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Uranium and arsenic dynamics in volcano-sedimentary basins – an exemplary study in north-central Mexico

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Abstract

Uranium and arsenic in deep groundwater of the volcano-sedimentary Villa de Reyes Graben around the city of San Luis Potosí in semiarid north-central Mexico (mean U: 7.6 µg L^{-1}, max. 138 µg L^{-1}; mean As: 11.4 µg L^{-1}) were shown to partly exhibit concentrations in excess of the WHO guideline values and thus to endanger the quality of the most important drinking water source in the area. To unravel the mechanisms for their enrichment in groundwater, the potential trace element sources – volcanic rocks and basin filling sediments – were characterized. A total of 131 solid and liquid samples were analyzed for major and trace element geochemistry/hydrochemistry and, partly, for As and U fractionation and mobilization potential. The As/U hydrogeochemical signatures, their behaviour during rock alteration and evidence from other major and trace elements distribution, especially rare earth elements, strongly argue for dissolution of acid volcanic glass to be the dominating process of U and As release into groundwater. Its hydrogeochemical fingerprint is modified by additional trace element (preferentially As) mobilization from the sedimentary basin filling, representing a secondary source, in the course of decarbonatization of playa lake sediments and desorption from Fe-(hydr)oxide coated clastic material. Common behaviour of both elements during magmatic differentiation and growing drift apart in sedimentary environments are important findings of this work. Comparison with recent studies in similar environments suggest a common primary trace element source identification but significant differences in the evolution of present day As and U distribution. The study area´s geological and climatic similarity to numerous volcano-sedimentary basins make the findings transferable to other semi-arid regions facing challenges of geogenically impacted drinking water quality.

Keywords

Uranium, arsenic, volcanic rocks, trace element distribution, mobilization, Mexico

1. Introduction

1.1. Background and objectives

Uranium (U) and arsenic (As) are potentially toxic trace elements leading to health problems in exposed populations, especially in areas with high concentrations in groundwater. While the toxicity of As is well documented and drinking water limitations are established and reconsidered for several decades (actually 10 µg L^{-1}, WHO 2006), U was neglected in this respect for a long time. It was shown that the risk of U exposure primarily arises from its toxicity as a heavy metal, leading to kidney deseases, rather than from its radioactive character (Orloff et al. 2004). Nevertheless, there is no fixed limitation for U concentrations in drinking water up to date, although intake with drinking water is by far the most important exposure mechanism. WHO announced a "provisional guideline value" of 15 µg L^{-1}, US-EPA a MCL ("maximum contamination level") of 30 µg L^{-1}, German legislation decided on a fixed limitation of 10 µg L^{-1} very recently, coming into effect in November 2011.

In addition to the large tropical, mainly deltaic regions with As-exposed populations (e.g. Bangladesh, West Bengal, Vietnam, Taiwan), (semi)arid As problem areas have been identified worldwide. Prominent examples can be found in Chile (e.g. Oyarzun et al. 2004) and the western U.S.A. (e.g. Welch and Lico 1998). There are also known occurrences in the northern part of Mexico, e.g. the Zimapán Valley (Armienta et al. 2001) and the Rioverde Basin (Planer-Friedrich et al. 2001). Endemic As poisoning was described in the Lagunera region (Del Razo et al. 1990). In Mexico, Tertiary volcanics have been identified as one potential carrier of elevated As concentrations, and thus a potential source rock, however, more detailed characterization of the source or mobilization processes remain unknown (Gutiérrez and Alarcón Herrera 2010). Recent studies in arid to semi-arid volcanic areas in Ethiopia (Rango et al. 2010) and Argentina (Nicolli et al. 2010, Bundschuh et al. 2004, Smedley et al. 2002) found high As concentrations (several hundreds of ppb) in groundwater to be accompanied by elevated U. Distinct positive correlations between the two trace elements in both areas led to the interpretation of rhyolites being a potential common source rock for As and U.

Very similar climatic and geological conditions prevail in north central Mexico, therefore San Luis Potosí was chosen for investigation to study trace element dynamics and the structure of their sources and sinks on the interface between magmatic and sedimentary processes and examine the common occurrence of As and U despite their opposite redox behaviour (As more mobile under reducing, U under oxic conditions). While groundwater quality problems in connection with As (Jiménez 1982, Landín 2006) and especially fluorine (F) (Carrillo-Rivera et al. 2002) in the study area have been recognized in the past (although information on the occurrence of As has not been published so far), we report here for the first time on elevated U concentrations in San Luis Potosí, thus adding another concern to the list of water quality problems as, like in most semi-arid zones of Mexico, groundwater is the main source for drinking, agricultural and industrial use.

1.2. Study area

The San Luis Potosí (SLP) study area is located in the semi-arid north-central part of Mexico, about 370 km north of Mexico City (Fig. 1a) and has around 1 million citizens. It is part of one of

several closed volcano-sedimentary basins on the western edge of the Sierra Madre Oriental. The rather flat valley morphology of the Villa de Reyes graben structure is bordered with abrupt relief by the surrounding mountains of the Sierra de San Miguelito (SSM) to the west, and the Sierra de San Pedro (SSP) to the east, which are composed of Tertiary felsic volcanic and Cretaceous calcareous rocks, respectively (Fig. 1a), and reflect the typical distensive features of a rift graben (Fig. 1b). The normal faults were partly used as conduits for volcanism and bound a regional horst and graben structure. The sierras have an elevation of more than +2300 m a.s.l. and steeply slope towards the plane of the drainage basin with an altitude of about +1900 m a.s.l. Annual precipitation is 386 mm and the mean temperature 17.5°C, potential evaporation is around 2000 mm a^{-1} (Carillo-Rivera et al. 2002). The following geological description is after Labarthe-Hernández et al. 1982, Tristán-Gonzalez 1986 and Aguillón et al. 1994.

The overall geological situation is governed by a thick (up to >1500 m) sequence of extrusive Tertiary volcanic rocks, covered by alluvial sediments, and covering a Cretaceous mainly carbonatic sequence outcropping in folded NW-SE structures in SSP. These conditions are well comparable to a number of similar basins in the Sierra Madre Occidental and other regions of north-western Mexico and the south-western U.S.A. The Tertiary volcanics are mainly felsic to intermediate in composition. In general, they show porphyric textures dominated by glassy matrix (80-85 vol.%) with main phenocrysts being quartz, sanidine and plagioclase. The phase of volcanic activity in the area was between 44 and 27 Ma BP with most abundant units (e.g. San Miguelito rhyolite) being formed during the Oligocene.

Volcaniclastic debris flow sediments resulting from the erosion of the surrounding volcanics syn-tectonically filled the graben structure. The complete sedimentary sequence is referred to as Tertiary Granular Undifferentiated (TGU). This basin filling consists of unconsolidated to moderately consolidated, well to poorly sorted beds of gravel, sand, silt, and clay deposited on alluvial fans (e.g. the "Halcones" alluvial fan, Fig. 1a), pediments, and playas, and comprises an average thickness of 250-300 m. Fine-grained aeolian (loess-like) and flood plain deposits formed a 50 to 150 m thick layer, referred to as "fine sand lens" (Fig. 1b), fully enclosed in the TGU and being present in the largest part of the study area (except from the margins of the plain).

The following hydrogeological and hydrochemical information is after Jiménez 1982, Carillo-Rivera 1992, Carillo-Rivera et al. 1996, Carillo-Rivera et al. 2002 and Cardona and Carillo-Rivera 2006. The aforementioned "fine sand lens" – a low-permeability layer – comprises two main hydrogeological units, a shallow and a deep aquifer. The former is unconfined and consists of alluvium material with Ca-Cl-HCO_3-type groundwater. It shows heavy hydrochemical (e.g. nitrate) and microbiological (e.g. faecal coliforms) contamination. The heterogenous deeper aquifer is confined below the fine-grained layer and hosted in both fractured volcanic rocks and granular material (TGU). Groundwater has a thermal character (T=30-40°C) and slightly alkaline pH of 7.5 on average. It is HCO_3^--dominated, with a hydrochemical character between Ca-HCO_3 and Na-HCO_3.

