, pure milliQ water was used as a stock solution, to ensure
157 that the input water is free of the trace elements that are under study. Importantly, the use of
158 milliQ water is not intended to mimic rainwater or groundwater. This simplification was
159 necessary to unravel the processes responsible for the release of the considered elements.
160 Once such process are correctly singled out, the extrapolation to different real conditions (i.e.
161 different rainwater or groundwater compositions) can be easily achieved by using geochemical
162 modeling software. The solution inside the reactor was continuously stirred so that the
163 concentrations and the temperature were theoretically homogeneous. The solution was
164 maintained at far-from-equilibrium conditions with respect to the dissolving phases because of
165 the continuous replenishment of the solution.

166 The experiment was designed to evidence the differences in elemental release
167 between samples of loess and calcrete. It was divided into two steps: the first testT1 and the
168 second test T2, in order to observe if the targeted elements are quickly and uniquely released
169 to the solution over T1 (corresponding either to desorption, or to the disappearance of
170 accessory minerals) or if they are continuously released over T1 and T2 (corresponding to the
171 congruent dissolution of trace elements that were coprecipitated in major rock-forming
172 minerals and/or minerals with slow dissolution kinetics). Drying the samples after collecting
173 them is required to stop the dissolution reaction of the samples, and limit the possible
174 precipitation of undesired secondary phases formed prior to the onset of the second
175 experiment. In that way, it was possible to decipher whether the trace elements are adsorbed
176 on solid particles or coprecititated as impurities in some minerals. For this purpose, the

177 samples of loess and calcrete were introduced two times in the reactor. First, 2 grams of
178 powder (loess or calcrete from the various above-mentioned locations) were introduced in the
179 reactor for 2 hours. Sampling of the outflowing aqueous solution was carried out at the
180 following duration steps: 1, 3, 5, 10, 15, 20, 30, 45, 60, 90 and 120 minutes. Those collected
181 aqueous samples correspond to the first testT1. Afterwards, the solid samples were recovered
182 at the end of the experiments, dried in an oven for 24 hours at 60°C. The dried solid samples
183 were then put back in the flow-through reactor for two additional hours. The collection of
184 aqueous samples in the second part of the experiment was carried out using the same
185 previous time steps. The collected aqueous samples correspond to the second testT2. The
186 experiments were repeated 3 times for each samples and each location. In all cases, the
187 aqueous samples were filtered through a 0.45 µmfilter and stored at -4°C prior to their
188 analyses.

189 3. **Aqueous sample analyses**

190 The aqueous solution samples recovered at the reactor outlet, from the experiments
191 realized with the loess and calcrete samples from the area of Mar del Plata, were analyzed to
192 quantify the concentration of calcium, sodium, potassium and magnesium by capillary
193 electrophoresis at the National Atomic Energy Commission (CNEA) laboratory (Buenos Aires,
194 Argentina) with a Beckman Coulter brand equipment using a 40 cm-long fused silica capillar
195 with a diameter of 75 µm(25 KV). The background electrolyte (BGE) was composed of a
196 deimidazole solution of 10 $mmol.l^{-1}$, and acetic acid (40 $mmol.l^{-1}$). BGE was used as a buffer
197 and is essential to stabilize the electro-osmotic flow and the migration time of the analytes.
198 Calcium, sodium, potassium and magnesium standard solutions of 0.1, 0.5, 1, 5, 10, and 15
199 ppm were injected to determine the time after which each element appeared and to obtain
200 the calibration curve of the peak area vs. the concentration. Sulfate, chloride and fluoride
201 concentrations of the aqueous samples were measured by high performance liquid

chromatography (HPLC) with a Thermo Separation Products, CA, USA team, with a Spectra SERIES P200 binary pump, and a UV-Vis UV100 detector. An HPLC anion exchange column, PRP-X100, HAMILTON® and a mobile phase of potassium biphthalate (4,5 mmol.l^{-1}) were used at the CNEA laboratory. Standard solutions of 0.5, 1, 2, 5, 10 and 15 ppm of fluorine, sulfate, and chloride were prepared to establish pattern curves in order to calibrate the concentration of each anion as a function of the area of the peak. The barium, vanadium, strontium, arsenic and silica concentrations of the aqueous samples were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Thermo ICAP 6000 brand equipment at the laboratory of hydrology and geochemistry of Strasbourg (France). In all analyses, pure milliQ water was used as a blank standard.

Arsenic concentrations of the aqueous samples obtained from the experimentsT1 and T2 realized with the calcrete samples from the area of Tandil and Tres Arroyos were determined by Total reflection X-Ray Fluorescence (TXRF), using a TXRF spectrometer S2 Picofox (Bruker, Germany).

4. **KIRMAT Modeling**

Fluorapatite was identified in the loess and calcrete samples (Vital et al, 2018) and fluorine has been detected as an impurity in the calcrete with concentrations ranging between approximately 220 µg.g-1 (García et al., 2006) and up to 1500 mg.kg-1 (Limbozzi, 2015). According to those observations, kinetic modeling was performed to assess the contribution of fluorapatite and fluoride-bearing calcite to the concentration of fluoride in the aqueous samples. Kinetic simulations coupled to mass transport were realized with the hydrochemical and thermo-kinetic code KIRMAT (KInetic Reaction and MAss Transfer), (Gérard et al., 1998). A phase of calcite with 0.1% of fluoride as an impurity with a solubility identical to that of pure calcite was added to the KIRMAT thermodynamic database. The concentrations of fluoride obtained in the flow-through experiments test 1 (T1) and test 2 (T2) with the samples of loess

from Mar del Plata, and the samples of calcrete from the four locations, were compared to dissolution simulations of loess and calcrete containing fluorapatite or F-bearing calcite (0.1% of fluoride). The BET surface area of each sample from (Vital et al., 2018) was used as well as kinetic rate laws gathered in Palandri and Kharaka, (2004). Other input parameters for the simulations include deionized water in equilibrium with atmospheric CO_2 (corresponding to a starting pH of 5.7), a temperature of 25ºC, and a flow rate of 5 ml.min^{-1}. The thermodynamic database used in KIRMAT comes from the THERMODDEM database of the Bureau de Recherche Geologique et Minière (BRGM - http://www.brgm.fr/).

