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CURSO: ESPELEOGÉNESIS Y EVOLUCIÓN DE ACUÍFEROS CÁRSICOS

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Hydrogeology and SiO_2 geochemistry of the Aonda Cave System, Auyan-Tepui, Bolivar, Venezuela.

Marco Mecchia, Leonardo Piccini

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Key-words: quarzite, speleogenesi, alterazione chimica, carsismo, quartzite, speleogenesis, chemical weathering, karst, Gran Sabana, Venezuela

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HYDROGEOLOGY AND SiO_2 GEOCHEMISTRY OF THE AONDA CAVE SYSTEM (AUYÁN-TEPUI, BOLÍVAR, VENEZUELA)

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RESUMEN

Hidrogeología y geoquímica del Sistema Sima Aonda, Auyán-tepui, Bolívar, Venezuela.

El Sistema Sima Aonda se localiza en la parte noroccidental del Auyán-tepui y es el complejo de cuevas desarrollado en rocas cuarcíticas mejor conocido del mundo. A pesar de la naturaleza silícea de la roca, el Sistema puede considerarse un sistema kárstico, ya que su origen se debe principalmente a procesos de disolución, donde el agua de escorrentía es drenado principalmente a través de conductos subterráneos. Las peculiares formas superficiales en Auyán-tepui son el resultado de la meteorización química. La importancia de la disolución química de las rocas es enfatizada por las pequeñas formas superficiales, típicas de terrenos kársticos de calizas, como acanaladuras, cubetas, huecos y otros. El Sistema representa la red de drenaje subterráneo de un curso superficial, el Río Superior, capturado en el extremo Este de la Plataforma de Aonda, finalmente resurgiendo en el acantilado exterior del tepui.

En el período investigado el caudal del río subterráneo varió entre 0,2 y 2,5 m^3/s. Con estos pocos datos, podemos asumir que durante la temporada de lluvias, las crecidas probablemente excedan 10-15 m^3/s, mientras que el caudal medio anual puede estar en el orden de 1 m^3/s.

Las muestras de agua analizadas fueron de varios tipos: lluvia, pequeñas pozas, corrientes superficiales y subterráneas, turberas y goteos. El pH, temperatura, conductividad eléctrica (CE) fueron medidos con equipos portátiles y las concentraciones de SiO2 se midieron con una prueba colorimétrica.

El pH del agua de lluvia fue siempre ácido, de 3,8 a 6,5. La CE fue baja (1,3 a 15,9 µS/cm) y SiO_2 no fue detectado. El agua de escorrentía al fluir a través de depósitos de turba se enriquece en materia orgánica derivada de la descomposición de la vegetación; el pH varía de 3,6 a 4,5 con una acidez siempre superior al agua de lluvia; la CE varía de 12 a 29 µS/cm; la concentración de SiO2 es muy variable de 0 a 0,43 mg/l y se deriva totalmente de la disolución de la roca, variando probablemente según el tiempo de contacto agua/roca y el grado de evaporación.

Los datos químicos señalan que el agua que procede de la superficie superior del tepui que fluye de rocas cuarcíticas y con corto tiempo de contacto tienen muy baja concentración de SiO_2. En las cuevas apenas se nota un pequeño incremento, mientras que en el Río Carrao a pié de la montaña su concentración es significativamente mayor ya que circula por rocas ricas en feldespatos.

La concentración de SiO_2 del agua que circula en el Systema Aonda mostró un incremento a medida que aumentaba el caudal durante un evento de inundación (máximo 0,48 mg/l, mínimo 0,17 mg/l). Esto implica que en un evento de este tipo, el agua enriquecida en SiO_2 retenida en los depósitos de turba, depresiones y fracturas, son arrastradas por el agua de lluvia.

El agua de percolación y gotéo subterráneo tiene una concentración de SiO_2 de alrededor de 1 mg/l, pero una sola muestra de agua goteando de una espeleotema de ópalo dio un valor de 7,1 mg/l, siendo la única muestra sobresaturada en sílice.