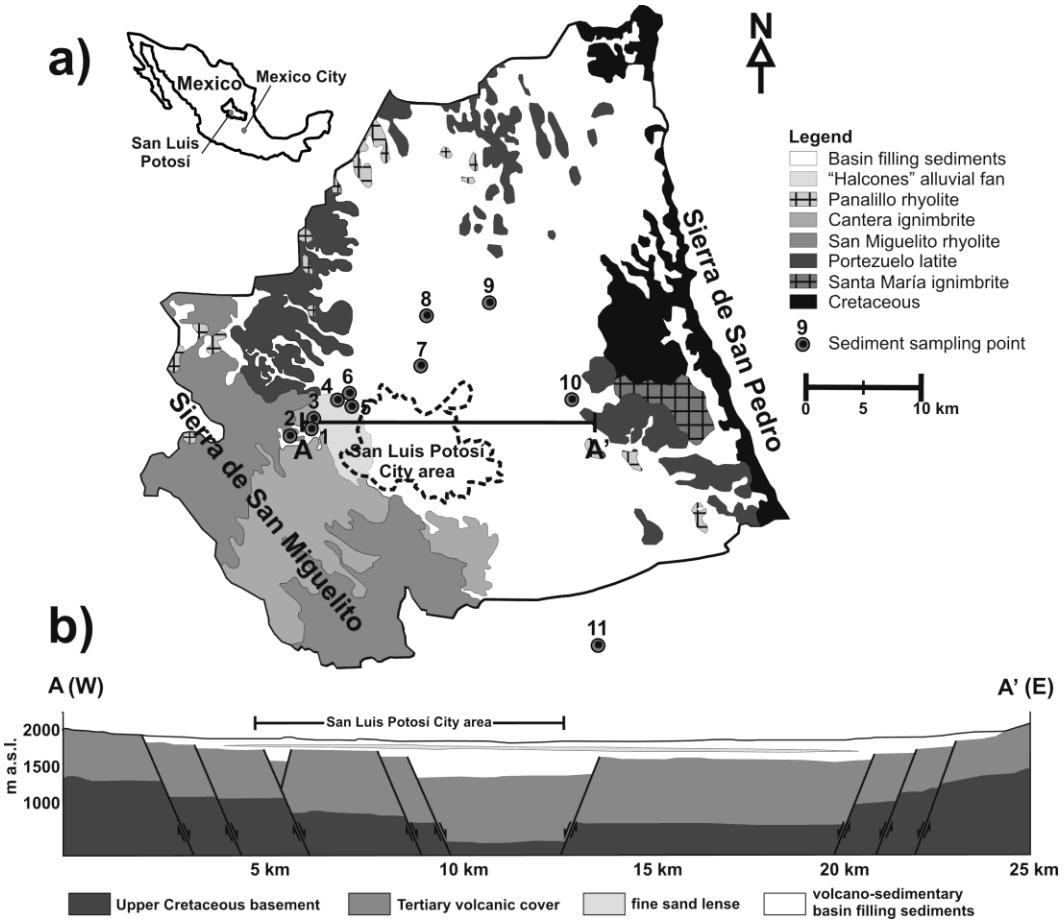


Fig. 1. Geological map of the study area **(a)** and simplified profile across the Villa de Reyes Graben **(b)**.

The deep aquifer has increasingly been subjected to intensive water extraction to supply the city, leading to a massive drawdown of the groundwater table in deep wells and production of regional old groundwater. While agriculturally and industrially contaminated groundwater could be avoided by exploiting the deep aquifer, other water quality problems related to high levels of F (up to 4 mg L^{-1}) and As (up to 65 µg L^{-1}) arose in some wells. Moreover, significant concentrations of dissolved ^{222}Rn indicate a possible U source and thus an additional potential threat for the water supply.

2. Materials and methods

Three compartments were studied to assess the different trace element reservoirs and their interdependencies: volcanic rocks, volcano-sedimentary basin fill sediments and groundwater.

The volcanic rock database consists of 40 samples (own outcrop sampling and analysis plus data from a previous local study, Rodríguez-Ríos 1997). The relevant units within the studied basin as well as some lithologies from its close surroundings were considered. Sample composition in our database ranges from trachyandesitic to rhyolitic, indicating that felsic volcanics are dominant in the study area (see chapter 3.1). The rocks are mainly of greyish to pinkish colour and show different forms and grades of alteration, including devitrification, partly refilled irregularly shaped cavities suggesting

glass dissolution, and oxidation of primary Fe phases to oxides. Figure 2 shows some of these phenomena.

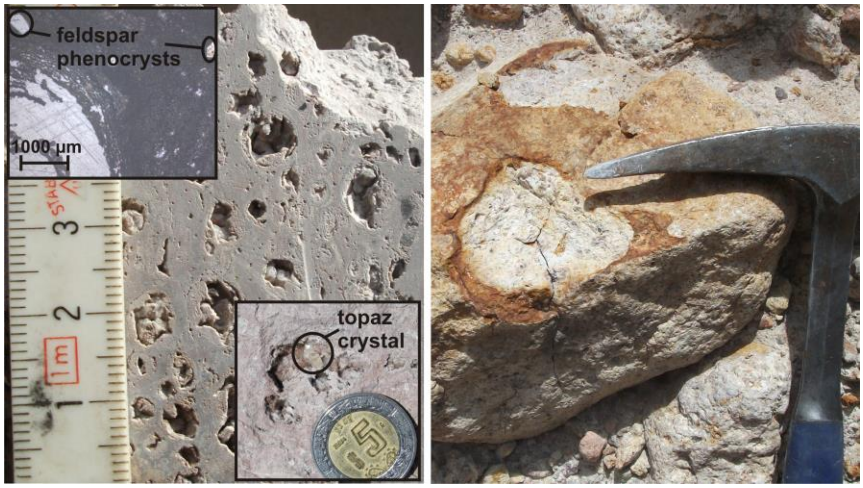


Fig. 2. Examples for volcanic rock appearance in the study area. Left side: sawn rhyolite with irregular cavities deriving from glass dissolution (upper inset: one cavity (light colour) in dense glassy matrix (dark colour) including few phenocrysts; lower inset: rhyolite surface cavity with idiomorphic topaz crystal). Right side: rhyolite block with reddish Fe oxides incrustation.

The basin filling sediments were sampled from outcrops (mainly sand and gravel pits of the little consolidated material with a depth of up to 35 m below ground surface (Fig. 3a), also some shallower outcrops and river beds) at 11 locations (Fig. 1a). A total of 30 sediment samples were obtained. These can be subdivided into two groups: (I) clastic sediments ranging in grain size from fine to coarse sand with differing portions of rounded rocks, especially near the Sierra de San Miguelito. Samples of this type consist of the material <2 mm only (obtained by sieving); rock pebbles were sorted out. In outcrops, dominant sediment colours are greyish to yellowish to dark orange indicating the presence of Fe-(hydr)oxides. (II) fine-grained light greyish to white sediments occurring in banks several meters thick or inter-bedded with the clastic sediments (Fig. 3b). They can be separated into two subgroups, (IIa) sediments showing a clear reaction after 10 % HCl treatment, indicating the presence of a significant amount of calcite and (IIb) optically very similar whitish sediments (Fig. 3c) which do not react with HCl, in the following referred to as “pseudo-caliche”. Group IIa represents caliche crusts and banks which we interpret to be the relicts of former ephemeral playa lakes in the valley. These secondary carbonates represent a typical feature in semi-arid basins and were identified in Argentinian As problem areas as well (Smedley et al. 2002). Group IIb is assumed to be the alteration products of IIa following meteoric decarbonatization.

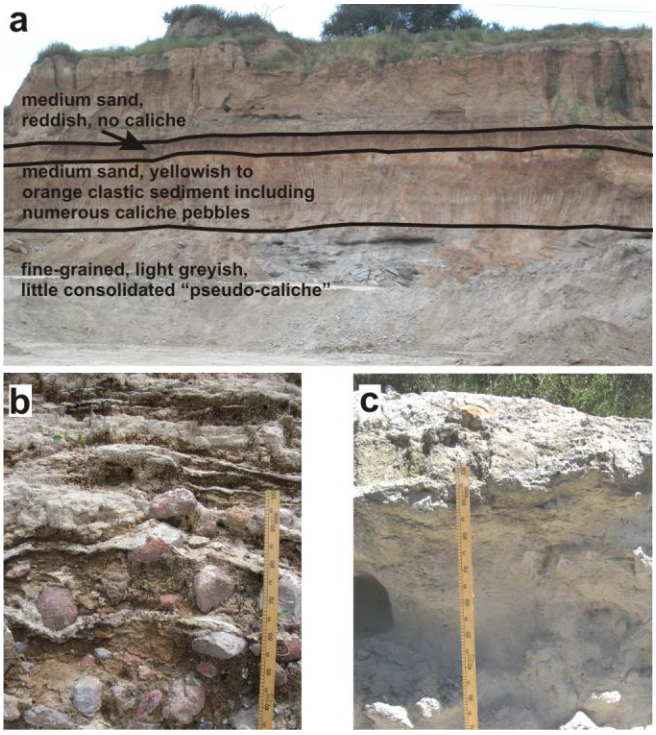


Fig. 3. Examples of basin filling sediments in the study area. **3a**: outcrop 7, typical appearance of sediment outcrop in the central part of the basin (cf. Fig. 1a), no rock pebbles, **3b**: outcrop 1, caliche crusts inter-bedded with clastic sediments including numerous rhyolite boulders due to proximity to Sierra de San Miguelito (cf. Fig. 1a), **3c**: outcrop 3, surface of ~4 m thick "pseudo-caliche", fine-grained, powder-like, little consolidated whitish sediment.

Groundwater samples were taken from wells completed in the deep aquifer. A total of 61 samples (spatially representative for the aquifer extent) were obtained by pumping. An in-line flow cell was applied to stabilize physico-chemical conditions during sampling. Water samples were stored at 4°C until analysis. The shallow aquifer was not sampled as this study does not deal with the evaporation effect on trace element concentrations, which surely is important for the shallow groundwater of the study area and has been well documented in climatically and geologically similar areas (e.g. Nicolli et al. 2010, Romero et al. 2003, Smedley et al. 2002, Welch and Lico 1998), but rather focuses on the impact of water-rock interaction processes leading to the hydrochemical signature of the groundwater, especially in terms of potentially hazardous trace elements like As and U. Moreover, the deep aquifer is of significantly higher importance for the water supply of San Luis Potosí, contributing 95 % of the total water usage (Carillo-Rivera et al. 1996).