RESULTS

To determine the source of trace elements and their relations to major ions, the evolution of the output concentrations of major and minor elements obtained from the flow-through experiments conducted with loess and calcrete samples from the area of Mar del Plata are presented in Table 1 and Figure 3.

1. Experiments conducted on loess samples

In the experiment conducted on loess samples, the major ions SiO_2(aq), Ca^{2+}, Na^+, SO_4^{2-}, Cl^- and K^+ are released in the solution following each of them a similar tendency, which consists of an initial peak of ion incorporation after the very first minutes of the experiment in the test T1. Then, the concentrations of SiO_2(aq), Ca^{2+}, Na^+, SO_4^{2-}, Cl^- and K^+ decrease to reach a constant final value after 120 minutes (TF1). A lower concentration of those ions is measured in T2 but also starting with an initial peak of release. In detail, the highest concentration of silica (0.24 mmol.l^{-1}) was measured in the sample collected during the first minute of contact with loess (table 1). Subsequently, the silica concentration dramatically decreases to reach 0.04 mmol.l^{-1} all over T1. In the second test(T2), a significant release of silica was observed in the first minute (0.21 mmol.l^{-1}) followed by a very significant decrease. Sodium and chloride ions are released

very quickly to the solution, with the highest concentrations reached during the first minute of T1(3.3 and 21 mmol.l^{-1}, respectively). A very significant decrease in the concentrations of these elements is observed to reach stable values in the first hour of T1(0.2 and 0.01 mmol.l^{-1}). Over the course of T2,the values measured in the samples in the first minute are significantly lower than the values measured in the first minute of T1 (0.09 and 0.1 mmol.l^{-1}). The same trend is observed for calcium and sulfate ions, with the highest concentrations reached in the first minutes of T1 of 4.8 mmol.l^{-1} and 0.7 mmol.l^{-1}.

The pH of the outflowing solution follows the patterns observed for the released ions. The pH of the initial input solution is 5.7. Initially, a fast increase from 5.7 to 6.6 is observed, but then pH decreases slowly to the initial input value after 180 min. The same behavior was observed for the TDS.

The behavior of trace elements is more complex (Figure3): while the concentration of some elements such as Sr and V follows a trend that is similar to that of major ions (i.e., initial peak after one minute in T1 and T2 followed by a decrease and the attainment of a steady-state concentration), the concentrations of other elements (e.g., Ba, F, As) steadily decrease throughout T1 and T2. The initial concentration of Sr^{2+} reached 8.72 µmol.l^{-1} in T1, with a decrease down to 0.2 µmol.l^{-1}, followed by another peak in T2 at 0.3 µmol.l^{-1}. The concentration of vanadium is 0.2 µmol.l^{-1} at the beginning of T1 and then, after an initial peak in T2 (0.07 µmol.l^{-1}), the final concentration of V is far below 0.1 µmol.l^{-1}. On the other hand, trace elements such as F^{-}, Ba^{2+}, and As start with a peak concentration in T1 (0.03 mmol.l^{-1}, 0. 51 µmol.l^{-1} and 0.027 µmol.l^{-1} respectively) to decrease in all T1 and T2, and As concentration is even below the detection limit in T2. These results provide a first indirect indication that these elements were either released from specific minor phases enriched in these elements that were completely dissolved by the end of T2, or that they have been rapidly desorbed from the solid samples.

Further treatment of the data was carried out for the determination of the origin of other trace elements. While only $Sr^{2+}$is linearly correlated with Ca^{2+} release (r^2 = 1) (Figure 4), the concentrations of $Sr^{2+}$and Ba^{2+}in the aqueous samples are linearly correlated with that of Na^+ ($r^2_{Na/Sr}$ = 0.999 and $r^2_{Na/Ba}$ = 0.96) and K^+($r^2_{K/Sr}$ = 0.93 and $r^2_{K/Ba}$= 0.97); (Figure 5). A lack of linear correlations between V and As concentrations and Na^+ or K^+ concentrations can be observed in Figure 5, as well as no linear correlation between $Ca^{2+}$and F^- in T1 (r^2 = 0.69) (Figure 6). On the contrary, a linear correlation is observed between the release of F^- and Ca^{2+} in the test T2 (r^2 = 0.95)

2. Experiments conducted on calcrete samples

In these experiments, the initial pH (5.7) quickly increased to stabilize at values comprised between 7.6 and 7.9, because of the $CaCO_3$ dissolution. These are the typical values of groundwater at the southeast of the province of Buenos Aires. The variation in concentrations in T1 and T2 of major ions are presented in Table 1. The highest concentration of calcium (0.64 $mmol.l^{-1}$) was obtained in the first minute of the test T1, and decreased down to 0.2 $mmol.l^{-1}$ after 20 minutes of reaction. In the second test, a peak of Ca^{2+} appears in the first minute of reaction (0.37 $mmol.l^{-1}$).A peak of sodium (3.3 $mmol.l^{-1}$) and chloride (21 $mmol.l^{-1}$) is observed in the first minute of the experiment and then the concentrations stabilized below 0.5 $mmol.l^{-1}$ and 0.1 $mmol.l^{-1}$respectively. In the test T2, a very similar trend is observed for the two elements. Similar trends were observed for SiO_2(aq) and SO_4^{2-}.

