

Geochemical processes controlling silica concentrations in groundwaters of the Salado River drainage basin, Argentina

P. Miretzky^a, V. Conzonno^b, A. Fernández Cirelli^{b,*}

^a*Departamento de Geología, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires, Argentina*

^b*Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires, Argentina*

Received 24 July 2001

Abstract

Chemical analyses of dissolved silica in the shallow groundwater of the lower part of the Salado River drainage basin indicate that silica values averaged 60 ppm. The groundwaters are oversaturated in relation to quartz, Na-plagioclase, K-feldspar, and the weathering of quartz and aluminosilicates appear to have little control on silica concentrations in solution. Groundwater is undersaturated with respect to amorphous silica present in the loessic sediments, and these sediments are specially important in the control of the groundwater composition. The sources of amorphous silica are volcanic glass shards and biogenic silica derived from plant (silicophytoliths, diatom frustules) or animal remains (sponge spicules) also present in the Pampean loess. Silicophytoliths and diatoms have also been reported in A soil horizon samples. The dissolution of amorphous silica most likely controls the high dissolved silica concentrations in groundwater. © 2001 Elsevier Science Ltd All rights reserved.

Keywords: Groundwater dissolved silica concentration; Weathering of silicate minerals; Silica solubility; Salado River drainage basin

1. Introduction

The study region is located between 35° 30′–35° 56′S and 57° 45′–58° 15′W in the lower part of the Salado River drainage basin, which is located in the Pampa Deprimida geomorphologic unit (Fig. 1).

Pampa Deprimida has a wet climate and a mean temperature between 13 and 16°C. The mean annual precipitation is between 850 and 950 mm. Although precipitation is higher in the summer, the precipitation–evaporation balance is negative in this season. The region is characterised by a very mild slope

(0.3%) and extremely low morphological potential that makes the runoff difficult during flooding periods (Kovacs, 1983).

From the geological point of view, the Salado basin is a sedimentary basin where Cretaceous, Tertiary (Lower and Upper), Plio-Pleistocene and Pleistocene (Middle and Upper) sediments are superimposed over the Precambrian crystalline basement. The geological characters are those of great plain areas with low topographic slope: little tectonic deformation, predominance of fine-grained sediments over coarse-grained ones, and continuity and areal extension of the geological units (Auge, 1983).

The Pampean sediments or Pampean loess (Middle and Upper Pleistocene) are of special importance in the chemical composition of the groundwater.

* Corresponding author. Tel.: +54-11-4511-8142; fax: +54-11-4511-8105.

E-mail address: afc@rec.uba.ar (A. Fernández Cirelli).

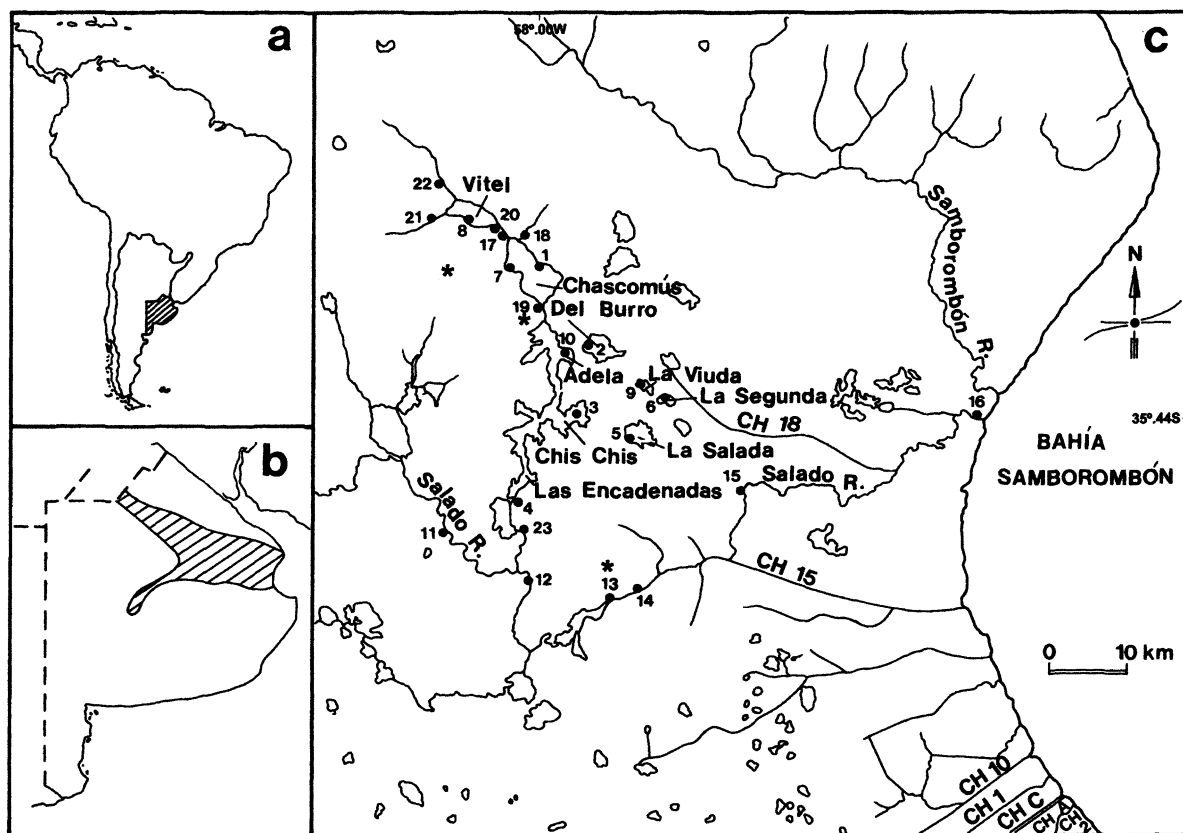


Fig. 1. (a) South America, Argentina, Buenos Aires Province; (b) Buenos Aires Province and Salado River drainage basin; (c) groundwater samples from wells (P1–P33) in the lower (1) Salado River drainage basin (CH: channel) * loess samples.