Estos datos permiten realizar un cálculo aproximado de la cantidad de sílice disuelto en la Plataforma de Aonda. Para ello utilizamos el caudal de la Resurgencia Alí Primera de unos 800 l/s para el 4 de marzo de 1993. La carga de sílice resulta en unos 184 mg/s, que resulta principalmente

del aporte superficial del Río Superior, en el orden de 144 mg/l; mientras que el sílice disuelto en su trayecto en el Sistema Aonda aporta unos 40 mg/l, a su vez compuesto de aproximadamente un 15% de la disolución superficial (turba, pozas, cubetas) y unos 85% de los procesos de disolución subterráneos
Palabras claves: Geomorfología, meteorización, cuarcita, karst, Gran Sabana.

ABSTRACT

The Aonda Cave System is located in the NW of the Auyán-tepui, it is the best known cave complex developed in siliceous rock in the world. Despite the nature of the rock, it can be regarded as a karst form, because its origin is mainly by solution processes. This System represents the underground drainage network of a surface stream captured through a sinkhole in the flat top of the tepui and out-flowing at a resurgence in the peripheral scarp. In the investigated period, the discharge of this underground stream ranged from a minimum of about 200 l/s to a maximum of 2500 l/s, but we can assume that during the rainy season floods the discharge probably exceeds 10-15 m^3/s, while the mean annual discharge should be around 0.5-1 m^3/s.
Temperature, pH, electric conductivity (EC) and SiO_2 concentration of water samples from rain, small ponds, surface or subterranean streams, peat deposits and cave drippings water have been measured. The pH of rainwater is always acid, EC is always very low (<15.9 µS/cm), and silica is absent. The runoff water, flowing trough peat deposit gets enriched with organic matter. The samples show a pH ranging from 3.6 to 4.5, the EC ranges from 12 to 29 µS/cm. Silica concentration ranges from about 0 to 0.43 mg/l.
Chemical data underline the very low concentration of SiO_2 of the surface water. Percolation and cave dripping waters has a SiO_2 concentration of about 1 mg/l. A water falling on a drip-stone of opal has a concentration of 7,1 mg/l SiO_2, being the only water sample over-saturated in silica.
The total silica load of the stream is 184 mg/s, mainly derived from surface solution removal in the upper platform. In the Aonda System, the SiO_2 dissolved, partly from surface solution (15 %) and partly from underground processes (85%), is 40 mg/s
Key words: Geomorphology, quartzite, weathering , karst, Gran Sabana.

INTRODUCTION

In 1993 and 1996 two speleological missions in the Auyán-tepui region, one of the widest table-mountain in southern Venezuela, were organised by the Associazione Esplorazioni Geografiche "La Venta", with the significant support from Sociedad Venezolana de Espeleología and Societá Speleologica Italiana. In 1993 the team of Italian and Venezuelan cavers explored three different areas. In that occasion, six new caves were discovered: at that time, one of these the Sima Auyán-tepui Noroeste (Venezuelan Cave Register number: Bo.87, SVE 1997) was the longest and deepest cave in the world developed in siliceous rock (depth -370 m, length 2950 m), now exceeded by Grutta do Centenario in Brazil. A new investigation of the Sima Aonda (Bo.8) and the exploration of new caves in the surrounding area were also carried on (BERNABEI *et al.* 1993, BERNABEI 1994).
In 1996, a second mission focused the efforts on the exploration of the active underground network of the Aonda Cave System. This aim was partially reached by the exploration of the “Resurgencia Alí Primera”, which represents the western part of the main collector (SVE 1997).