The experiments conducted with calcrete exhibited large release of strontium and barium during the first minutes of reaction in the first test (T1) and second test (T2), followed by a progressive decrease in the release rate of these ions during the subsequent hours (Figure 3). Of note, the maximum concentrations of $Sr^{2+}$and Ba^{2+}at the beginning of T2 are equivalent to those reached at the beginning of T1. Conversely, vanadium concentration peaks to a higher value in the first test (0.9 $\mu mol.l^{-1}$) compared to the second test (0.1 $\mu mol.l^{-1}$). Arsenic is

301 detected in T1 (0.027 µmol.l^{-1}) and only at the beginning of T2 (0.013 µmol.l^{-1}). A linear relation
302 was evidenced between the concentration of calcium and the trace elements Ba^{2+} (r^2 = 0.97),
303 As (r^2 = 0.93), and Sr^{2+}(r^2 = 0.99), (Figure 7a), and to a lesser extent, V (r^2 = 0,84).No linear
304 relationship between $Ca^{2+}$and F^- concentrations was evidenced in T1. Conversely, the linear
305 relationship was retrieved inT2 (r^2 = 0,86), (Figure 7b).

306 **3. Confirmation of the control of As mobilization by calcite contained in calcrete**

307 Flow-through experiments were repeated with calcrete from three other places of the
308 province of Buenos Aires: Otamendi, Tres Arroyos, and Tandil. Arsenic concentrationswere
309 measured by TXRF, which is a method less sensitive than ICP-AES. Semi-quantitative values
310 were obtained, indicating that arsenic was detected in almost all the aqueous samples (Table
311 2). In the first and second tests, the concentration ranged from 0.002 to 0.005 mg.l^{-1} (0.026
312 µmol.l^{-1} to 0.067 µmol.l^{-1}).This experiment showed that As is most certainly incorporated into
313 calcite, as supported by the linear correlation between Ca^{2+} and As previously reported in
314 Figure7a.

315 **4. Unravelling the source of fluoride using reactive transport modeling**

316 The fluoride concentrations measured in T1 and T2 conducted with loess and calcrete were
317 compared with the outputs of simulations of sediment (calcrete or loess) dissolution
318 containing F-calcite and fluorapatite (Figure 8). Fluorapatite was previously detected by SEM
319 observations reported in Vital et al. (2018) but could not be identified by XRD. Because it was
320 estimated that the detection limit of our XRD was ~2 wt. %, we ran the kinetic simulations
321 using this value as an upper bound for fluorapatite content in the solid sample. Also, calcite
322 containing 0.1 wt. % of F was added (calcite represent >90% of the weight of the calcrete
323 sample, and 1-2% of the loess sample). Following Kitano and Okumura (1973), 0.1 wt. % is the

maximum concentration of F that can be incorporated into calcite. We used this value as an upper bound for the F content of calcite.

Figure 8ashows the results of the fluoride concentrations obtained in T1 and T2 flow-through experiments for the loess sample. As can be seen, the model successfully predicts the concentration of fluoride measured by the end of experiment T2. It further reveals that calcite is the main contributor to this agreement, as testified from the simulation performed with 0 wt. % of F-calcite and 2 wt. % of fluorapatite. Nevertheless, the first peak in T1 could not be fitted, which is an indirect evidence for a two-step process: (i) desorption of F at the beginning of the experiment T1 (not taken into account in the simulation), and (ii) continuous release from F-bearing phases.

A similar approach was used for calcrete from Mar del Plata, Otamendi, Tandil and Tres Arroyos flow-through experiments. The simulations were conducted with 2 wt. % of fluorapatite and considering F-bearing calcite instead of pure calcite (Figure 8b). The outputs of the simulations are in good agreement with the concentration plateau observed in T2, but, again, the initial peak of fluoride release at the beginning of T1 could not be fitted.

DISCUSSION

1. Experiments conducted on loess samples

An initial peak of major ion such as SiO_2(aq), Na^+, Cl^-, Ca^{2+} is systematically observed in the flow-through experiments of loess in test 1. This may result from the rapid dissolution of the finest particles of the primary rock forming minerals (e.g., Schott et al., 1981). In T2 series, these elements are still released to the solution, with a steady-state concentration close to the concentration reached at the end of T1. Not surprisingly, these results indicate that these elements must have been released by mineral phases that were not completely consumed by the end of the T1, i.e., most likely the dissolution of primary rock-forming minerals. In a

348 previous study (Vital et al., 2018), we showed that the release of major ions from loess is
349 related to the presence of minerals such as quartz, albite and accessory minerals such as
350 halite, gypsum and calcite. An initial peak of strontium, vanadium, barium, fluoride and arsenic
351 is also observed in T1. The concentrations of those elements decrease all along T1 and T2.

352 The presence of vanadium, strontium, barium and arsenic in groundwater has been related to
353 loess deposits (Farías et al., 2003; Fiorentino et al., 2007; Nicolli et al., 2012a), mainly due to
354 the release from volcanic glass shards and Al/Fe oxides (Steinhauser and Bichler, 2008; Nicolli
355 et al., 2010; Nicolli et al., 2012a; Nicolli et al., 2012b; Bia et al., 2015; Barranquero et al., 2017;
356 Alvarez and Carol, 2018), which could explain the behavior of the trace elements in the flow-
357 through experiments T1 and T2 conducted on loess. The desorption of As and F from Fe/Mn
358 oxides has been mentioned in many other studies focused on aquifers in China(Currell et al.,
359 2011), or Korea (Kim et al., 2012), and Argentina (Smedley et al., 2002; Smedley et al, 2005;Bhattacharya et al., 2006;Borgnino et al., 2013). Currel et al., 2011 showed that
361 increasing the duration of the interaction between water and loess samples generally did not
362 result in an increase in F or As concentrations in solution and indicated that these ions are
363 most likely mobilized by de-sorption rather than dissolution of F- or As-bearing minerals. Our
364 results with the loess sample of the area of Mar del Plata are consistent with this previous
365 study, suggesting that the rapid release of As could be the consequence of the desorption from
366 those solid surfaces.