For the volcanic rock samples taken for this investigation, whole rock samples were analyzed for major elements using a Siemens SRS 3000 X-ray wavelength dispersive spectrometer, a large suite of trace elements was quantified using ICP-MS (Perkin Elmer ELAN 9000). Thin sections were produced from three rhyolite samples (San Miguelito rhyolite) and studied under an optical microscope using transmitted light.

Sampled basin filling sediments were sieved to <2 mm grain size, ground in an agate mortar and analyzed for bulk rock chemistry by either Instrumental Neutron Activation Analysis or digestion ($HClO_4$-HNO_3-HCl-HF at 240°C) followed by ICP-OES analysis (Varian 735ES). Four sediment

samples (1 from group I, 2 from group IIa, 1 from group IIb) were subjected to a four-step sequential extraction procedure (SEP, Table 1) to assess As and U fractionation and mobilization potential. Aliquots of the samples (1 g) were ground in an agate mortar and placed in 50 mL centrifugation tubes. Extraction solutions (25 mL) were added in each step and the respective treatment was conducted (Table 1). After centrifugation (15 min at 3000 rpm) and filtration (0.45 µm) of the supernatant solution, the remaining sediment was subjected to the subsequent step. The extracted solutions were analyzed for U and As using AAS (PerkinElmer AAnalyst 800), and for Ca and Fe with ICP-OES (PerkinElmer Optima 2000 DV).

Table 1. Applied sequential extraction procedure (SEP).

Fraction no.	Targeted fraction	Extractant	Procedure	Reference
1	Easily soluble	NH_4NO_3 (1 M, pH 7)	30 min shaking, 20°C	Han and Banin 1995
2	Bound to carbonates	NaOAc/HOAc (1 M, pH 5)	16 h shaking, 20°C	Han and Banin 1995
3	Bound to Fe-(hydr)oxides	NH_4-oxalate (0.2 M) + ascorbic acid (0.1 M), pH 3.25	30 min in a water bath (96°C)	Wenzel et al. 2001
4	Residual	element (total) – element (sum steps 1-3)		

Groundwater samples were collected in double acid washed, low-density polyethylene bottles, filtered (0.45 µm) and stabilized to <pH 2 with 1 % ultrapure HNO_3. Trace element concentrations were determined by ICP-MS (Perkin Elmer ELAN 9000).

Geochemical and hydrochemical results were statistically analyzed, especially for potential correlations of As and U, and trends with other elements. To assess the impact of rock alteration on trace element remobilization, the Chemical Index of Alteration (CIA) was calculated for the volcanic rocks after Nesbitt and Young (1982). Chondrite-normalized Rare Earth Elements (REE) patterns were produced and compared for the potential trace element reservoirs rock-sediment-groundwater. The data were compared to a recent study in a geologically similar area showing elevated trace element concentrations in groundwater (Nicolli et al. 2010).

3. Results and Discussion

3.1. Volcanic rocks – Primary source and trace element mobilization

Volcanic rocks sample groups were organized according to a petrographical classification by applying the approach of Le Bas and Streckeisen (1991) who defined lithological fields in a scatter plot of SiO_2 vs. Na_2O+K_2O (TAS diagram, Fig. 4).

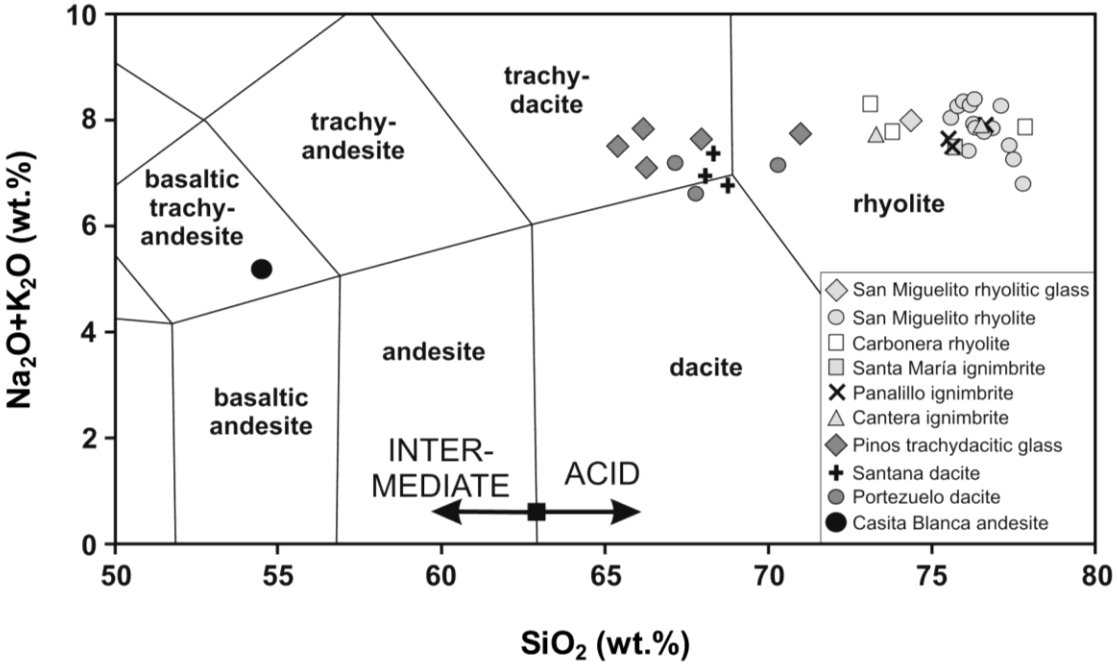


Fig. 4. Petrographical classification (after Le Bas and Streckeisen 1991) of the studied volcanic rock samples.

Except for one trachyandesite (Casita Blanca andesite), all samples can be classified as well differentiated, acid rocks (>63 wt.% SiO_2). All studied ignimbrites (Santa María ignimbrite, Panalillo ignimbrite and Cantera ignimbrite) show a rhyolitic composition. The Santana and Portezuelo units were combined as trachydacites, glass separates from the Pinos dome as trachydacitic glass (although in both groups, there is a slight overlap with the rhyolite field). The San Miguelito and Carbonera units represent rhyolites.

The occurrence of selected trace elements in the volcanic rocks, arranged according to the aforementioned petrographical groups, is presented in Table 2. Furthermore, the chemical index of alteration (CIA) calculated as CIA = Al_2O_3 / (Al_2O_3+Na_2O+K_2O+CaO) * 100 (Nesbitt and Young 1982) is shown.

Table 2. Statistics on trace element concentrations, As/U ratios and chemical indices of alteration (CIA) for the volcanic rocks in this study, and for comparison, rhyolitic glass data from the Salí River Basin/Argentina (Nicolli et al. 2010). DL: detection limit.

	As µg g^{-1}	U µg g^{-1}	Th µg g^{-1}	Pb µg g^{-1}	Zn µg g^{-1}	Cr µg g^{-1}	Ni µg g^{-1}	Cu µg g^{-1}	V µg g^{-1}	As/U	CIA
DL (this study)	0.5	0.5	0.2	3	1	1	0.5	2	2		
Trachyandesite (n=1)											
	2.50	1.26	6.00	18.0	123	68.0	27.0	<DL	143	1.99	56.5
Trachydacite (n=6)											
mean	5.2	4.7	20.0	24.8	84.1	6.4	6.3	11.0	20.6	1.1	61.2
median	5.1	4.5	20.3	23.6	80.6	6.1	4.9	9.7	20.5	1.1	62.2
min	2.06	4.09	18.0	22.2	70.5	2.00	3.26	6.20	17.4	0.44	52.9
max	9.00	5.44	20.9	29.1	104	11.5	11.5	19.0	24.0	2.08	64.0
Rhyolitic ignimbrite (n=6)											
mean	11.9	4.2	29.9	34.3	92.7	2.0	10.7	22.4	23.3	2.9	58.3
median	11.7	4.1	25.6	32.0	91.2	1.9	13.0	28.5	28.8	2.9	58.6
min	7.47	3.23	24.0	26.1	58.0	1.00	1.48	4.21	12.0	1.64	57.0
max	18.2	5.38	40.0	49.0	127	3.26	20.0	34.0	29.1	4.21	59.7

Rhyolite (n=21)											
mean	15.0	6.8	37.0	40.3	83.2	3.3	2.9	10.5	8.0	2.2	61.1
median	12.2	7.1	33.8	39.2	65.2	3.2	1.4	7.0	6.3	1.8	60.5
min	5.00	3.60	16.0	28.3	42.8	1.00	0.50	2.00	<DL	0.83	58.0
max	77.2	10.1	79.0	54.0	228	14.5	24.0	35.0	23.0	11.1	70.1
Glass separates (trachydacitic) (n=5)											
mean	8.9	4.7	17.2	26.5	123	3.4	3.1	6.8	12.9	1.9	59.4
median	8.7	4.5	16.6	25.1	93.7	3.3	2.6	7.4	13.5	1.9	59.1
min	7.45	4.22	15.3	25.0	66.7	2.11	0.96	3.85	7.97	1.77	58.2
max	11.2	5.60	21.5	30.5	273	5.64	7.29	8.17	15.6	2.00	61.2
Glass separates (rhyolitic) (n=1)											
	21.1	11.0	35.7	38.0	62.2	1.26	1.48	3.69	3.00	1.92	58.2
All rocks (n=40)											
mean	12.4	5.5	28.8	33.3	92.9	5.3	5.7	12.0	16.5	2.1	59.2
median	9.8	5.3	24.4	31.6	81.4	3.3	3.1	7.6	13.5	1.9	59.7
min	2.06	1.26	6.00	18.0	42.8	1.00	0.57	<DL	<DL	0.44	52.9
max	77.2	11.0	79.0	54.0	273	68.0	27.0	35.0	143	11.1	70.1
Glass separates (rhyolitic) (n=13) (Nicolli et al. 2010)											
mean	6	15	n.a.	n.a.	59	/	/	19	8	0.4	58.4
median	6	10.6	n.a.	n.a.	55	/	/	14	8	0.6	57.6
min	<5	4.3	n.a.	n.a.	36	<20	<20	<10	<5		
max	8	27.7	n.a.	n.a.	107	273	<20	74	17		