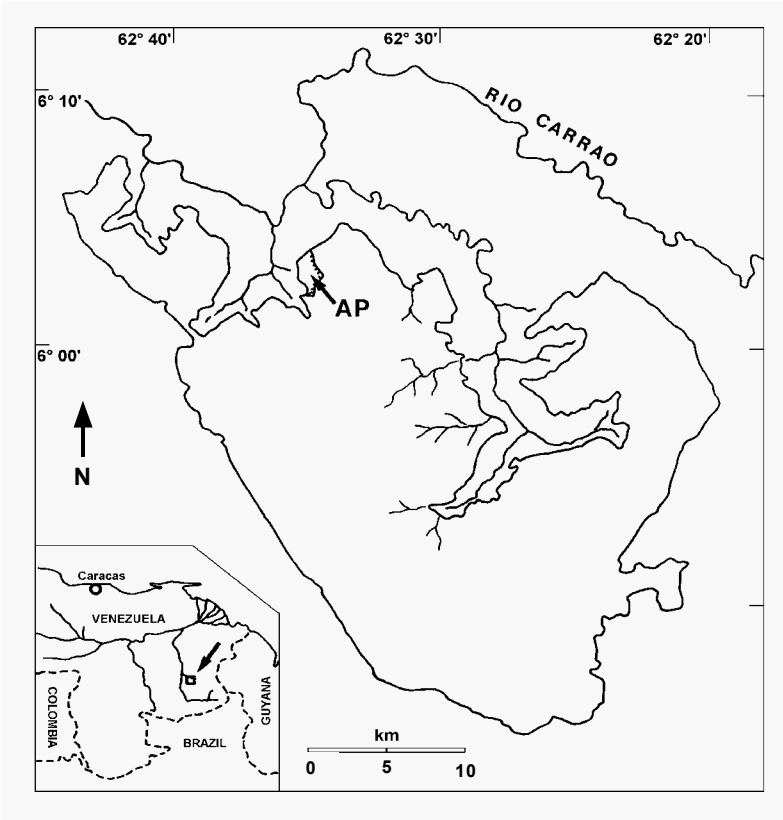

Fig. 1. Sketch map of the Auyàn-tepui and location of the Aonda platform (AP).

Currently, the Aonda System is the best known cave complex developed in siliceous rock in the world. The System is located in the NW of the Auyán-tepui (Fig.1). It consists of several caves not yet completely connected by explored passages; the connection exists from a hydrogeologic point of view. The System represents the underground drainage network of a stream (Río Superior) captured through a sinkhole at the E border of the Aonda platform. The water flows out from a spectacular resurgence in the peripheral scarp of the tepui.
Presently 11 caves have been explored in the Aonda platform, but many other deep shafts are waiting to be investigated. Although we do not know yet the exact pattern of the underground drainage network, the speleological and hydrogeologic surveys allow a first hypothesis about the hydrodynamic behaviour of the System. A first analysis of the water chemical data allows to better understand the development processes of endokarst in siliceous sedimentary rock.

GEOGRAPHIC AND GEOLOGIC OVERVIEW

The Aonda platform is a small secondary bench, 1.5 km long and about 1 km wide, located in the northern part of the Auyán-tepui, about 10 km NW from the Angel Fall (Fig.1). The geographic co-ordinates are 6° 02' of N latitude and 62° 36' of W longitude, the elevation is about 1500 m a.s.l. The platform is limited to the NE and SE by a rock-wall of about 100-150 m, to the W by the rim of the plateau, which falls with a drop of about 500 m facing the valley of the Río Aonda.
From a geologic point of view, the Auyán-tepui belongs to the Roraima-Canaima Province, where the silico-clastic rocks of the Roraima Group widely outcrop (REID 1974, GOSH 1985). The arenaceous formations of this group display continental to peri-continental facies, whose age ranges from 2.3-1.8 Ga of the granitic basement to the 1.4-1.8 Ga of the basaltic dikes and sills that cross