Pampean loess is of volcanic pyroclastic origin and has been transported by winds to the actual place of deposition. Fluvial and paludal Holocene deposits cover the loessic sequences or intermingle with them. Argentine loess is similar in field appearance and texture to the North American and European loess. However, the mineralogical composition is completely different, especially in the coarse fraction where an assemblage of volcanic minerals is predominant. Imbellone and Teruggi (1993) indicate that the volcanoclastic ancestry of Pampean loess is reflected in its sand size mineralogy: abundant medium to basic plagioclase grains, scarce quartz and K-feldspars, abundant lithoclasts of volcanic rocks (andesites, basalts, lacites) and frequent glass shards usually unaltered or etched by dissolution. Heavy minerals are mainly ortho- and clinopyroxenes, amphiboles

and titaniferous magnetite. A small proportion of opal particles, derived from plant (phytoliths, diatom frustules) or animal remains (sponge spicules), is normally present. The clay minerals are mainly illitic and montmorillonitic with kaolinite as a subordinate constituent. The Pampean loess composition also reveals 2–4% of calcium carbonate as calcite. The Pampean loessic sequences show small variations in texture composed predominantly of a silty clay loams or a silty loams, either primary or reworked.

In previous reports, we have characterised the shallow groundwater of this drainage basin. Sodium (meq/l) accounts for 70.5% and calcium for 11.9% among the cations, and bicarbonate for 62.0% among the anions (Miretzky et al., 1998). The local groundwater drainage supplies the base discharge of surface waters and maintains the perennial discharge of

stream beds (Sala, 1975). As groundwater is one of the sources of surface water, it is necessary to study the geochemical processes that affect the groundwater chemistry in order to achieve better understanding of surface water chemistry. The processes that seem to be responsible for groundwater hydrochemistry are: cation exchange process in the loessic sediments of the basin where calcium is replaced by sodium, the dissolution of ancient marine sediments from Platense and Querandinense Holocene marine incursions (Frenguelli, 1957) and aluminosilicate weathering.

The differences observed between surface water and shallow groundwater composition with respect to an enrichment in sodium in the former may be attributable to the evaporation–precipitation process promoting calcite precipitation (Miretzky et al., 2000).

The shallow groundwater in the Pampean aquifer is characterised by high concentrations of dissolved silica, which are nearly constant and average 60.2 ppm. In contrast, the dissolved silica concentration in streams is about 10 ppm and in ponds less than 5 ppm. The aluminium concentration is less than the detection limit of 0.050 ppm in all samples. There are no previous studies on the groundwater content of dissolved silica in the region and the high values found, raise questions about its possible origin. Similar contents (ca SiO₂ 50–70 ppm) from the same aquifer but to the southeast of the Buenos Aires Province have also been reported (Martínez and Osterrieth, 1999).

The aim of the present paper is the study of the geochemical processes responsible for high SiO₂ concentrations in groundwater in the region.

2. Materials and methods

Water samples from stations shown in Fig. 1 of the shallow groundwater of the lower Salado River drainage basin and of local rainwater were collected during February (summer) 1998. Groundwater samples were taken from wells used by rural population for human consumption by means of molinos and pumps sapo (average depths 7–15 m estimated according to construction characteristics). The samples were filtered using 0.45 micron acetate

cellulose membrane (Micro Separations Inc., MSI), and were stored in polyethylene bottles.

Temperature and pH were determined in the field by means of a portable pH meter (Hanna HI 9025). Major ions were determined by conventional methods: carbonates and bicarbonates by acid titration, chloride by AgNO₃ titration, sulphate by precipitation titration with BaCl₂ using sodium rodizonate as an indicator in water–acetone medium; Na and K were determined by atomic spectrophotometric emission and Ca and Mg by atomic spectrophotometric absorption (Varian Techtron Model AA275). Silica was determined by spectrophotometric analysis (APHA 4500–E, 1993) using 1-amino-2 naphthol-4 sulfonic acid as a reducer at $\lambda = 815$ nm (1 cm path length Jasco 7850 spectrophotometer) and aluminium by atomic absorption spectrophotometry AAS-AET (Shimadzu 6801 with autosampler).

Determinations were performed in duplicate with a relative error <1.0% for all the elements analysed. The accuracy of the analysis for major ions was estimated from the electroneutrality condition (Appello, 1997) and ranged between –0.3 and 7.0% and mean value 1.30%. Total dissolved solids (TDS) were calculated as the sum of the above ion concentrations.

Saturation indexes were calculated using the computer program WATEQF (Plummer et al., 1978). Mass balances were performed by means of the computer program NETPATH (Plummer et al., 1994)

Three loess samples (Fig. 1) were taken from a *calicata* (1-m³ well in the soil) having in consideration the Chascomús Soil Map 3557-5 (INTA, 1982) and analyzed by optical microscopy and by X-ray diffraction. Once the loess samples were attacked (alkaline fusion for SiO₂ and Al₂O₃ determination and HF–H₂SO₄ attack for the other elements), the chemical percent composition of the loess was determined (Shapiro, 1975). Na₂O, K₂O, CaO, MgO and SiO₂ were determined in a similar way to water samples. Al₂O₃, Fe₂O₃, TiO₂, P₂O₅ and MnO₂ by spectrophotometric determination (1 cm path length Jasco 7850 spectrophotometer) after complexation with alizarin S ($\lambda = 475$ nm), o-phenantroline ($\lambda = 560$ nm), tiron ($\lambda = 420$ nm), respectively, P₂O₅ by the blue phosphomolybdate complex after reduction with ascorbic acid ($\lambda = 815$ nm) and MnO₂ by oxidation to MnO₄[–] with KIO₄ ($\lambda = 525$ nm). H₂O[–]

was determined at 105°C and H_2O^+ at 1200°C (Shapiro, 1975). CO_2 was determined by volumetric titration. Determinations were performed in duplicate being the relative error <1.0% for the total loess samples analyses.