The median As concentration in all rock samples is 9.8 µg g^{-1} with highest values in rhyolites (median 12.2 µg g^{-1}, one outlier with 77.2 µg g^{-1}, the second highest value – 21.1 µg g^{-1} As – was measured in the rhyolitic glass separate). Uranium median concentration is 5.3 µg g^{-1} (1.26-11.0 µg g^{-1}) for all rocks. Like for As, the highest median value (7.1 µg g^{-1}) is found in rhyolites, the highest single value in the rhyolitic glass. Compared to the rhyolitic glass separates studied by Nicolli et al. (2010), the highly differentiated rocks in this work show significantly higher As concentrations while U contents are slightly lower, resulting in a typical As/U ratio of ~2 in San Luis Potosí volcanic rocks, compared to ~0.5 in the Argentinian glasses. CIA values ranging from 53-70 (median ~60) document different grades of chemical rock alteration. Fresh rhyolites yield a CIA of 49, dacites between 46 and 50, while highly alterated rocks approach 100 (i.e. pure kaolinite CIA), this development is caused by successive loss of geochemically less stable oxides and thus, a relative enrichment of Al_2O_3 (Dawood et al. 2004).

Figure 5 illustrates the distribution and interrelation of U and As in the different volcanic rock groups.

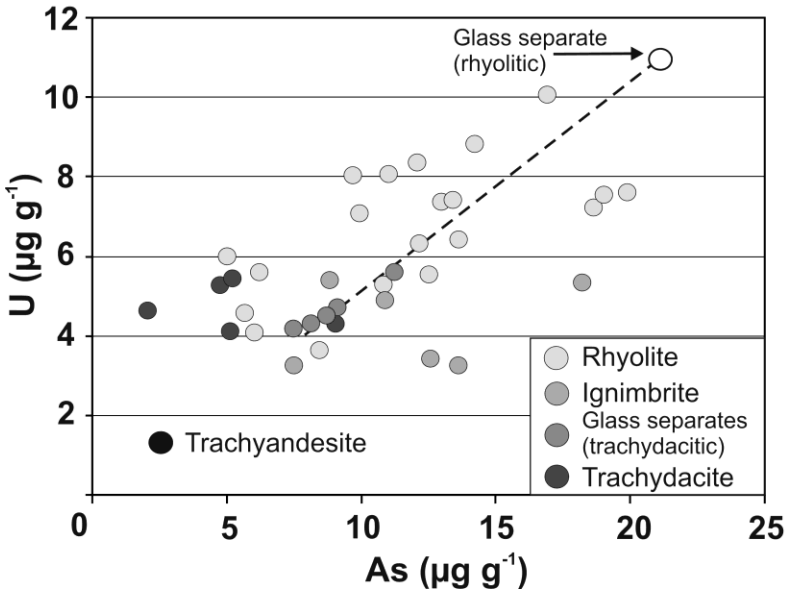


Fig. 5. As vs. U scatter plot for the volcanic rock samples.

In the scatter plot (Fig. 5), the rock samples cluster between two end members of low (trachyandesite) and high (rhyolitic glass) As and U concentrations. Rhyolite whole rock samples display a positive correlation between U and As (R=0.62) and thus suggest a potential common host rock of both trace elements. Even more distinct, the trachydacitic glass separates yield R=0.99 between As and U, although with lower absolute concentrations on average. The rhyolitic glass sample is situated in extension of this trendline (indicated by the dotted line in Fig. 5), suggesting general common occurrence of the trace elements in the volcanic rocks´ glassy matrix with enrichment towards more acid rocks. These findings support the incompatible character of U and As during magmatic differentiation and their accumulation in the latest cooling products. Rhyolites and especially their glassy components may consequently be considered a potential primary source of the studied trace elements in the investigation area.

We developed "double correlation" scatter plots (i.e. correlation coefficient R for As with other parameters vs. correlation coefficient R for U with the same parameters) for this project (Fig. 6) and introduce them here. This form of data presentation allows for approaching a number of questions and offers information and interpretability significantly in excess of standard binary scatter plots:

- What is the degree of geochemical similarity in occurrence and behaviour of two elements (in this case As and U) in a given environment? Common trends of both elements towards other major and trace elements or parameters (negative or positive), and also their absence, hint to mutual geochemical distribution. If analyzed for a sufficiently large set of elements and/or parameters, high degrees of geochemical similarity between two elements are expressed by a) high correlation coefficients $R_{\text{corr coeff with element 1 vs. corr coeff with element 2}}$ and b) trendlines of this correlation through the origin of the diagram (cf. Fig. 6).

- Which are the elements or parameters mainly responsible for similarity or dissimilarity in geochemical distribution of two elements? Common positive behaviour of both elements towards another element hints to mutual occurrence of all three parameters. In contrast, common negative trends indicate the both studied elements prefer to stay away from where the third element prevails. Examples for this are given in the following discussion (below Fig. 6). Therefore, diagnostic parameters governing the occurrence of one or both of the characterized elements may be identified from the plot and used for interpretation of the geochemical system.
- Which are the processes responsible for the observed distribution of the two studied elements? Given some previous background knowledge of the studied system and general comprehension of different elements´ hydrogeochemical behaviour (e.g., (in)compatibility, (im)mobility, preferential mineral host phases, speciation and transport characteristics under prevailing conditions, etc.), much can be learned from "double correlation" plots about these processes. Some examples of processes derived from interpretation of these plots for As and U in the studied volcanic rocks (e.g., common behaviour in magmatic differentiation, common occurrence in the volcanic glass phase, common mobilization during rock alteration) are discussed in the following. In contrast, examples for low degrees of geochemical similarity and associated explanatory approaches derivable from "double correlation" plots are found in Fig. 9 and the respective discussion.

We believe that the mode of data presentation introduced here offers the possibility to describe, compare and interpret occurrence and behaviour of two elements in a studied system with only one diagram. Although a sufficiently large suite of elements/parameters has to be determined to support this statistical approach, it can represent a tool for the concise characterization of environmental compartments.

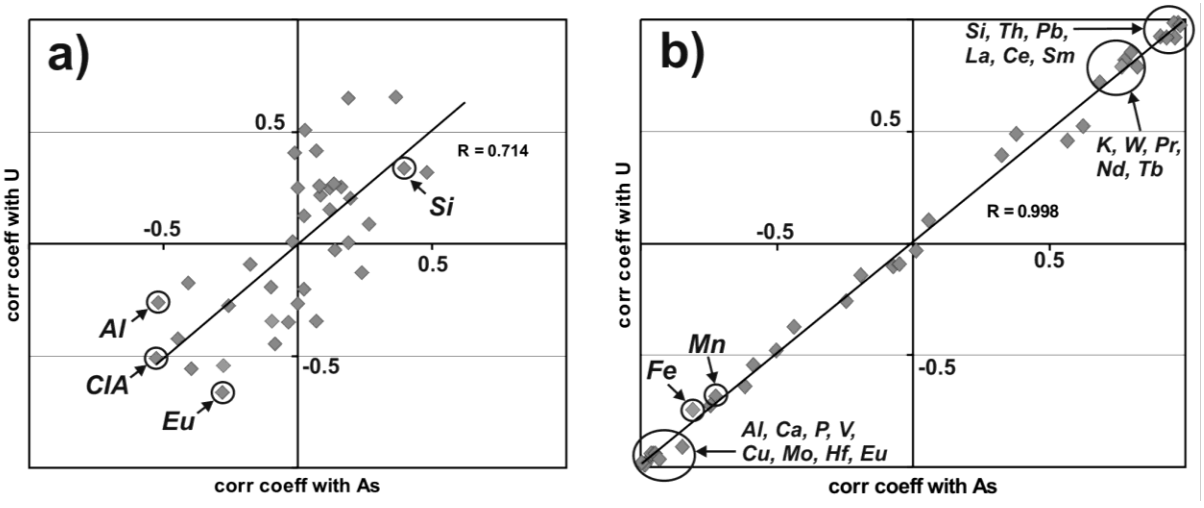


Fig. 6. "Double correlation" diagrams, **(a)** for rhyolite samples and **(b)** for trachydacitic glass separates.