the Roraima Group (BRICEÑO *et al*. 1990). A low-grade metamorphism, with quartz-pirophillyte paragenesis of the shaly beds, is the result of the load of a now eroded thickness of almost 3 km of rock (URBANI *et al*. 1977).
The scarps and the plateau of the Auyán-tepui are formed by orthoquartzites to subarkoses with subordinate middle-fine grained lithic wackes (Matauí Formation), that rest onto protoquartzites, arkoses and wackes with beds of chert, lutite and siltite (Uaimapué Formation) which form the pediment of the table-mountain. The wide plain at the base of the tepui, where the Río Carrao flows, is formed by the siltstones and shales of the Kukenam Formation (BRICEÑO 1985). The flat top of the Aonda bench is caused by the occurrence of a hard bed of fine quartzose arenite (PICCINI *et al*. 1994). This hard "cap" lies over a sequence of medium to coarse quartzose arenites, white or ocraceous in colour, with cross-laminated beds. About 80-90 m below the surface a 1 m thick level of red-white banded shale is found; an x-ray analysis has shown the presence of pyrophillyte (URBANI 1996), chlorite and talc.
The structural setting of the area is very simple, being the beds almost perfectly horizontal. The main tectonic features are sets of vertical fractures, which cut the platform into rectangular to rhombic prisms some meters wide. In the Aonda platform the main sets of fractures are oriented NNW-SSE and NE-SW.

KARST GEOMORPHOLOGY

Despite the siliceous nature of the rock, the landscape of the Auyán-tepui plateau shows typical karst solution landforms: karren-like forms, stone-forests, dolines, sinkholes, caves and impressive shafts which underline that the runoff waters are mainly drained through subterranean paths.
The geomorphic setting of the tepui has been widely described by several authors (SZCZERBAN & URBANI 1974, URBANI 1986, 1991a,b, GALÁN 1988, 1991, GALÁN & LAGARDE 1988, BRICEÑO & SCHUBERT 1990, 1992, GORI *et al.* 1993, PICCINI 1995, DOERR 1999). The most of them agree that the development of a karst-like landscape has been possible because the environmental conditions have restricted the effects of mechanical weathering, allowing, in a very long time, the development of endokarst forms (URBANI 1986, GALÁN 1991, WRAY 1997).
This karst landscape is the result of chemical weathering processes. The importance of the chemical solution of quartzarenite is well emphasised by small-scale solution forms: rills, pans, pits, and small pockets of phyto-corrosion origin covered by algae. Mechanic-erosive processes are active too, but their effect is significant only along the streams, close to the rim of the plateau, and inside the active caves. Presently, a fully effective evolutionary model of karst systems is still missing, and the time of development of so impressive underground networks is still matter of debate. Actually, these plateau are affected by weathering from Cretaceous, in a state of almost absolute tectonic quiescence (BRICEÑO & SCHUBERT 1990), and thus the time of formation of caves could entail several millions of years.
The great shafts, called with the Spanish word "*simas*", are the most important landscape features of the Aonda platform (SVE 1986, 1997). Their origin is largely due to collapse of deep shafts, enlarged by basal erosion in correspondence of underground water flow (SZCZERBAN & URBANI 1974, PICCINI 1995). The huge Sima Aonda (360 m deep, 500 m long and about 100 m wide), for instance, formed by the joining of different shafts (SVE 1983).
According to the evolutionary model of SZCZERBAN & URBANI (1974) and PICCINI (1995), the *simas* of the Aonda System show different evolutionary stages. The Sima Aonda 2 (Bo.83, -360) displays an initial stage, where rock-collapse does not yet occur, whereas the Sima Aonda 3 (Bo.84, - 335), represents a young-middle stage where collapsing of the lower part of the cave is now in progress. The Sima Aonda and the Simas Este 1 (Bo.27) and 2 (Bo.28) represent the final stage, which follows the full collapse of the underground cavities.