3. Results and discussion

The groundwater chemical composition at the sample stations shown in Fig. 1 is given in Table 1. Average concentrations are Na^+ : 13.9 meq/l (318.8 ppm), K^+ : 0.6 meq/l (24.6 ppm), Ca^{2+} : 2.2 meq/l (44.3 ppm), Mg^{2+} : 2.6 meq/l (31.8 ppm), Cl^- : 5.4 meq/l (190.7 ppm), SO_4^{2-} : 11.8 meq/l (85.2 ppm), HCO_3^- : 11.5 meq/l (700.3 ppm); 37.9% of the groundwater samples are alkaline (>50% meq/l $\text{Na}^+ + \text{K}^+$), 55.2% strongly alkaline (>75% meq/l $\text{Na}^+ + \text{K}^+$), 37.9% bicarbonated (>50% meq/l HCO_3^-) and 41.4% strongly bicarbonated (>75% meq/l HCO_3^-).

The groundwaters dissolved silica concentration range from 19.6 to 72.9 ppm (average concentration 62.2 ppm) (Table 1). Of the samples, 79.3% possess a silica content of 60–70 ppm SiO_2 .

A knowledge of the evolution of the chemical composition from rainwater to groundwater in the study region is required to explain the high SiO_2 values present in the latter. Reactions in the edaphic zone involve the dissolution and redistribution of CO_2 (g) due to root and microbial respiration and to a lesser extent to oxidation of organic matter, 4–6% in these soils (INTA, 1982). As a consequence, soil CO_2 partial pressures are larger than the atmospheric value. One direct result of dissolving CO_2 in water is a rapid increase in the carbonic acid content and a decrease in the pH promoting dissolution of carbonates and aluminosilicates. Also, groundwater is able to dissolve halite bearing sediments originated in Holocene marine intrusions (Querandino), which contribute to high salinity values and to sodium and chloride equivalent amounts. Weathering reactions will also take place in the sandy and clay fractions of pampean loess percolated by groundwater.

Table 2 shows the chemical composition of pampean loess in the study area. Taking in consideration % Na_2O , % K_2O and % SiO_2 values, pampean loess presents a dacitic chemical composition.

In the sandy fraction, the acid mesosilicic volcanic lithic fragments constitute 39% of the felsic suite, the volcanic glass 22%, plagioclases 25%, quartz 7% and potassium feldspar 7%. The heavy components constitute a mafic suite and represent only 0.4% of the sand fraction, the principal components being: amphiboles (hornblende) 25%, pyroxene (hypersthene and augite) 33%, opaque minerals (magnetite, hematite, ilmenite) 29%, basic lithic volcanic fragments (andesites and basalts) 4%, epidote, 6% and zircon, rutile and mica 3%. An X-ray study of the clay fraction reveals a montmorillonite content of 30%, illite 50%, interlayer illite smectite 10%, chlorite 5% and kaolinite 5%. The pampean loess composition also possesses 8% of calcium carbonate as calcite (Teruggi, 1957) and gypsum as concretions (Frenguelli, 1955).

The main potential sources of dissolved silica in the groundwater waters are the weathering of quartz, amorphous silica and aluminosilicate minerals. Quartz (7% in the sandy fraction) has little control on silica concentrations in solution, due to the slow reaction kinetics (Lasaga, 1984). Quartz is soluble at high temperature and pH above 9.5, undissociated orthosilicic acid being the major species present below this pH. The solubility of quartz is only 5% that of amorphous silica at room temperature, but it rises much rapidly with temperature than does opal solubility (Siever, 1962).

The weathering of an aluminosilicate mineral is a slow and complicated hydrolysis reaction, in which the overall effect is the solubilization of cations and part of the silica and an increase in the pH. The aluminium and the remaining silica stay as a clay mineral. The formation of secondary products is due to the insolubility of Al compounds. Increasing intensities of leaching are associated with the removal of increasing amounts of silica and cations: moreover, the type of weathering products depends on the hydrological conditions as well as on the rate of mineral weathering, kaolinite being favoured by acid solutions and good drainage, montmorillonite by alkaline solutions containing Ca^{2+} , Mg^{2+} , and Fe^{2+} , and illite by abundant K^+ (Krauskopf, 1979).

The high silica content in the shallow groundwater of the region under study indicates active degradation of silicate minerals. Volcanic rocks present in pampean loess are more reactive than granitic ones.