367 The results also show that only Sr is linearly correlated with Ca release. Vital et al., 2018
368 showed that the loess samples could contain up to 2% of calcite. Therefore, the strontium was
369 likely coprecipitated with calcite, and its release to the solution results from calcite dissolution.
370 In addition, the concentrations of Sr^{2+} and Ba^{2+} in the aqueous samples are linearly correlated
371 with that of Na^{+} and K^{+}. The correlation of $Ba^{2+}$and $Sr^{2+}$with Na^{+} and K^{+} could also suggest that
372 these trace elements were incorporated into the main rock-forming minerals of the loess

sample (feldspars). Conversely, the absence of linear correlations between V and As concentrations and Na^+ or K^+ concentrations supports the assumption that these trace elements were not released from the congruent dissolution of feldspars. Instead, it is suggested that they were carried by minor phases that have almost disappeared by the end of the experiment T2. Furthermore, Nicolli et al., (1989), Bhattacharya et al. (2006), Fiorentino et al. (2007), Heredia and Cirelli (2009), Puntoriero et al. (2015), showed that V is strongly correlated with As in groundwaters in the Pampean Region. This result indicates that those elements may have similar sources, mobilization and transport processes and could be mainly desorbed from Al/Mn oxides.

Finally, no linear correlation between Ca and F was evidenced in the T1 test, questioning the possibility that F was released congruently from a putative F-bearing calcite. Instead, the mechanism of fluoride release may be the rapid desorption from the particle's surface. Conversely, a linear correlation can be observed between Ca and F concentrations in the T2 test. Therefore, it is likely that the loess sample contains a second pool of fluoride, which might have been released through the congruent dissolution of a Ca-rich phase, such as the putative F-bearing calcite. The ability of calcite to be either a substrate for fluoride adsoption/desorption, or to incorporate fluoride during the course of its precipitation has been supported by the works of Kitano and Okumura (1973); Turner et al. (2005); Budyanto et al. (2015); Padhi and Tokunaga (2015).

2. Experiments conducted on calcrete samples

Calcium and trace elements were released all over the experiments conducted on calcrete, with an initial peak at the beginning of each test T1 and T2. The observed linear correlation between the concentration of calcium and the trace elements Ba, As, Sr and V, suggests that these elements were coprecipitated in calcite and their release results from calcite dissolution. This suggestion is supported by the work of Dietrich et al. (2016), who showed that carbonates

were the main As-bearing minerals in the carbonate-rich unsaturated zone from a large plain environment (Pampean plain, Argentina). Moreover, Renard et al. (2015) showed that As(V) was mostly incorporated in the calcite structure. When calcite dissolves, these elements are released stoichiometrically to the solution. In numerous studies, it has been demonstrated that calcite is able to retain trace elements, delaying their transport (Zachara et al., 1991; Stipp et al., 1992; Paquette and Reeder, 1995; Elzinga and Reeder, 2002; Rouff et al., 2004). The results obtained in the present work confirm the conclusions of these previous studies. An absence of linear relationship between Ca and F concentrations in the T1 test conducted with calcrete was observed, while this correlation was evidenced in the second T2 test. These latter results are very similar to those previously discussed for loess: At the beginning of T1, the main mechanism is F desorption from minerals surface (Kumar et al., 2016). The second mechanism, which prevails after the F on particles surface is totally desorbed, could be the release of fluoride that was incorporated in calcite.

3. Confirmation of the control of trace elements mobilization by calcite contained in calcrete

A significant difference was observed in the behavior of the trace elements released from loess or calcrete samples. The highest concentrations of vanadium, barium and arsenic have been measured for the experiments conducted with loess. These elements were released quickly to the solution in the first minute of T1 before decreasing sharply, while for calcrete, a continuous release is observed, and these trace elements are still released to the solution over the course of T2. This behavior was observed in four location of the province of Buenos Aires. The mechanisms of trace elements release from volcanic glass shards or Fe/Al/Mn oxides mentioned above could explain the higher concentration of trace elements in the aqueous samples collected for the experiments conducted with loess.

Conversely, trace elements may have been coprecipitated in calcite, which would explain their continuous release to the solution throughout the experiments conducted with calcrete. The experiments conducted with calcrete samples from different location (Tandil, Otamendi, Tres Arroyos) show that the release of trace elements from calcrete may apply throughout the Buenos Aires province. Importantly, the present results demonstrate that calcium carbonate may play a prevailing role in controlling the trace elements distribution for the study site. To the best of our knowledge, this aspect had never been proposed before in this area. Depending on the solution composition, calcium carbonates can therefore act as a sink for As if precipitation occurs, or asa source during dissolution. Alexandratos et al. (2007)suggested that arsenates are substituted in carbonate sites of calcite in most of the calcrete that is present in the Pampean aquifer. Sø et al. (2008) measured that the adsorption of arsenate increases with decreasing alkalinity, indicating a competition between arsenate and (bi)carbonate for sorption sites. These authors also observed that the mobility of arsenate in calcite bearing aquifers is greatly reduced due to sorption on calcite, whereas sorption on calcite in aquifers with low calcite content affects the mobility of arsenate to a lesser extent. Another study (Romero et al., 2004) focused on the carbonate-rich aquifer at Zimapán, México showed that carbonates play an important role in As mobility, and proved the high capacity of As(V) retention from this material. It was also shown that at alkaline pH (between 7 and 9), the carbonate-rich sample had a higher retention capacity of As.

Considering the presence of thick layers of calcrete and groundwater pHs around 7.5 to 8.0, it is possible to conclude that the coprecipitation and desorption from calcretes are factors controlling the As and other trace elements mobility and distribution in the aquifer. The experimental results showed that calcrete dissolution can be the most important source for As over long time periods, when the solution is undersatured with respect to calcite. On the contrary, when the solution is supersaturated with respect to calcite, it can precipitate with trace-elements and act as a sink for these elements. It is expected that the calcite saturation

index of water samples could be considered as a proxy of As contents for some zones, as shown by Calvi et al. (2016), who reported a correlation between calcite supersaturation areas and low fluoride concentrations.