In the rhyolite sample group (Fig. 6a), U and As exhibit a similar geochemical behaviour, not only towards each other (cf. Fig. 5) but also towards most other chemical parameters as indicated by R (R(As/parameter) vs. R(U/parameter))=0.714. Common positive correlation with Si, together with the negative trends towards Al, support occurrence in the glassy matrix and not in silicate host minerals, especially feldspars. This finding is supported by Mahood and Hildreth (1983) who found partition coefficients significantly smaller than unity for $U_{sanidine/rhyolitic\ glass}$, and enhanced by the negative behaviour towards Eu which is incorporated as Eu^{2+} in feldspars during magmatic differentiation (e.g. Weill and Drake 1973) and thus withdrawn from the depleted melt (see also chapter 3.4). A striking outcome of the plot is the common negative correlation of U and As with CIA, i.e. the concentrations of both trace elements in the rocks decrease with increasing alteration intensity. They are mobilized together (CIA does not show any trend against the As/U ratio) from the volcanic rocks during weathering. Additional noteworthy features of CIA behaviour include a negative trend with Si (R=-0.54) which is remarkably similar to $R_{CIA/U}$=-0.51 and $R_{CIA/As}$=-0.53 and suggests parallel mobilization of the three elements from the volcanic rocks. Further negative correlations of CIA with K (R=-0.78), most probably due to the breakdown of feldspars, as well as with Cr (R=-0.41), V (R=-0.34) and W (R=-0.45) indicate also these elements´ loss during weathering. Positive interrelations with CIA displaying relative refractory enrichment of elements during rock alteration are observed for Al (R=0.69, retained in clay minerals resulting from feldspar transformation which, nevertheless, do not represent effective secondary trace element sinks (Zielinski 1982)), Hf (R=0.52, most probably in refractory zircon) and Zn (R=0.60, likely to be retained in secondary Fe phases). Rare earth elements behave trendless to slightly negative towards CIA (R=0.00 to -0.30, exception: Eu with R=0.27) indicating rather limited mobilization potentials.

Evaluating the separated trachydacitic glass samples in the same way (Fig. 6b), an even more significant geochemical similarity of U and As becomes obvious, expressed by R=0.998 in the "double correlation" plot. The rhyolitic glass sample was not implemented in the calculations. It substantially supports and increases the geochemical trends but would exaggerate the correlation coefficient values in this data cohort due to significantly higher As and U concentrations, compared to the trachydacitic glass (cf. Fig. 5). The aforementioned relations in rhyolites towards Si, Al and Eu are clearly approved and enhanced, suggesting that the glassy matrix is the main host that is largely responsible for As and U signatures in whole rock volcanics. A common occurrence with other incompatible elements (Th, W, REE except Eu) is observable while distinct negative correlations with Ca, P and Hf indicate that U and As are unlikely to be hosted within accessory mineral phases like apatite and zircon, both of which represent potential hosts in general (e.g. Zielinski 1981, Mahood and Hildreth 1983, Lee et al. 2009). Moreover, common negative behaviour towards Fe and Mn argues against primary (e.g. biotite) or secondary (e.g. hematite, Fe/Mn oxyhydroxides) phases of these elements to be significant hosts. While it has long been known that acid volcanic glasses represent sinks and potential sources of U (e.g. Rosholt and Noble 1969, Zielinski 1977; exploration-related U research was triggered

substantially in the 1960s and 70s), it was only recently shown for the first time by Borisova et al. (2010) that As is present in silicate glasses as As(III)-hydroxide species (similar to its preferential forms in aqueous solutions) and that concentrations can exceed 400 µg g^{-1} (study of Peruvian rhyolites). Zielinski (1981) found that U removal from volcanic glass mainly happens via glass-network dissolution, especially under high T and alkaline pH conditions of the dissolving solution, and that U and Si are mobilized in approximately equal proportions. Those findings are in good agreement with this study, considering the behaviour of U and Si discussed above and the observation of glass dissolution structures in the studied rocks (cf. Fig. 2). For the investigation area, we can extend these statements to As in view of the geochemical similarity to U and the U-analogue behaviour towards Si and CIA.

In conclusion from the data so far, U and As seem to be dispersely distributed in the amorphous volcanic glass, representing their primary source, and from there, remobilized together in the course of rock alteration (with glass dissolution as dominant mobilization mechanism), with subsequent release into sedimentary environments.

3.2. Basin filling sediments – Primary sinks, secondary sources

Analytical results of basin filling sediments, classified according to the sample groups defined in section 2, are presented in Table 3, together with loess sediment data from the Salí River Basin/Argentina taken from Nicolli et al. (2010).

Table 3. Statistics on trace element concentrations and As/U ratio for the basin filling sediments in this study, and their enrichment factors (median sediment compared to median volcanic rock composition). For comparison, loess basin sediment data from the Salí River Basin/Argentina (Nicolli et al. 2010) are also implemented. DL: detection limit.

	As µg g^{-1}	U µg g^{-1}	Th µg g^{-1}	Pb µg g^{-1}	Zn µg g^{-1}	Cr µg g^{-1}	Ni µg g^{-1}	Cu µg g^{-1}	V µg g^{-1}	As/U
DL (this study)	0.5	0.5	0.2	3	1	1	0.5	2	2	
Group I (clastic sediments) (n=18)										
mean	11.7	4.2	16.9	24.0	85.7	17.7	8.8	9.7	30.0	2.9
median	11.7	4.3	17.2	21.5	87.0	18.0	7.0	10.0	34.0	2.7
min	5.70	2.70	13.2	14.0	49.0	11.0	3.00	5.00	6.00	1.33
max	19.2	5.90	21.4	47.0	137	31.0	20.0	18.0	51.0	4.96
EF vs. median volcanics	1.19	0.81	0.70	0.68	1.07	5.45	2.28	1.32	2.52	1.41
Group IIa (caliche sediments) (n=7)										
mean	13.1	4.9	9.7	11.7	61.2	18.0	9.0	7.3	24.7	2.5
median	10.2	3.2	9.1	12.0	66.0	10.0	10.0	7.0	27.0	2.7
min	5.50	2.70	6.30	5.00	21.0	<DL	5.00	3.00	13.0	1.22
max	37.4	14.0	15.8	20.0	99.0	59.0	19.0	13.0	36.0	4.89
EF vs. median volcanics	1.04	0.60	0.37	0.38	0.81	3.03	3.26	0.93	2.00	1.41
Group IIb ("pseudo-caliche") (n=5)										
mean	7.4	4.6	18.0	13.4	86.0	8.4	5.4	3.4	18.2	2.0
median	8.5	4.3	16.1	11.0	80.0	8.0	2.0	2.0	9.0	2.2
min	4.60	1.70	9.70	8.00	58.0	<DL	2.00	1.00	<DL	0.66
max	10.4	7.00	27.3	25.0	113	21.0	17.0	11.0	38.0	5.12
EF vs. median volcanics	0.87	0.81	0.66	0.35	0.98	2.42	0.65	0.26	0.67	1.16
All basin fill sediments (n=30)										
mean	11.3	4.4	15.4	19.5	80.2	13.4	8.6	7.9	27.0	2.8
median	10.4	4.3	15.7	20.0	79.0	13.0	7.0	9.0	28.5	2.6
min	4.60	1.70	6.30	5.00	21.0	<DL	2.00	1.00	<DL	0.66
max	37.4	14.0	27.3	47.0	137	59.0	20.0	18.0	51.0	5.12
EF vs. Median volcanics	1.06	0.80	0.64	0.63	0.97	3.93	2.28	1.19	2.11	1.35

Basin sediments (loess) (n=18) (Nicolli et al. 2010)										
mean	10	4.9	n.a.	n.a.	78	46	/	21	84	2.1
median	10	3.88	n.a.	n.a.	81	45	/	20	85	2.6
min	7.00	3.60	n.a.	n.a.	<30	29	<20	13	53	
max	14.0	12.4	n.a.	n.a.	125	58	37	26	99	

The median As concentration in all basin fill sediment samples is 10.4 µg g^{-1} with highest median values in the clastic sediments (11.7 µg g^{-1}). Nevertheless, the single highest value was detected in the most Ca-rich caliche sample (37.4 µg g^{-1} As, 21.6 wt.% Ca). Uranium median concentration for all sediments is 4.3 µg g^{-1} (1.7-14.0 µg g^{-1}) and, like for As, with the peak single value in the same caliche sample while the minimum U content was observed within the "pseudo-caliche" group. Arsenic and U concentrations (and their ratios) in the Argentinian sediments are comparable to those obtained in this study while the former yield significantly elevated values for Cr and V (Table 3). In the Villa de Reyes Graben, As exhibits a slight enrichment (especially in the clastic sediment group) together with Cu, Ni, V and Cr, while U is slightly depleted (same for Th and Pb), compared to the volcanic source rocks characterized in chapter 3.1. Consequently, the median As/U ratio is higher in the sediments, indicating growing differences in geochemical behaviour between As and U. Figure 7a shows the As-U scatter plot for the basin filling sediments.