Table 1
Shallow groundwater chemical composition in the region under study

S	Temperature (°C)	pH	SiO ₂ (ppm)	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	Cl (ppm)	SO ₄ (ppm)	CO ₃ (ppm)	HCO ₃ (ppm)	TDS (ppm)
P2	17.7	7.85	70.5	249.0	30.0	84.0	48.0	195.0	58.0	0.0	751.0	1485.5
P4	17.9	7.56	60.7	439.0	63.4	89.1	69.7	399.0	228.0	0.0	851.2	2200.1
P5	21.0	8.04	60.3	424.0	26.6	73.8	66.3	455.0	114.5	13.0	643.9	1877.4
P7	19.2	6.95	63.1	625.0	30.0	117.9	68.0	653.5	345.6	0.0	804.9	2708.0
P8	21.6	7.34	19.6	260.0	25.0	58.0	26.0	129.0	57.0	0.0	748.0	1322.6
P9	19.3	6.85	65.4	487.6	19.2	24.0	34.0	325.1	211.3	0.0	671.0	1837.6
P10	22.7	7.23	72.9	399.0	18.0	9.0	34.0	214.0	38.0	0.0	702.0	1486.9
P11	20.2	7.15	63.1	105.6	19.9	58.0	31.0	56.0	19.2	0.0	492.3	845.1
P12	22.3	7.99	68.6	343.0	12.0	7.0	6.0	102.0	38.4	0.0	713.7	1290.7
P13	21.4	7.85	63.1	263.3	12.0	6.0	17.0	56.0	67.0	0.0	617.1	1102.6
P14	19.5	7.26	68.2	234.6	25.0	18.0	38.0	56.7	38.4	0.0	640.5	1119.4
P15	22.0	7.85	61.1	216.2	12.9	15.0	10.0	37.2	57.6	0.0	536.8	946.8
P16	24.2	7.64	67.0	220.0	17.0	14.0	14.0	46.0	19.0	0.0	590.0	987.0
P17	18.8	6.63	63.5	281.1	43.0	136.9	73.0	613.3	57.6	0.0	429.4	1697.8
P18	19.0	9.10	63.5	357.0	27.0	22.0	32.0	204.0	77.0	106.0	563.4	1451.9
P19	20.4	8.18	53.7	224.0	16.0	18.0	14.0	55.7	57.6	13.2	563.4	1015.6
P20	17.7	7.56	63.1	512.0	16.0	14.0	15.0	120.7	182.4	0.0	1126.9	2050.1
P21	17.5	7.15	63.1	392.0	21.0	49.0	34.0	120.7	124.8	0.0	1046.4	1851.0
P22	18.1	8.13	63.1	386.0	10.0	11.0	10.0	92.9	76.8	5.3	847.8	1502.9
P23	18.0	7.89	63.1	158.0	28.0	54.0	36.0	65.0	48.0	0.0	617.1	1069.2
P24	21.5	8.07	68.2	96.0	50.0	99.0	58.0	92.9	57.6	0.0	670.8	1192.5
P25	21.6	8.89	64.9	214.0	23.0	32.0	18.0	37.1	57.6	39.6	563.4	1049.6
P26	22.8	8.40	61.1	264.0	25.0	40.0	29.0	92.9	76.8	5.3	713.7	1307.8
P28	18.4	7.02	63.3	350.0	33.0	101.0	48.0	538.5	38.4	0.0	536.6	1708.8
P29	21.9	8.20	49.1	228.0	22.0	49.0	22.0	92.9	38.4	5.3	660.0	1166.7
P30	18.2	7.88	63.3	409.0	24.2	9.9	11.3	141.4	48.0	0.0	939.3	1646.4
P31	17.7	6.98	67.8	409.0	24.0	31.9	28.4	251.5	96.0	0.0	750.0	1658.6
P32	15.8	7.43	72.2	416.0	12.0	13.3	11.8	147.6	95.2	0.0	850.2	1618.3
P33	18.4	7.89	58.5	283.0	27.0	31.0	19.0	139.3	48.0	0.0	667.9	1273.7

Table 2
Pampean loess chemical composition of three samples in the region under study (Fig. 1)

S	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	TiO ₂ (%)	MnO (%)	P ₂ O ₅ (%)	MgO (%)	CaO (%)	Na ₂ O (%)	K ₂ O (%)	H ₂ O ⁺ (%)	H ₂ O ⁻ (%)	CO ₂
CH2	60.91	14.51	6.00	0.60	0.05	0.20	1.34	2.95	2.83	2.28	2.72	2.28	3.05
UD2	63.36	14.15	5.99	0.59	0.06	0.20	1.35	2.56	2.88	2.55	1.90	3.22	2.04
Abb	60.49	12.83	6.95	0.69	0.11	0.10	1.64	2.34	2.70	2.15	2.26	4.51	2.40

Excess sodium not balanced with equivalent amounts of chloride, as might be expected by dissolution of halite marine sediments, is derived from weathering of Na-feldspar such as albite or any member of the plagioclase solid solution series between albite and anorthite (Ca-feldspar). Plagioclase weathering releases Ca, although also weathering of amphiboles and pyroxenes may contribute to the Ca concentration.

Nevertheless, Miretzky et al. (2000) showed the importance of cationic exchange processes between clay adsorbed Na⁺ and Ca²⁺ in solution taking place in the Pampean loess sediments in the chemical composition of groundwater and also the role of the halite (due to Holocene marine intrusions) dissolution. Therefore, Ca²⁺ and Na⁺ concentration can not be used as simple indicators of plagioclase weathering. Moreover, excess Na⁺ from cationic exchange will reduce the amount of plagioclase dissolution.

Mg, which accounts for 13.2% meq/l of the cationic groundwater composition may be derived from mafic minerals and from Holocene marine sediments. As mafic minerals make up only 0.4% of the loess sand fraction, it is possible that magnesium is released faster in the dissolution process than are calcium and sodium from the plagioclases (Siegel and Pfankuch, 1984). As a consequence of the aluminosilicate weathering, groundwater will show an increase in alkalinity, cation and silica concentration.

The presence of montmorillonite and illite as mineral products in the basin under study is explained by their preferential crystallization in relatively dry climates, with rainfall <2000 mm/year and, therefore, relatively longer residence times of water in the soil, so that the concentration of dissolved ions are relatively high (Berner, 1971). Montmorillonite and illite formation is favoured when rapidly dissolving material such as volcanic rock is available, mainly from Pampean loess sediments in the present area (Appelo and Postma, 1993).