4. Unravelling the source of fluoride using reactive transport modeling

The results of the KIRMAT modeling showed that the neither fluorapatite nor F-calcite dissolution can account for the initial peak of F observed in T1for loess and calcrete experiments, leaving F desorption as the best explanation for the observed F release when the sample is put in contact with water for the first time. Of note, several studies indicated that fluorine comes from surface desorption, as it was found adsorbed on calcite particles (Turner et al., 2005), iron oxides (Borgnino et al., 2013), or associated with volcanic glasses (Bundschuh et al., 2004; Bhattacharya et al., 2006; Nicolli et al., 2012a; García et al., 2014). These observations are in good agreement with the very fast release of fluorine to the solution and further suggest that when the sample was put in contact with water for the first time, the initial mechanism of F release is surface desorption.

Interestingly, the concentration of fluoride measured in the T2 for both loess and calcrete samples match the simulations of KIRMAT. This result confirms that in T2, a second mechanism of F release occurs and is most probably the release from F-bearing minerals such as fluorapatite and F coprecipitated in calcite. Therefore, we suggest that the two mechanisms of F release (desorption and dissolution from calcite and fluorapatite) may superimpose. Again, this confirms that calcrete plays an important role in the release of trace elements.

CONCLUSION

In this study, flow-through experiments associated to kinetic modeling were used in order to assess the specific role of calcite in the control of the mobility of trace elements in the Pampean aquifer. Samples of loess and calcrete from different areas of the province of Buenos

Aires (Mar del Plata, Tandil, and Tres Arroyos) were collected. In the experiments, the solid samples were first reacted with water in a flow-through set-up, dried, and then put again in contact with water. The chemical composition of the aqueous solution varied with the type of solid sample reacting (loess or calcrete). Regarding experiments conducted with loess, arsenic and other trace elements (V, Ba, Sr) were rapidly released during the first minute of reaction, likely due to their desorption from solid particles in loess. These observations agree with the results of other studies suggesting that the original source of those trace elements could be the volcanic glass or the Al/Fe/Mn oxides shards present in the loess sample. On the contrary, regarding experiments conducted with calcrete, those trace elements were released to the solution for several minutes, but also in the second experiment performed with the dried samples recovered from the first experiment. It has been shown in this work that arsenic, barium, vanadium and strontium have a strong correlation with Ca during the first part of the experiment, suggesting that they are released to the solution as a result of calcite dissolution. This work shows that calcite plays an important role in the migration of inorganic contaminants such as arsenic in the environment. The mobilization of contaminants from calcium carbonates can occur by desorption from the solid surface or by dissolution of the coprecipitated elements. In the Pampean aquifer, those trace elements can be coprecipitated in the calcrete banks and can be re-mobilized by calcite dissolution as a result of variation in physicochemical changes in the groundwater (i.e. pH, saturation index).For both loess and calcrete samples, fluorine release occurred through two different mechanisms. In a first step, the fluoride that is most likely adsorbed to the surface of the particles is released to the solution. Afterwards, fluorine coprecipitated in calcite is released to the solution. The use of reactive transport modeling allowed validating this model. In the future, it would be interesting to expend this study on loess and calcrete from different locations and different depths of the very great territory of Argentina. Because it was demonstrated in this study that trace elements adsorbtion/desorption and precipitation/dissolution from calcrete are

498 important processes impacting the groundwater chemistry, it would be necessary to include
499 them in the geochemical simulations. This would allow to improve the knowledge of the
500 mobilization and distribution of As and other trace elements in groundwater.

501

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Table 1. Highest concentrations of major elements in the first test (T1) and second test (T2) of the flow-through and final concentration of the first test (TF1) conducted with the samples of loess and calcrete collected in the area of Mar del Plata.

	LOESS			CALCRETE		
	T1	TF1	T2	T1	TF1	T2
Ca^{2+}	4.8	0.06	0.16	0.64	0,2	0,37
Na^{+}	3.3	0.2	0.09	3.2	0,5	0,58
SiO_2	0.24	0.04	0.21	0,29	0,20	0,16
SO_4^{-2}	0.7	0.02	0.01	0,40	n/d	0,05
K^{+}	0.14	0.05	0.015	0.1	0.03	0.08
Cl^{-}	21	0.01	0.1	7,99	0,1	0,1

* $mmol.l^{-1}$

Table 2. Arsenic content of solutions in contact with calcrete in flow-through experiments with tests T1 and T2 from 3 locations of the Buenos Aires Province.

	T1				T2			
	t1	t5	t30	t60	t1	t5	t30	t60
Otamendi	det <0.005	det <0.005	no det <0.002	no det <0.002	det <0.005	det <0.005	det <0.005	det <0.005
Tandil	det <0.005	det <0.005	det <0.005	no det <0.002	det <0.005	det <0.005	no det <0.002	no det <0.002
Tres arroyos	det <0.005	det <0.005	det <0.005	no det <0.002	det <0.005	det <0.005	no det <0.002	no det <0.002

T1: Test 1 - T2: Test 2
t: time in minutes
Det: detected - No det: not detected
* $\mu mol.l^{-1}$