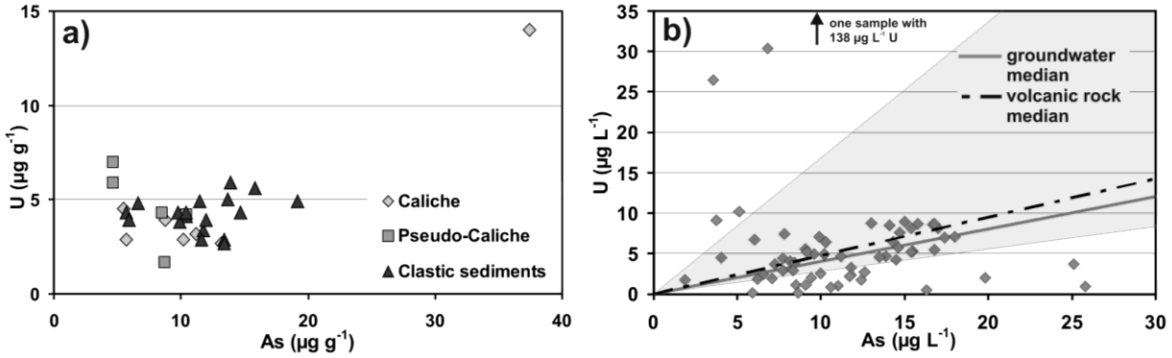


Fig. 7. As vs. U scatter plots for **(a)** basin filling sediments and **(b)** groundwater, the greyish zone in (b) indicates an area defined by average volcanic rock As/U ratio +2 standard deviations (lower line) and -2 standard deviations (upper line).

The observation of highest concentrations of both As and U in the most Ca-rich caliche sample and lower values in the other members of the caliche (Ca: 3.84-14.7 wt.%) and the "pseudo-caliche" (Ca: 0.19-1.06 wt.%) group (Fig. 7a) may lead to the assumption that trace element loss from these sediments occurs during decarbonatization, i.e. that U and As may be preferentially hosted in the relatively soluble carbonate fraction, especially when considering that calcite is able to incorporate both trace elements (Sturchio et al. 1998, McCall et al. 2001, Di Benedetto et al. 2006). To assess this question and the general mineralogical fractionation of both trace elements, the applied sequential extraction procedure (SEP) contains a step targeting the carbonate fraction in the sediments.

Figure 8 illustrates the results of the SEP with an approach to evaluate potential preferences in leaching either As or U. Samples subjected to the SEP include the aforementioned high-Ca caliche with highest trace element concentrations, a second caliche sample with lower Ca (7.84 wt.%), one

unconsolidated whitish "pseudo-caliche" (Ca: 0.32 wt.%) and a reddish fine sand sample representative for the clastic basin fill sediments.

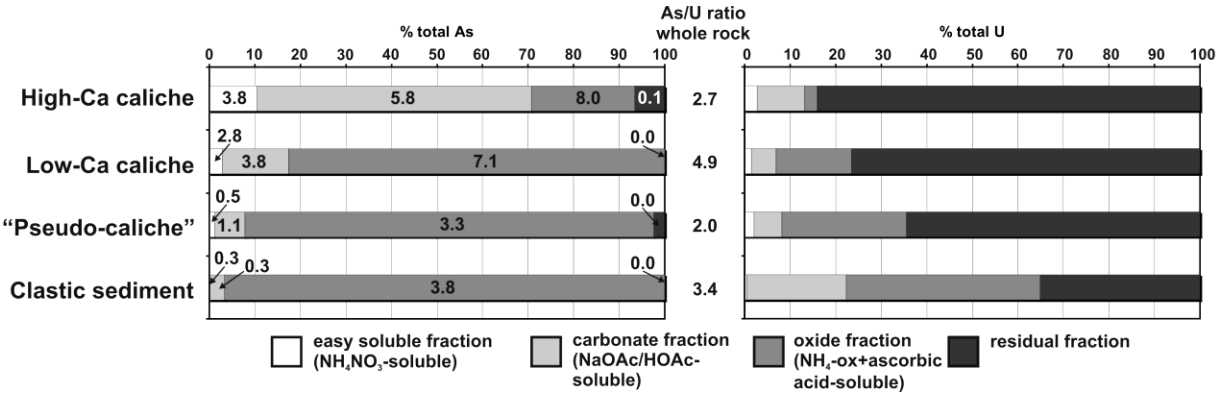


Fig. 8. Sequential extraction procedure (SEP) results for As (left side) and U (right side) and whole rock As/U ratios of the studied samples. Figures in the left diagram are As/U ratio factors (i.e. the As/U ratio in the different fractions divided by the whole rock As/U ratio whereby factors >1 indicate preferential As leaching, <1 preferential U leaching and =1 congruent As and U leaching in the respective steps).

A significant proportion of NH_4NO_3-soluble As (~10 % As_{tot} corresponding to 3.9 µg g^{-1} As) was observed in the high-Ca caliche only, other samples yielded <3 % for both U and As. The carbonate fraction of As decreases with decreasing Ca in the sample (i.e. with increasing decarbonatization) from 60 % As_{tot} (i.e. 22.5 µg g^{-1}, largest As fraction) in the high-Ca caliche to 7 % in the "pseudo-caliche" suggesting that indeed, As is mobilized from the sediments during calcite dissolution. This trend is less distinct for U whose NaOAc/HOAc-soluble portion is 10 % U_{tot} in fresh caliche and 5-6 % in the more altered samples. Factors of As/U ratio between NaOAc/HOAc-leachate and whole rock suggest clearly preferential As over U leaching in high- and low-Ca caliche and virtual congruent mobilization from the "pseudo-caliche". Mobilization potential for As in this rather easy soluble fraction is clearly higher than for U, an equilibration seems to be reached when decarbonatization is completed. In contrast, U leaching in this step is favoured over As from the clastic sediment sample (22 % U_{tot}; 3 % As_{tot}). In the NH_4-oxalate-soluble trace element fraction, preferential As over U mobilization is obvious in all samples, most prominently in the high-Ca caliche (ratio factor 8.0). In the other samples, this fraction is the most important for As, accounting for 86 % (low-Ca caliche) to 97 % (clastic sediment) of As_{tot}. Obviously, there is a shift in the mineralogical As fractionation during decarbonatization from carbonates to Fe oxides, supported by a significant negative trend between Ca and Fe in the caliche sample group (not shown) indicating Ca loss and Fe relative enrichment. Considering the As concentration difference between fresh and altered caliches, nevertheless, the oxides are not able to effectively retain the As mobilized from carbonates which, in consequence, will be lost from the sediments to solution. In the applied SEP, virtually all As was dissolved from the samples, the residual fraction is negligible.

Similar to As, the U fraction bound to oxides is more important than the carbonate fraction (except for the high-Ca caliche, see above), it represents the dominant U portion in the clastic

sediment (43 % U_{tot}). Preferential U over As mobilization, expressed by a ratio factor of 0.3, occurs most noticeably in the relatively easy soluble steps 1 and 2 for the clastic sediment. In contrast to As, total U leachability in this SEP is significantly lower, ranging from 16 % U_{tot} in fresh caliche to 65 % in the clastic sediment, resulting in large residual fractions. Thus, an important part of the U seems to be effectively retained, especially in the caliche sediments. Sphene, known as a uraniferous accessory mineral (Zielinski 1981), might offer an explanation for this phenomenon, as concluded from a positive trend between U and Ti in the caliche group. Another possible explanation, derived from the observation that the playa sediments, in contrast to the clastics, contain at least measurable concentrations of sulphide-S (350 µg g^{-1} on average, maximum value: 1000 µg g^{-1} in the high-Ca caliche), may be U accommodation in reduced accessory mineral phases like pyrite (Descostes et al. 2010) or uraninite (Leach et al. 1980). Assuming the latter, the U portion allocated to the applied SEP´s residual fraction would at least partly be remobilizable in the course of meteoric oxidative alteration of the sediments.

Leach et al. (1980) studied playas for their geochemical U exploration potential, examining playa sediments from the U.S. Basin and Range Province, an area with very similar climatic and geological conditions as in the Mexican example in this work. They concluded that evaporation processes in the playa lakes may lead to U enrichment in the carbonaceous sediments (up to 58 µg g^{-1}, median: 3.9 µg g^{-1}, cf. Table 3) even with low U inflow water, but vulnerability to alteration and remobilization limits the U exploration potential substantially. Large residual U fractions in sediments (after treatment with 1 M HCl; up to 95 % U_{tot}) is another similarity between the studies. Those results are supported by the data in this work, the genetic model may thus be transferred to the playas in San Luis Potosí and extended to As enrichment therein.

In summary, a quite heterogenous dissolution behaviour with a preference for As mobilization from the studied basin fill sediments is observable, compared to the rather homogenous common mobilization of both trace elements via glass dissolution from volcanic rocks as discussed in the previous chapter.

3.3. Groundwater – Secondary sink, drinking water source

Selected trace element results for the groundwater samples are presented in Table 4 and compared to the study of Nicolli et al. (2010).

Table 4. Statistics on trace element concentrations and As/U ratios for the groundwater samples in this study, and comparison with WHO guideline or recommended values. Groundwater data from the Salí River Basin/Argentina (Nicolli et al. 2010) are also implemented (n.a. – not analyzed). DL (ts): detection limit (this study).