The stability of the weatherable minerals like quartz, plagioclases, K-feldspars, amorphous silica, montmorillonite and illite in the groundwater system can be evaluated by calculating the saturation state of the groundwater for a given mineral. The saturation indices (SI) have been calculated using the WATEQ program. As is shown in Fig. 2, subsaturation is observed for anorthite and amorphous silica, while

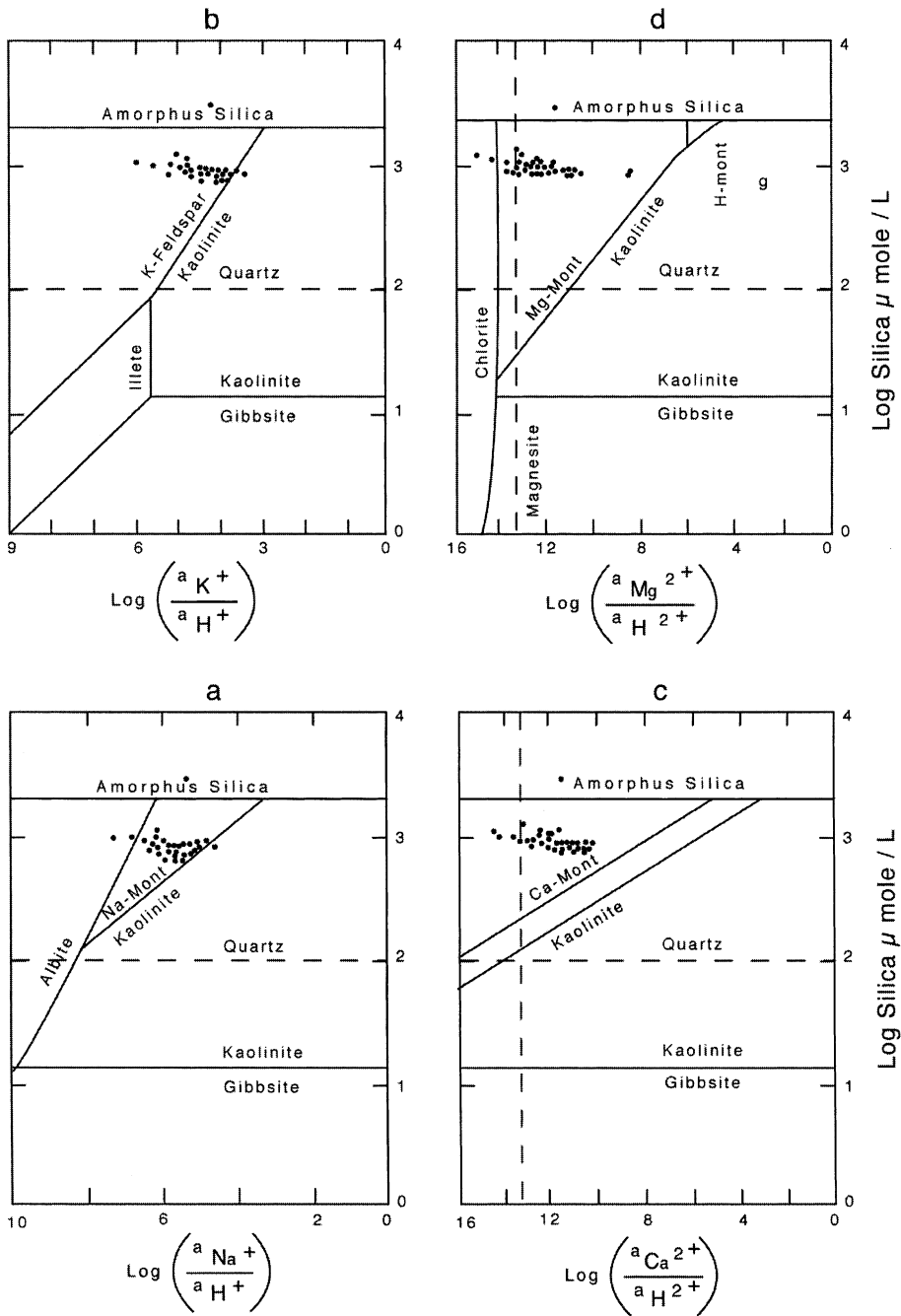


Fig. 2. Saturation indices (SI) vs TDS (g/l).

oversaturation is observed for albite, quartz, K-feldspar and also for illite, montmorillonite, and kaolinite (present in pampean loess clay fraction). It seems probable that one or more of these aluminosilicates controls aqueous aluminium and silica concentrations. Moreover, dissolution of amorphous silica and anorthite is expected to take place.

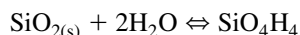
It is well-known that reactions in nature may not achieve equilibrium but run to exhaustion if one of the products escapes from the system, for example when ions are removed by the movement of the water in which the reaction is taking place (movement of groundwater in response to hydraulic gradient). Aluminosilicate weathering reactions remove H^+ from the solution and increase the pH. If the supply of H^+ is large and if the soluble products are removed, the reaction can run to completion. Another fact that must be taken into account is the water/rock ratio. Reactions taking place in large bodies of water and in aquifers with high percolation rates having large water/rock ratios are more likely to run to completion than to achieve equilibrium, whereas reactions in a small volume of pore water may achieve a localised state of equilibrium between ions and solids.