Figure1

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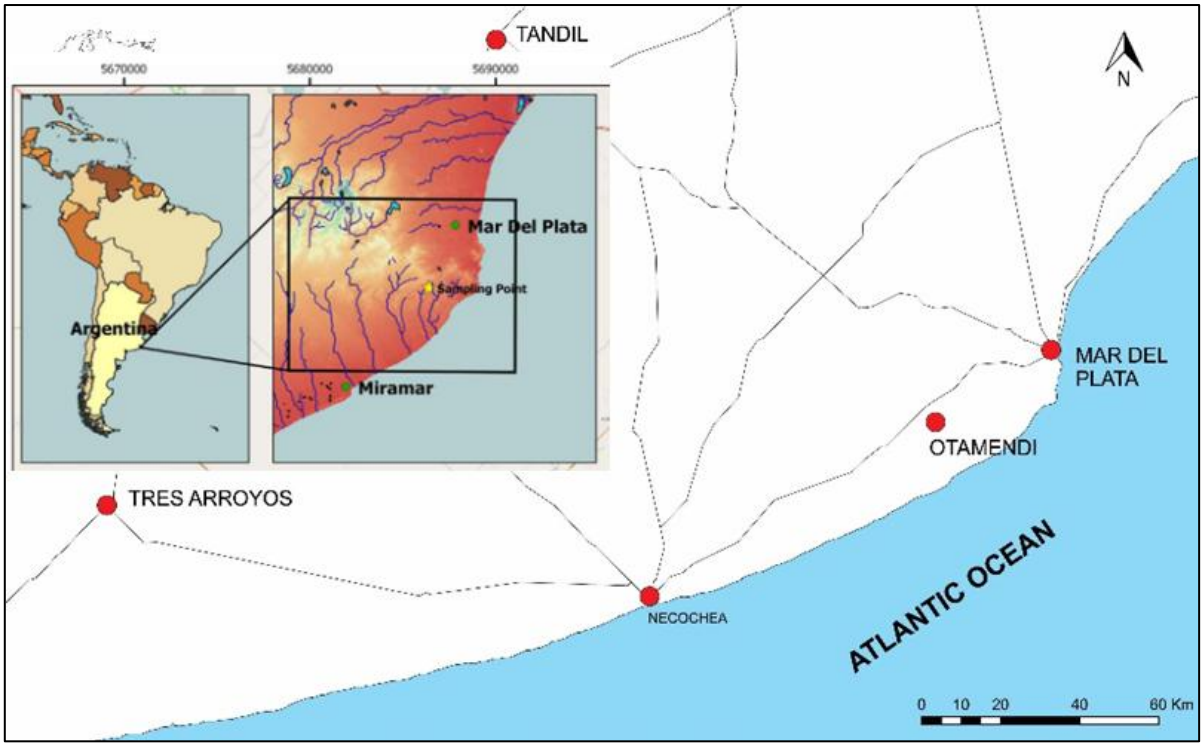

Figure 1. Location of the sampling points (indicate by red dots on the map)

Figure2
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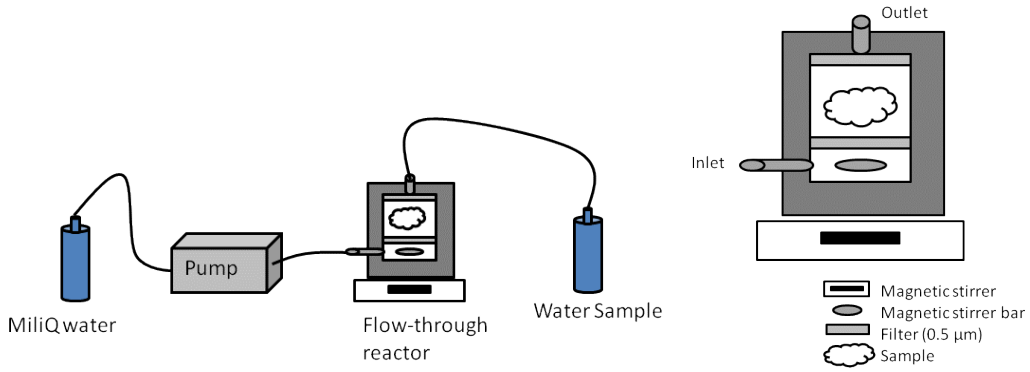

Figure 2. Schematic diagrams of the flow-through experiment and reactor. The deionized water (pH 5.7) is continuously pumped through the reactor at a flow rate of 5 $ml.min^{-1}$ where the loess or calcrete samples were previously introduced.