HYDROGEOLOGY OF THE AONDA SYSTEM

The Aonda platform is the best investigated area in the Auyán-tepui quarzitic massif (GALÁN 1986, 1988, 1991, SVE 1983, 1986, 1997, Bernabei, 1994). Currently, although only eleven of the many deep shafts have been explored, the hydrogeologic setting of the System is well depicted (MECCHIA *et al*. 1994). It is commonly accepted that many of the caves in the Aonda platform are joined in a single system but, presently, only two caves, the Sima Aonda and the Sima del Bloque, are connected by a man-accessible path (Fig. 2).

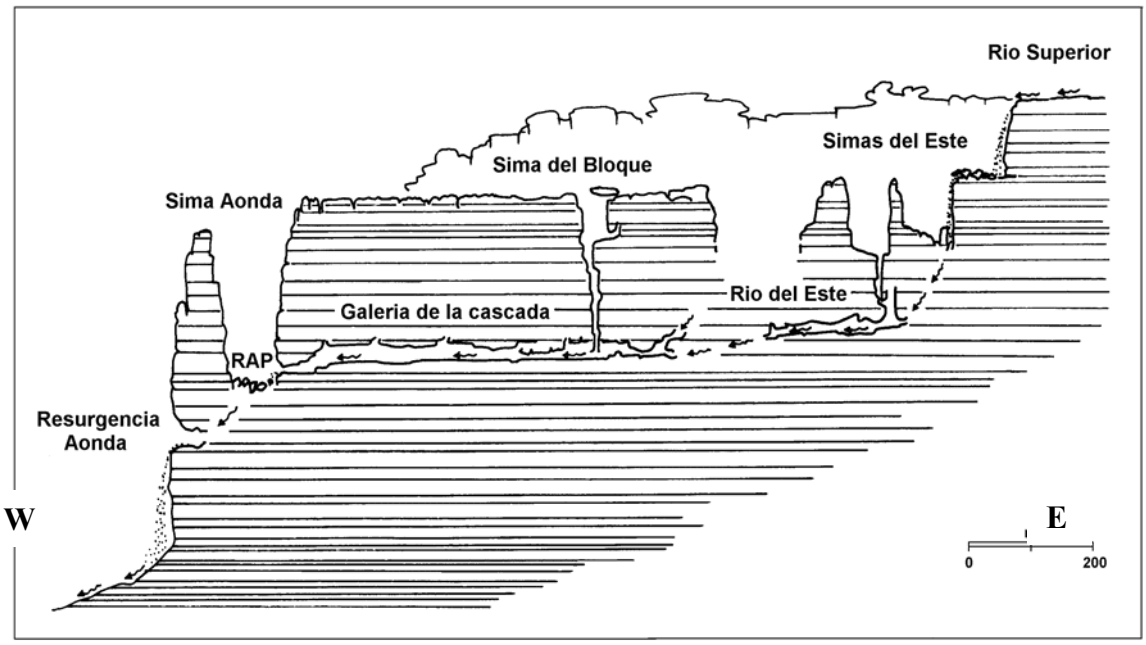

Fig. 2. Sketch profile of the Aonda Cave System (RAP = Resurgencia Ali Primera).

In the E of the Aonda platform, a waterfall, about 100 m high, falls from the rim of the upper plane (Aonda upper platform). It is fed by the Río Superior, a surface stream whose basin extends over an area probably larger than 10 km^2. At the base of the waterfall the water disappears beneath a pile of large rock-blocks. After a path of 120 m the river emerges with a waterfall of 120 m in the close Sima Este 1 (Bo.27). The water loose again in the floor of the shaft, and flows out in the basal tunnel of the Sima Este 2 (Bo.28) (SVE 1983, 1986, GALÁN 1986). In this cave the stream is accessible for about 250 m, along a narrow rectilinear canyon, until it flows into a small lake.