Stability field diagrams, which assume that aluminium is conserved in the minerals of the system, were used to evaluate the saturation of water with respect to aluminosilicates. The slopes of the phase boundaries shown on the diagrams are fixed by the stoichiometry of the reactions. The intercepts of the boundaries, however, depend on the free energies of formation of the mineral and aqueous species involved in the reactions between mineral and water. Because the reported free-energy values of a given species differ, especially for weathering products such as clays, the theoretical position of the boundaries can vary depending on the sources used.

Fig. 3(a)–(d) show that Na-montmorillonite, K-feldspar, Ca-montmorillonite and Mg-montmorillonite are the stable phases and that the groundwater is oversaturated in relation to quartz and subsaturated in relation to amorphous silica. The different results in the albite stability obtained comparing Figs. 2 and 3(a) are probably due to the fact that the aluminium concentration must be far below the detection limit, and as a consequence the ionic product is overestimated. It must be noticed that in Fig. 3(b)

montmorillonite could not be realistically shown on the diagram, because its stability depends on other variables, particularly the concentrations of Na^+ and Mg^{2+} .

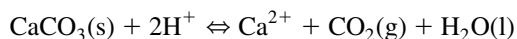
The SiO_2 (quartz and amorphous silica) solubility is described by the reaction



Assuming that SiO_4H_4 remains predominantly undissociated at pH values below 9.5, and the solubility of $SiO_{2(s)}$ phases for $pH < 9.5$ is given by the solubility product $K = [SiO_4H_4]$. For quartz, $K = 10^{-4}$ and for amorphous silica $K = 10^{-2.74}$ and $K = 10^{-2.69}$ according to different authors at 25°C (Alexander et al., 1954; Greenberg and Price, 1954; Siever, 1962). Lines indicating the solubility of both quartz and amorphous silica are shown in Fig. 3(a)–(d).

Although thermodynamically it is possible to reach a 6 ppm dissolved silica concentration in a solution in equilibrium with quartz, the latter has extremely slow reaction kinetics and, therefore, rarely appears to control dissolved silica concentration (Lasaga, 1984). As in other cases where the most stable mineral reacts very slowly, a range of less stable forms of $SiO_{2(s)}$ exists which may control the dissolved concentration (e.g. amorphous $SiO_{2(s)}$ or opal, chalcedony, cristobalite). The most soluble is amorphous silica, which places the upper constraint on dissolved silica concentrations at 122.5–109.2 ppm.

In addition, the activity of Ca^{2+} in aqueous solutions reacting with anorthite is limited by the solubility of calcite, which depends on the fugacity of CO_2 and the pH according to the reaction



$$K = 10^{-9.85}$$

If $(CO_2) = 3 \times 10^{-4}$ atm, then $\log(Ca^{2+}) - 2 \log(H^+) = 13.38$ and this line is shown in Fig. 3(c). Groundwaters are in equilibrium in relation to calcite (55.2% of the samples) and oversaturated (37.9% of the samples) preventing a further dissolution. As a result, anorthite cannot be stable in contact with water and, therefore, dissolves incongruently to form gibbsite or kaolinite, depending on the silica concentration in the solution.