Figure3

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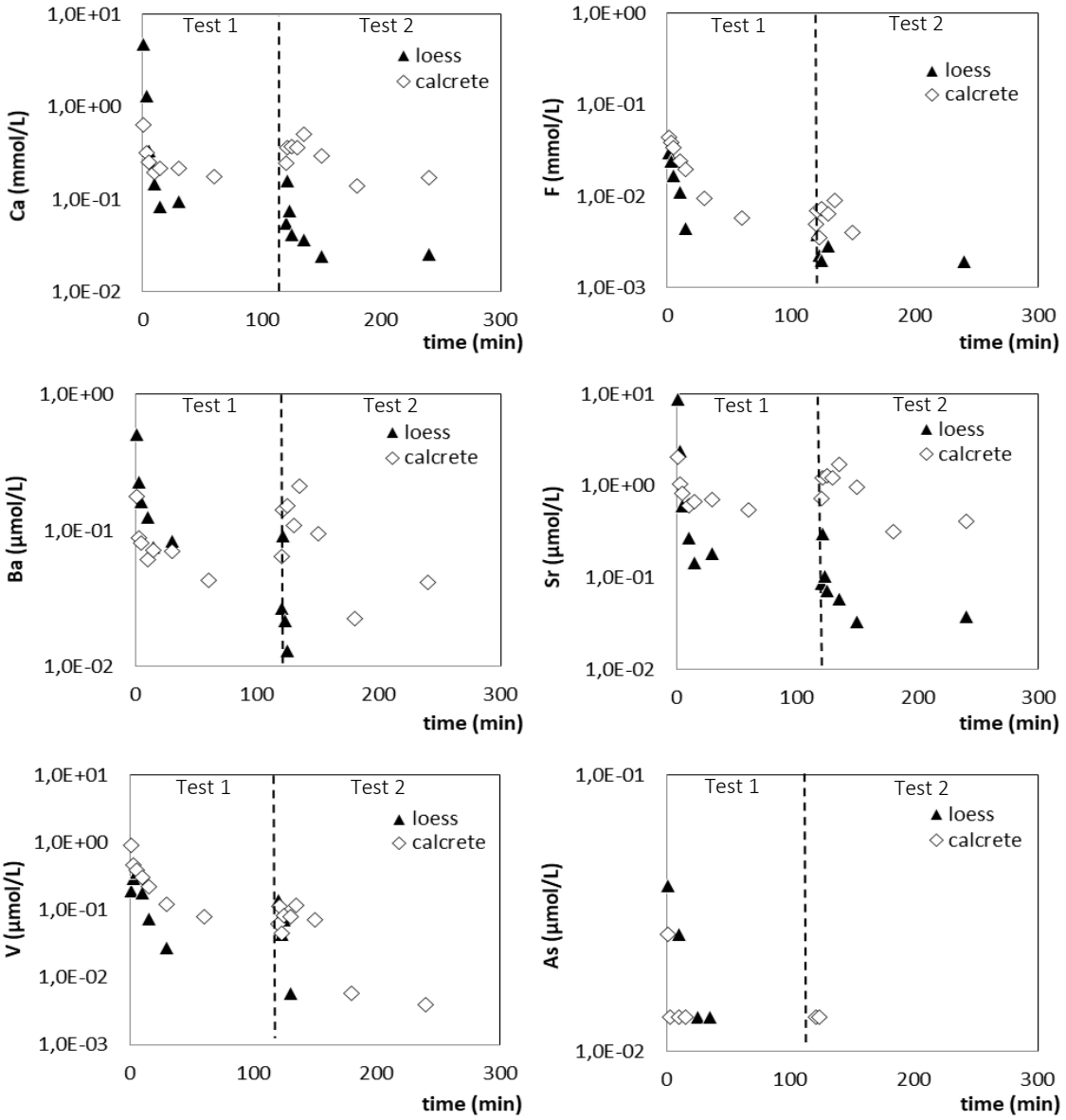

Figure 3. Release of trace elements in the flow-through experiment test 1 (T1) and test 2 (T2) conducted with the loess and calcrete samples from the area of Mar del Plata.

Figure4

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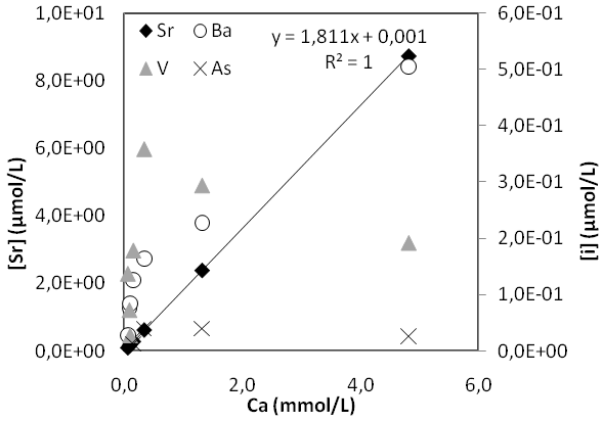

Figure 4. Correlation between Ca and trace elements (Ba, Sr, V, As) in the flow-through experiment test T1 conducted with loess.

Figure5

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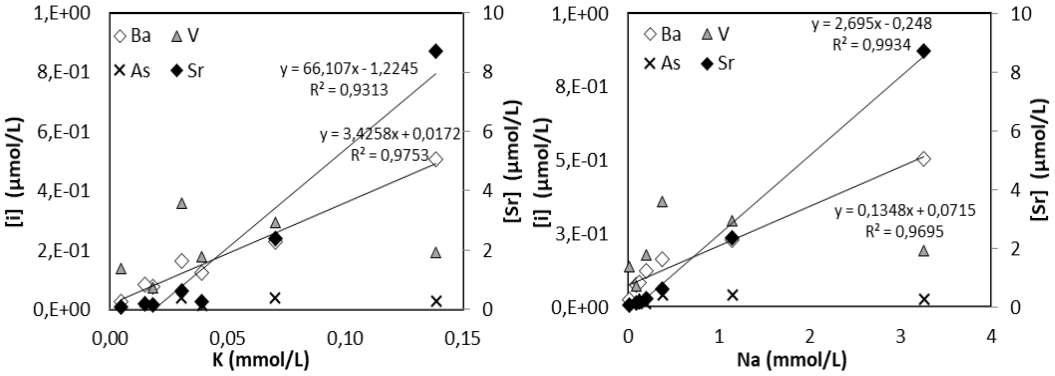

Figure 5. Correlation between Na^{+}, K^{+} and trace elements (Ba^{2+}, Sr^{2+}) in the flow through experiment

Test T1 conducted with loess.

Figure6
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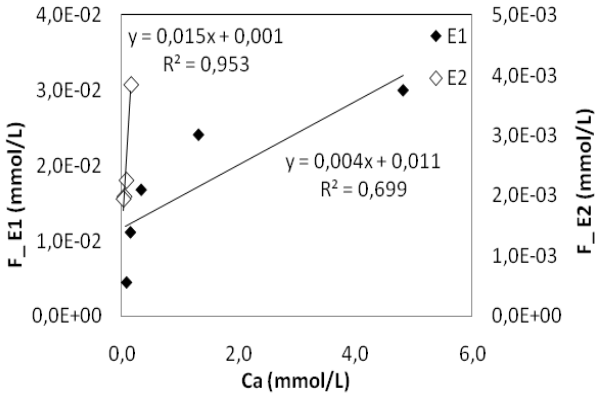

Figure 6. Correlation between Ca^{2+} and F^- release in T1 and T2 flow-through experiments conducted with loess.