The exploration of the Sima del Bloque in 1996 (SVE 1997), have allowed to know another important segment of the underground stream which connects the sinkhole with the resurgence in the Sima Aonda. In the unknown path the stream does not seem to change significantly its discharge. But, lacking of simultaneous measurement of discharge, we cannot rule out the presence of tributaries coming from different part of the platform or, conversely, the loss of water towards another unknown resurgence.

At the bottom of the Sima del Bloque (-325 m), the stream emerges from narrow submerged fissures. From here, the subterranean stream flows towards NNW along a large canyon (Galería de la Cascada), which features long sand banks in the middle part. Along all the pathway, the stream receives only a tributary from left. After about 700 m, the water falls out near the bottom of Sima Aonda with a waterfall named Resurgencia Alí Primera (Fig. 2).

The large depression of Sima Aonda drains also the water of the small surface streams, which fall in

it with a drop of more than 350 m. All the waters flow together and emerge from the peripheral scarp of the Auyán-tepui, through the spectacular Resurgencia Aonda, about 100 m above the foot of the wall. We presume that beneath the chaotic accumulation of rock-blocks at the bottom of the Sima Aonda, a non-fractured bedrock collects the water from other undetectable underground streams, coming from the Sima del Sur area and from the Sima Aonda 3 area. The confluence of another hypothetical collector from N, where unexplored *simas* and sinkholes exist, is probable because no others springs are visible at the base of the W scarp of Aonda platform. This could explain the increase of discharge that the stream displays from Resurgencia Alí Primera to the Resurgencia Aonda .

The discharge of streams can be estimated on the ground of the few measurements of Venezuelan and Italian cavers. These measurements refers only to the dry season. The authors report the following discharges: Río Superior - from a minimum of about 200 l/s to a maximum of 2500 l/s (MECCHIA *et al.* 1994); Resurgencia Alí Primera - from 50-100 l/s to more than 2000 l/s (SVE 1983). In 1996, after two days of rain, a significant increasing of discharge of the Río Superior and of Resurgencia Alí Primera had been observed. Both probably reached a discharge of more than 5-6 m^3/s. In the underground stream of the Sima Aonda, the hints of the flood were found 4-5 m above the usual water level. According to these few data, we can assume that during the rain-season floods the discharge probably exceeds 10-15 m^3/s, while the mean annual discharge should be about 0.5-1 m^3/s.

SILICA GEOCHEMISTRY OF SURFACE AND UNDERGROUND WATER

During the 1993 and 1996 field researches, several water samples, collected in the NW part of the summit plateau of the Auyán-tepui (Fig. 3), and along the Carrao River valley had been analysed. The samples concerned different kinds of water: rain, ponds, surface or subterranean streams, peat deposits and cave drippings.