	As µg L^{-1}	U µg L^{-1}	Th µg L^{-1}	Pb µg L^{-1}	Zn µg L^{-1}	Cr µg L^{-1}	Ni µg L^{-1}	Cu µg L^{-1}	V µg L^{-1}	Se µg L^{-1}	Sb µg L^{-1}	Mo µg L^{-1}	Al µg L^{-1}	Fe µg L^{-1}	Mn µg L^{-1}	SiO_2 mg L^{-1}	As/U
DL (ts)	0.03	0.001	0.001	0.01	0.5	0.5	0.3	0.2	0.1	0.2	0.01	0.1	2	10	0.1	0.2	
WHO (2008) guideline or recommended values																	
	10	15	-	10	-	50	20	2000	-	10	20	70	200	-	400	-	
Groundwater Villa de Reyes Graben/Mexico (deep aquifer, T=30-40°C, n=61, this study)																	
mean	11.4	7.6	0.0	0.9	20.7	1.5	0.6	3.0	4.4	1.7	0.2	1.7	25	72	1.9	80.7	5.9

median	10.6	4.7	0.0	0.7	12.6	0.9	0.3	2.2	4.2	1.2	0.2	1.7	17	20	0.9	76.3	2.5
max	25.8	138	0.03	5.2	250	5.3	2.9	12.9	22.4	8.7	1.37	4.1	92	2470	29.8	117	87.2
min	1.86	0.1	0.00	0.16	2.9	<DL	<DL	0.5	0.8	0.4	0.04	0.2	5	<DL	0.2	18.6	0.1
							% dataset exceeding guideline value										
	54	5		0		0	0	0		0	0	0	0		0		
	Groundwater Salí River basin/Argentina (deep artesian aquifer, T=21-45°C, n=17, Nicolli et al. 2010)																
mean	36.4	1.8	n.a.	n.a.	n.a.	178	n.a.	n.a.	77.5	2.1	0.11	10.1	8.7	170	16.1	41.4	20.4
median	26.5	1.3	n.a.	n.a.	n.a.	178	n.a.	n.a.	63.8	2.1	0.09	5.5	7	183	8.3	35.2	20.5
max	76.9	6.19	n.a.	n.a.	n.a.	218	n.a.	n.a.	162	3.6	0.29	29.9	22	365	90.6	74.3	
min	16.2	0.10	n.a.	n.a.	n.a.	110	n.a.	n.a.	44.8	0.2	0.03	0.4	2	40	0.5	21	
							% dataset exceeding guideline value										
	100	0				100				0	0	0	0		0		

More than half of the analyzed groundwaters exhibit As concentrations exceeding the WHO guideline value (median As: 10.6 µg L^{-1}) which demonstrates the extent of the As-related water quality problem in the study area. Only 5 % of the U dataset exceed the actual WHO recommended guideline value of 15 µg L^{-1}. Nevertheless, in view of an extreme value of 138 µg L^{-1} and nearly half of the samples being above 5 µg L^{-1} (for comparison: a national survey in the U.S.A. found a mean U groundwater concentration of 1.86 µg L^{-1}, Longtin 1988), the study area´s groundwater U can be characterized as elevated. As/U ratios are variable at a median value of 2.5. Low concentrations of Fe and Mn support the oxidizing character of the groundwater, albeit one Fe outlier (~2.5 mg L^{-1}, but no elevated As or U) indicates the presence of local reducing conditions.

Arsenic and U exhibit a positive relationship in groundwater samples (Fig. 7b) which is in agreement with Nicolli et al. (2010). Nevertheless, outliers from this trend with elevated As or U are observable. In Fig. 7b, the greyish zone is defined by the average As/U ratio in volcanic rock samples +2 standard deviations (lower boundary) and -2 standard deviations (upper boundary) to approach a confidence area in which dissolution from volcanic rocks may be made responsible for the As/U signature in groundwater. Two-thirds of the samples plot within this field, ~25 % show more elevated As concentrations, 8 % exhibit disproportionally high U. This distribution is responsible for the displacement of median groundwater As/U ratio towards the “As side” displaying As sources in addition to volcanic rocks. These are likely to be found in the basin filling sediments that were shown to have a higher As than U mobilization potential (see previous chapter), especially the playa caliches. Arsenic loss from Fe oxides in carbonate or clastic sediments may also contribute to this shift of the As/U ratio. Preferential U over As input lowering groundwater As/U ratios may be expected in early stages of mainly clastic sediment alteration, as concluded from SEP results (Fig. 8).

To follow up the development of As and U hydrogeochemical behaviour after mobilization from their common primary source, “double correlation” diagrams were produced, as it was already done for volcanic rocks (Fig. 6), for clastic basin filling sediments (Fig. 9a), and groundwater (Fig. 9b).

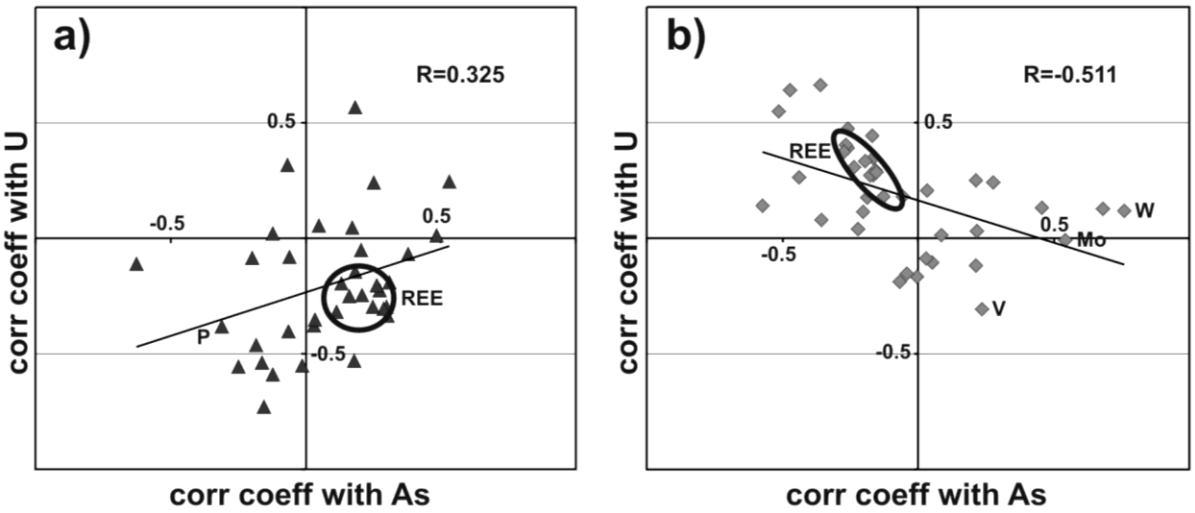


Fig. 9. „Double correlation“ diagrams (i.e. correlation coefficient R for As with other parameters vs. correlation coefficient R for U with the same parameters). **(a)** for clastic basin filling sediments and **(b)** for groundwater samples.

The positive trend between U and As behaviour towards other elements, compared to the findings for volcanic rocks and especially the glass separates, is significantly less distinct for the clastic basin fill sediments (Fig. 9a). Moreover, the trendline shows an offset from the center of the diagram. Both observations argue for a less similar geochemical behaviour of the trace elements and thus a beginning differentiation of As and U in the sedimentary environment. Negative trends towards P suggest that also in the sediments, accessory apatite is unlikely to host important amounts of the trace elements.

A similarly diffuse, but negative trend is exhibited by the groundwater “double correlation” plot (Fig. 9b). Although, as discussed before, As and U still occur together in the water, their chemical speciation is known to differ in solutions, dependent on their unequal affinity towards complexing reagents. It is most likely that under the hydrochemical conditions prevailing in the studied aquifer (chapter 1.2), U is transported as carbonate complexes. This assumption is supported by rare earth elements´ (REE) positive relation towards U (and negative towards As, Fig. 9b), as REE tend to form carbonate complexes under the given conditions as well (Luo and Byrne 2004). In contrast, As will preferably be present as oxyanion species which is underlined by rather positive As trends towards other mobile oxyanion forming elements like W, Mo or V (Fig. 9b).

In consequence, the geochemical behaviour of As and U, being very similar in volcanic primary host rocks, is successively decoupled after crossing the interface between magmatic and sedimentary environment, although the primary source´s fingerprint is still clearly visible in absolute trace element concentrations.

3.4. Rare earth elements

As another approach to study the interrelations between the different potential As and U reservoirs in the study area, REE plots were produced for the compartments volcanic rocks (Fig. 10a),

basin fill sediments (Fig. 10c) and groundwater (Fig. 10d). Additionally, the intensity of the observed Eu anomaly was plotted against U concentrations in volcanic rocks (Fig. 10b).