Figure7

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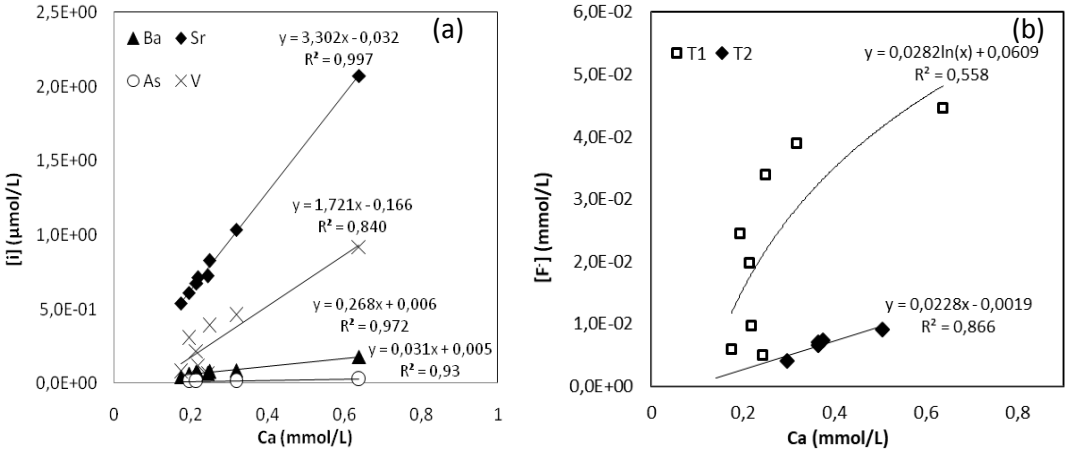

Figure7. Correlations between Ca^{2+} and Ba^{2+}, Sr^{2+}, As, V in the flow through experiments T1 (a) and between Ca^{2+} and F^- (b) in the test T1 and T2 conducted on calcrete samples.

Figure8
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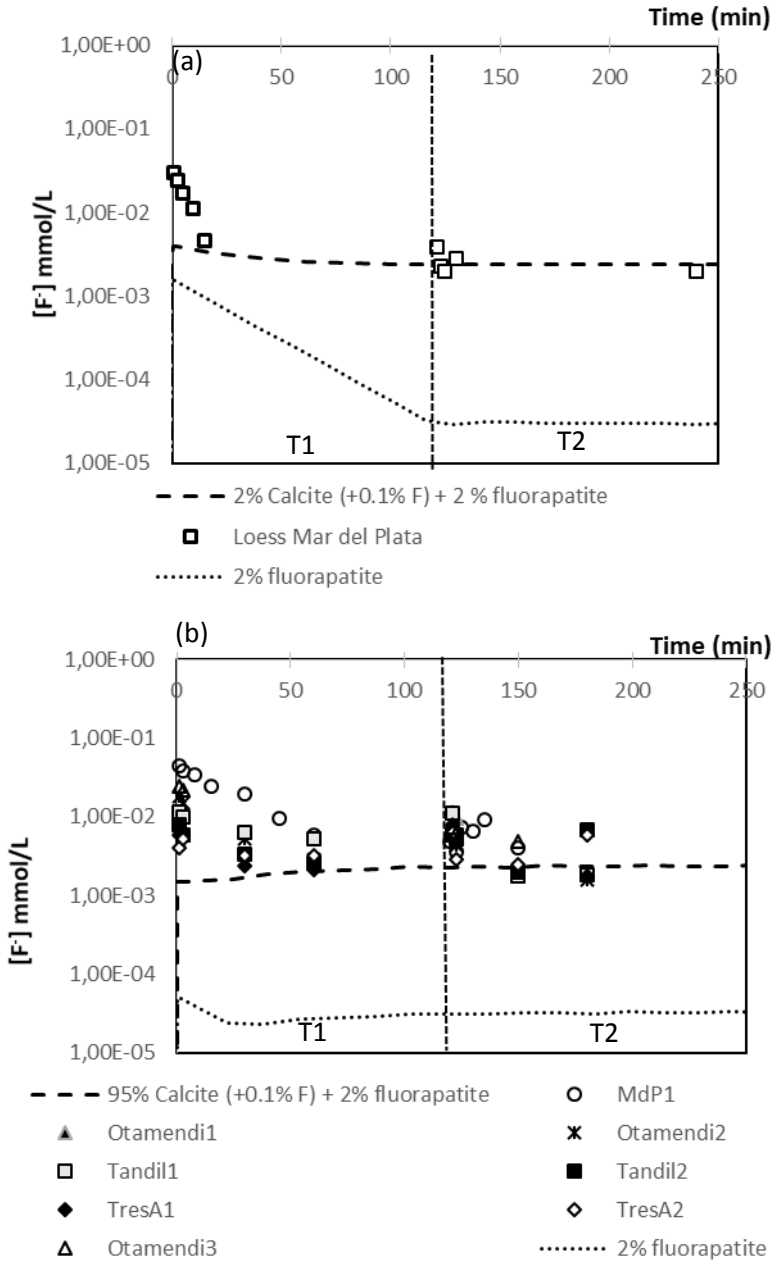

Figure 8. Simulations of fluoride release for loess (a) and calcrete (b) experiments including accessory minerals. The kirmat simulation for loess and calcrete were first realized with 2% of fluorapatite. Then, another kirmat simulation for loess was realized with 2% Calcite containing 0.1% impurity of fluoride and 2% of fluorapatite. Another kirmat simulation for calcrete was realized with 95% Calcite containing 0.1% impurity of fluoride and 2% of fluorapatite. The Kirmat simulations were compared to the flow-through experiments T1 and T2 on the loess sample from Mar del Plata (MdP) and the calcrete samples from Mar del Plata (MdP), Otamendi, Tandil and Tres Arroyos (TresA), in the province of Buenos Aires.