The activity diagrams of K-feldspar [Fig. 3(b)] and

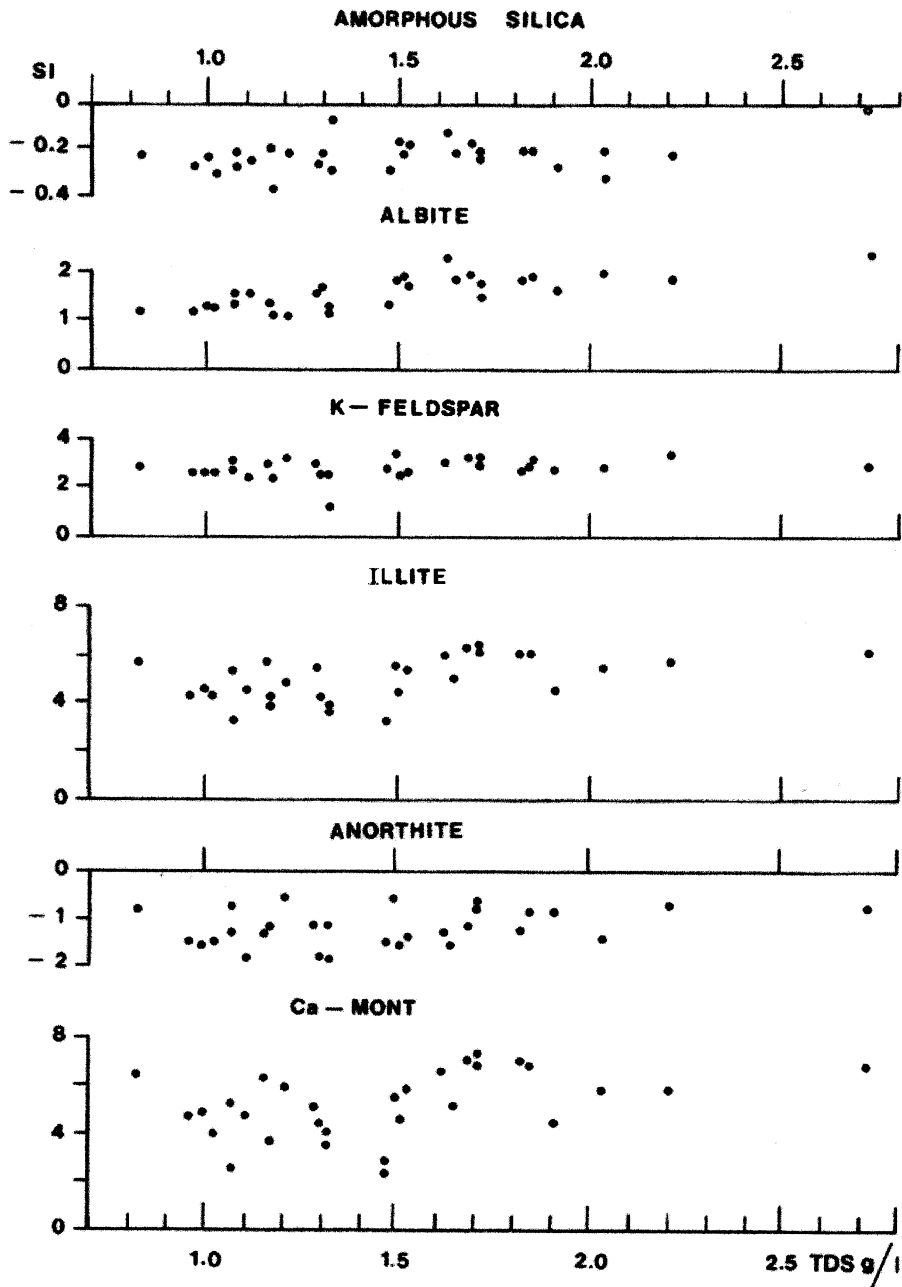


Fig. 3. Stability diagrams (Von Damm and Edmond, 1984) (a) Na-montmorillonite; (b) K-feldspar; (c) Ca-montmorillonite; (d) Mg-montmorillonite.

Table 3
Chemical composition of local rainwater (initial) and groundwater (final)

Constains	Final well (mM)	Initial well (mM)
C	15.358	0.020
S	1.023	0.006
Ca	0.780	0.005
Al	0.002	0.000
Mg	1.145	0.196
Na	17.439	0.082
K	0.602	0.006
Cl	7.261	0.113
Si	1.130	0.020

albite [Fig. 3(a)] do not contain solubility limits other than that of the amorphous silica and quartz, because the carbonates of alkali metals are soluble. Consequently the K^+/H^+ and Na^+/H^+ ratios of natural solutions can rise until the solutions are in equilibrium with K-feldspars and albite, respectively. Hence, these minerals may be stable in contact with water and, therefore, the weathering process is slower than the one for anorthite and Ca-bearing plagioclase. Therefore, certain minerals such as anorthite do not form as authigenic minerals at earth surface temperatures.

The differences in susceptibility to weathering among Mg-bearing silicates (olivine, pyroxene, amphibole) is restricted by the solubility limits imposed by magnesite, serpentine and sepiolite. Therefore, natural waters cannot be in equilibrium with olivines, pyroxenes and amphiboles. Olivine is more susceptible to weathering than pyroxene, which is more susceptible than amphibole, as implied also by Bowen's reaction series (Goldich, 1938; Berner, 1971).

As a consequence, Ca^{2+} , Mg^{2+} and SiO_2 concentrations in natural waters are restricted by the solubility limits of amorphous silica, calcite and magnesite. Groundwaters are in equilibrium in relation to the latter (69.0% of the samples) and oversaturated (20.7% of the samples).

It is interesting to note the presence of highly altered silicophytoliths (amorphous silica present in plant tissues taking the shape of the cells which it fills) in the A horizon of soils and paleosols of the region, but not in the B horizon (Osterrieth and Martinez, 1993) suggesting that they are dissolved by the pedogenetic processes and as a consequence, groundwater becomes enriched in dissolved silica.

Table 4
ETPATH mass balance possible models

Phase	Reaction	Model 1 (mM)	Model 2 (mM)
Exchange	Ca/Na	6.272	6.272
Calcite	Dissolution	6.031	6.03
Gypsum	Dissolution	1.017	1.017
Halite	Dissolution	4.812	4.898
Organic matter	Redox	9.308	9.308
O ₂ gas	Redox	9.42	9.421
K-feldspar	Dissolution	0.596	0.596
Amorph. SiO ₂	Dissolution	0.258	0.258
Mg-montomor.	Precipitation	- 0.255	- 0.255
MgCl ₂	Dissolution	1.168	1.126

This source of amorphous dissolved silica adds to the silica derived from volcanic glass shards and from opal particles, and to that derived from plant (silicophytoliths, diatom frustules) or animal remains (sponge spicules) normally present in the local loessic sediments. The presence of silica derived from dissolution of amorphous silica will displace the aluminosilicate weathering equilibrium to the left.

Martinez and Osterrieth (1999) have shown by use of the code PHREEQC (Parkhurst, 1995), that the incongruent dissolution of anorthite produces 0.3 ppm SiO_2 in equilibrium with Ca-montmorillonite. Therefore, the dissolved silica resulting from weathering of aluminosilicates will be even less, and will not account for the high values found in the shallow groundwater.

Dissolution of amorphous silica present in volcanic glass or biogenic silica seems to be responsible of the high values found in the groundwater.

We used the NETPATH computer program to interpret net geochemical mass-balance reactions between an initial and final water along a hydrologic flow path. We considered as initial water the local rainwater, as final water the shallow groundwater compositions and the following constrains: Na, K, Ca, Mg, Al, C, S, Cl and Si (Table 3).

Taking into account the major element geochemistry, pH, saturation indices and aquifer mineralogy, we propose several mineral phases and chemical reactions that may control the groundwater chemistry (Table 4). The following reactions and phases were taken in consideration: dissolution of NaCl and MgCl₂, gypsum, K-feldspar, anorthite, amorphous silica and calcite (because $IS < 0$);

precipitation of illite, montmorillonite (because $IS > 0$), aerobic organic matter oxidation and ionic exchange between Na-clay and Ca-groundwater. Twelve models were found which satisfy our requirements. Two possible models are shown in Table 4. Positive mass transfers calculated by NETPATH indicate that the phase entered the aqueous solution, indicating dissolution (of a phase) or ingassing (of a gas). Negative mass transfers indicate precipitation or outgassing. The ‘exchange’ phase is used to define the exchange of 2Na^+ by 1Ca^{2+} . Positive mass transfers indicate that the exchange takes place and Na^+ is released to the solution.