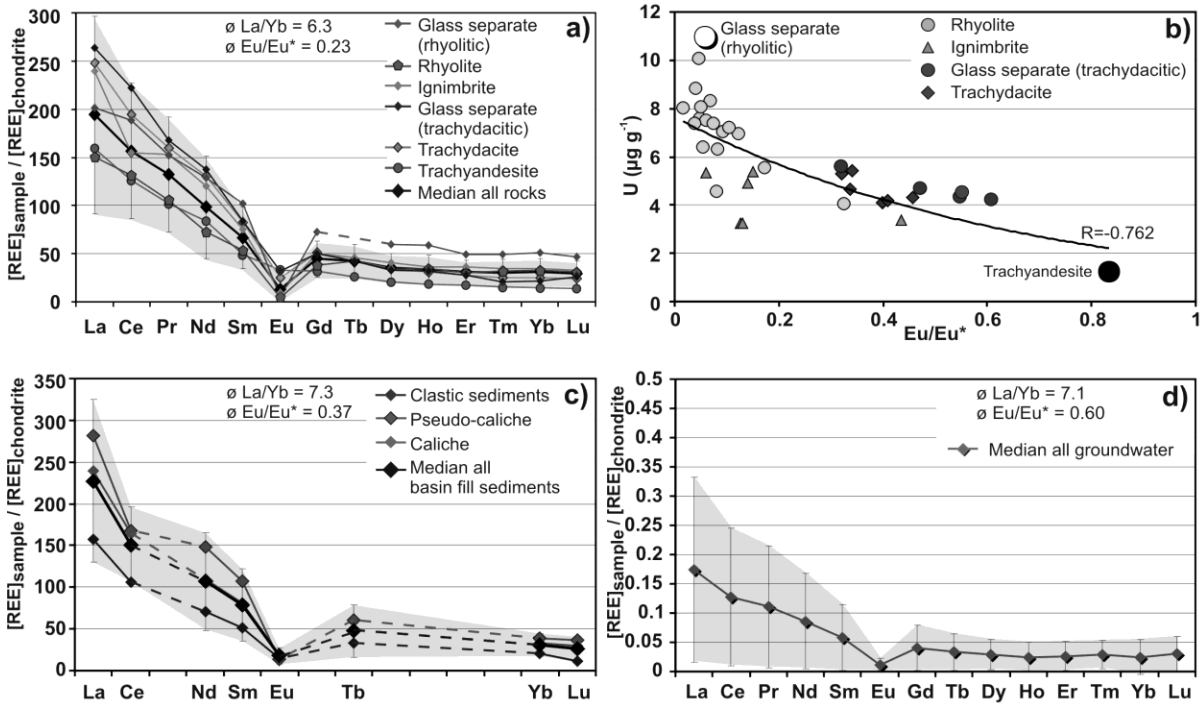


Fig. 10. Rare earth element (REE) plots normalized to C1 chondrite data (after Evensen et al. 1978) and some REE proxies for volcanic rocks **(a)**, basin filling sediments **(c)** and groundwater **(d)**, greyish zones indicating standard deviation from median compartment values, and plot of U vs. intensity of Eu anomaly (Eu/Eu*) for volcanic rocks **(b)**.

Several features can be identified in the chondrite-normalized REE pattern of the volcanic rocks (Fig. 10a): light rare earth elements (LREE) are enriched compared to the heavy ones (HREE), expressed by an average La/Yb ratio of 6.3. A distinct negative Eu anomaly is developed in all volcanic units except for the trachyandesite. There is a significant negative correlation (R=-0.762) between U concentrations and depths of the Eu anomaly (Eu/Eu*) for the volcanic rocks (Fig. 10b) with end members being trachyandesite and rhyolitic glass, clearly expressing once more that most differentiated rocks have the highest potential for U enrichment. The same trend is observable, slightly less distinct (R=-0.583), for As. In highly evolved acid magmas, feldspar fractionation removed large amounts of Eu^{2+}, leaving the remaining melt Eu-depleted but enriched in incompatible elements like U and As. Highest accumulation levels are then reached in most differentiated magmas and especially their latest cooling products, represented in this study by the rhyolitic glass.

Both basin filling sediments (Fig. 10c) and groundwater share the most striking features of the volcanic rocks´ REE pattern – LREE > HREE with comparable La/Yb ratios and a clear, even though less steep) negative Eu anomaly (Eu/Eu* may be overestimated for the sediments as Gd data is not available and the parameter was calculated on the basis of Sm and Tb). These patterns must have been inherited from the source rocks as in systems <200°C, especially oxidizing ones, Eu anomalies cannot

be generated (Bau and Möller 1992). Consequently, hydrogeochemistry of sediments and groundwater in the studied basin is dominated by supply from, and interaction with, the acid volcanic rocks.

3.5. Comparison with a recent study in a similar environment

In the study from Argentina (Nicolli et al. 2010), median U concentrations are lower than in the Villa de Reyes Graben and quantitatively clearly below the WHO guideline (at least in the deep aquifer best comparable to the studied Mexican aquifer). In contrast, As is >10 µg L^{-1} in 100 % of the groundwater samples from the Salí River Basin studied by Nicolli et al. (2010), resulting in high As/U ratios of above 20 on average. Besides fluoride, being a water quality problem in both study areas discussed here, elevated Cr concentrations (100 % of the samples above the WHO guideline value of 50 µg L^{-1}) are obvious in Salí River Basin groundwaters studied by Nicolli et al. (2010), while low concentrations prevail in San Luis Potosí. This observation is in accordance with comparably much higher Cr contents in basin loess sediments in the Argentinian case study (cf. Table 3), potentially representing a Cr source. The following paragraph attempts to explain some of the observed hydrogeochemical differences between the deep artesian aquifer in the Salí River Basin/Argentina and the deep aquifer in the Villa de Reyes Graben/Mexico.

The Argentinian deep groundwaters contain significantly higher concentrations of dissolved Fe and Mn, compared to the studied Mexican aquifer, both being elevated by ~factor 9 (Table 4). Apart from the aforementioned much more abundant Cr (factor 200!), also V shows concentrations elevated by ~factor 15, while SiO_2 contents are substantially higher in the Mexican case. Together with the distribution of As and U and the geochemical data from both study areas, these observations lead to the following interpretation of the different hydrogeochemical signatures: inheritance of As/U ratios in groundwaters from rocks as well as high dissolved SiO_2 and low Fe and Mn argue for volcanic glass dissolution as dominant trace element mobilization mechanism in the Mexican case, compared to desorption from metal hydr(oxides) in basin filling sediments. Nevertheless, the latter water-sediment-interaction (desorption) acts as modifier of the superior hydrogeochemical fingerprint derived from water-rock-interaction (glass dissolution). In contrast, As abundance in the Argentinian deep groundwater is clearly favoured over U (ratios >20) while rhyolitic glasses separated from basin sediments show As/U ratios <1. Direct inheritance of groundwater As/U signatures from volcanic rocks is therefore unlikely. Loess basin sediments as whole rock samples, on the other hand, clearly exhibit As/U>1 (Tables 2-4), documenting preferential secondary accumulation of As over U, most likely in metal (hydr)oxides. Together with higher Fe and Mn and lower SiO_2 in groundwater, these findings argue for trace element (and here mainly As) desorption from secondary metal (hydr)oxides under high pH to be the dominating mobility control and thus support the genetic model of Nicolli et al. (2010). Additional evidence is provided by comparison of oxyanion forming elements (besides As): high Cr and V contents are found in loess sediments and groundwater, and not in the rocks, a distribution not observed in the study at hand. These hydrochemically similar elements are likely to

share source and mobilization mechanism with As. In the shallower aquifers in both areas, growing influence of evaporation effects lead to further enrichment of trace elements. Elevated fluoride concentrations in groundwater, being comparably high in both regions, may contribute to enhanced As release from the primary sources by anion exchange processes or fluoride complexing (Casentini et al. 2010).

The described differences in trace element mobilization modes (glass dissolution vs. desorption from metal oxides) may partly be explained by the configurations of the aquifers themselves: the deep aquifer in the Villa de Reyes Graben/Mexico includes the uppermost part of the fractured volcanic rocks with the glassy matrix accounting for 80-85 vol.% of the whole rocks in addition the volcanic glass shards present in the basin filling sediments. Access to rhyolitic glass in the quaternary deep aquifer of the Salí River Basin/Argentina is limited to its proportion in the sediments (25-50 %, Nicolli et al. 2010). Moreover, differences in T and pH between the two aquifers may contribute to the observed diversities: median groundwater pH in the Argentinian case is 8.1 (7.5 in the aquifer studied here), while groundwater T is higher in the Mexican case (30-40°C compared to a median of 23.6°C in the Salí River Basin). More alkaline pH contributes significantly to enhanced desorption of As from metal (hydr)oxides (e.g. Smedley and Kinniburgh 2002) while the removal rate of trace elements and Si during volcanic glass dissolution is more sensitive to temperature than to solution pH (Zielinski 1981).

4. Conclusions

Elevated concentrations of U and As, partly exceeding WHO guideline values for drinking water, were identified in deep groundwater of the volcano-sedimentary Villa de Reyes Graben around the city of San Luis Potosí/semiarid north-central Mexico. Hydrogeochemical characterization of the trace element reservoirs volcanic rocks – basin filling sediments – groundwater allowed for the derivation of the As and U sources and sinks structure. The chemical signatures of sediments and groundwater are largely dominated by interaction with acid volcanic glass representing the primary trace element source in the study area. The glass is shown to be enriched in incompatible trace elements during magmatic differentiation, its congruent dissolution is the principal mechanism of As and U release into groundwater, modified by additional input from basin fill sediments. The latter exhibit preferential As over U mobilization potential during meteoric decarbonatization of playa lake sediments and desorption from Fe-(hydr)oxide coated clastic sediments. The hydrochemical fingerprint of volcanic glass dissolution, widely controlling the As/U signature in groundwater, is thus slightly shifted towards the As side.

The study illustrates the common destiny of U and As during magmatic processes and the successive dissociation in hydrogeochemical behaviour when crossing the interface between magmatic and sedimentary environments. The trace element situation in the study area shows similarities with known high-As regions under comparable climatic and geological conditions. Nevertheless, also important differences in the evolution of present day As and U distributions were observed. Therefore,

this study contributes to the understanding of natural trace element dynamics in semiarid volcano-sedimentary regions where groundwater often represents the only drinking water resource. Its anthropogenically as well as geogenically influenced quality is a major concern to a large and continuously growing population worldwide.

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