In the two models considered, dissolved silica concentration is derived from the dissolution of amorphous silica and not from quartz and all the assumptions made previously then remain to be valid. It is important to note the high amounts of oxygen needed for aerobic oxidation of organic matter that could only be obtained in the unsaturated zone were the system is open to atmospheric oxygen.

4. Conclusions

The shallow groundwater of the Salado River drainage basin contains high concentrations of dissolved silica, averaging 60 ppm in samples taken in different stations during the summer of 1998.

The principal process controlling the groundwater silica concentration is the dissolution of silicate minerals. Quartz has little control on silica concentration in solution. The weathering of plagioclases and K-feldspar do not account for the high dissolved silica concentration in groundwater although the groundwater is undersaturated in relation to anorthite. The solution is undersaturated in relation to amorphous silica indicating that silica is not in equilibrium with the solution (SiO_2 equilibrium value: 109.2–122.5 ppm). The sources of amorphous silica are volcanic glass shards present in loess sediments and biogenic silica derived from plant (silicophytoliths, diatom frustules) or animal remains (sponge spicules) also present in Pampean loess and in the A soil horizon.

It is concluded that amorphous silica minerals, from volcanic or biogenic origin, are likely to be

responsible for the high dissolved silica values in groundwater in the study region.

Acknowledgements

We are grateful to the Universidad de Buenos Aires and to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for the financial support for this project. We thank the Departamento de Geología, Universidad de Buenos Aires for the mineralogic analyses and the Centro de Investigaciones en Suelos y Aguas (CISAUA)—Centro de Investigaciones Geológicas (CIG), Universidad Nacional de La Plata for the X-ray analyses. Also, we thank Dr Ofelia Tofalo for helpful discussions on pampean loess compositions.

References

- Alexander, G., Heston, W., Iler, R., 1954. The solubility of amorphous silica in waters. *J. Phys. Chem.* 58, 453.
- Appelo, C., Postma, D., 1993. *Geochemistry, Groundwater and Pollution*. Balkema, Rotterdam, Netherlands pp. 536.
- Berner, R., 1971. *Principles of Chemical Sedimentology*. McGraw-Hill, New York pp. 240.
- Frenquelli, J. 1955. Loess y limos pampeanos. *Revista del Museo de La Plata. Serie técnica y didáctica no. 7*, pp. 88.
- Goldich, S., 1938. A study in rock-weathering. *J. Geol.* 46, 17–58.
- Greenberg, S., Price, E., 1954. The solubility of silica in solutions of electrolytes. *J. Phys. Chem.* 61, 1539.
- Imbellone, P., Teruggi, M., 1993. Paleosols in loess deposits of the Argentine Pampas. *Quaternary International*. 17, 49–55.
- INTA, 1982. Carta de suelos de la República Argentina. Hoja 3557-25. Chascomús.
- Krauskopf, K., 1979. *Introduction to Geochemistry*. 2nd ed McGraw-Hill, New York pp. 617.
- Lasaga, A., 1984. Chemical kinetics of water-rock interactions. *J. Geophys. Res.* 89, 4009–4025.
- Martínez, D., Osterrieth, M., 1999. Geoquímica de la sílice disuelta en el acuífero Pampeano en la vertiente sudoriental de Tandilia. *Hidrología subterránea*. Tineo, A. Serie de Correlación Geológica 13, 241–250.
- Miretzky, P., Herrero, A., Galindo, G., Fernández Cirelli, A., 1998. Caracterización de los recursos hídricos en la zona del sistema de las lagunas Encadenadas de Chascomús, Provincia de Buenos Aires. *Estudios preliminares*. *Rev. Geol. Apl. Ing. y Amb.* 12, 85–100.
- Miretzky, P., Conzonno, V., Fernández Cirelli, A., 2000. Hydrochemistry of pampasic ponds in the lower stream bed of Salado River drainage basin (Argentina). *Environm. Geol.* 39, 951–956.
- Osterrieth, M., Martínez, G., 1993. Paleosols on late Cenozoic

- Loessic Sequences in the Northeastern Side of the Tandilia Range, Buenos Aires, Argentina. *Quaternary International* 17, 57–65.
- Parkhurst, D., 1995. PHREEQC. A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. U.S. Geol. Surv. Water Resources Investigations Report 95-4227, Colorado, USA, pp. 127.
- Plummer, L., Blair, F., Truesdell, A., 1978. WATEQF A computer program for calculating chemical equilibrium of natural waters. US Geol. Surv. Water Resources Investigations Report 76-13. 69 pp. Virginia. USA.
- Plummer, L., Prestemon, E., Parkhurst, D., 1994. An Interactive code NETPATH for modeling net geochemical reactions along a flow path. Version 2.0. U.S. Geol. Surv. Water Resources Investigations Report 94-4169, Virginia, pp. 132.
- Shapiro, L., 1975. Rapid analysis of silicate, carbonate, and phosphate rocks. *Geol. Survey Bull.*, 1401.
- Siegel, D., Pfankuch, H., 1984. Silicate dissolution influence on Filson Creek chemistry, northeastern Minnesota. *Geol. Soc. of American Bulletin* 95, 1446–1453.
- Siever, R., 1962. Silica solubility, 0°–200°C and the diagenesis of siliceous sediments. *J. Geol.* 70, 127.
- Von Damm, K., Edmond, J., 1984. Reverse weathering in the closed-basin lakes of the Ethiopian rift. *Am. J. Sci.* 284, 835–862.