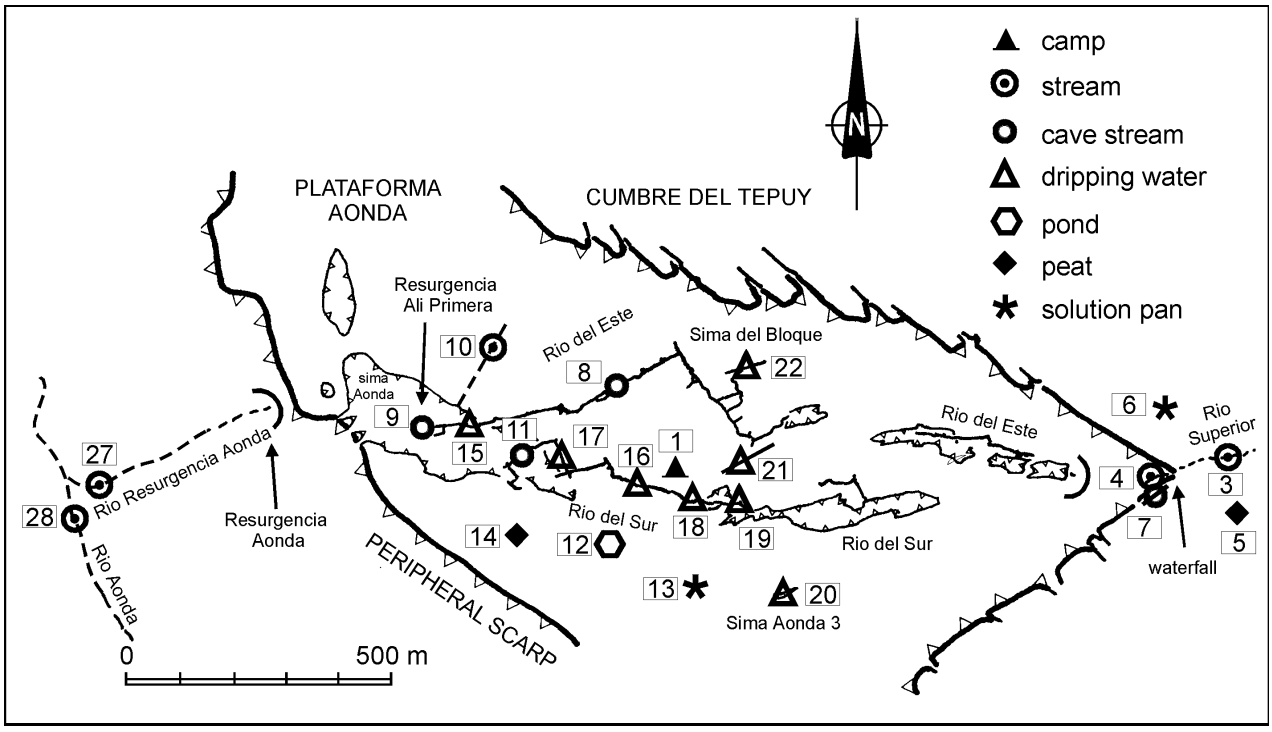

Fig. 3. Sampling stations of water.

Temperature, pH, and electric conductivity (EC) were measured by field portable instruments. SiO_2 concentration has been measured, as soon as possible, by the colorimetric test Aquaquant 14410 Silicon by Merck, because the low concentration (<1 mg/l) requests a measure no later than 8 hours (UNESCO-WHO, 1978). The kit-test allows the analysis in the concentration range 0.01-0.25 mg/l, with an error probably lower than 20%. The samples with a higher concentration were analysed by dilution with distilled water. The reaction of analytic test depends on the temperature: below 20°C we obtain a concentration progressively lower than the real one. Anyway, the low EC of water is a further warranty that the method is sufficiently selective to rule interference out of other chemical elements.
Some water samples were carried to Italy for laboratory analysis of Ca, Mg, Li, Mn, Na and K, by atomic absorption spectrophotometry.

Rainwater

During the season February-March 1993, after a first period with only some middle-intensity rains, in the March 1-2 a storm yielded more than 30 mm of water. According to the data from the Auyán-tepui meteorological station, which reports a total mean rain of 65 mm in February and 73 mm in March (GALÁN, 1992), during the investigated period the rain was probably greater than the average.
A sampling of rainwater was performed in February 20, 22 and 23 and in March 1 and 5, 1993; the results of pH, EC and silica concentration are reported on table 1. The pH of rainwater is generally acid, ranging from 3.8 to 6.5. EC is always very low (1.3 - 15.9 µS/cm), and silica is absent. Such a low EC is due to the high distance from the sea (the natural spring of salty aerosol) and from human activities and industries (spring of dust and pollution).
A relationship between EC and rainfall seems to exist (Fig. 4). Namely, the first sample of rain, after a week of no rain, has an anomalous EC = 15,9 µS/cm, whereas the water of the more intensive rain has a very low EC = 1,3 µS/cm (i.e., pure water). With the increasing of EC the pH fall. This behaviour is typical of rain water and it indicates a storage of Sulphur and Nitrate oxides in the atmosphere, which increases the acidity of rainwater.

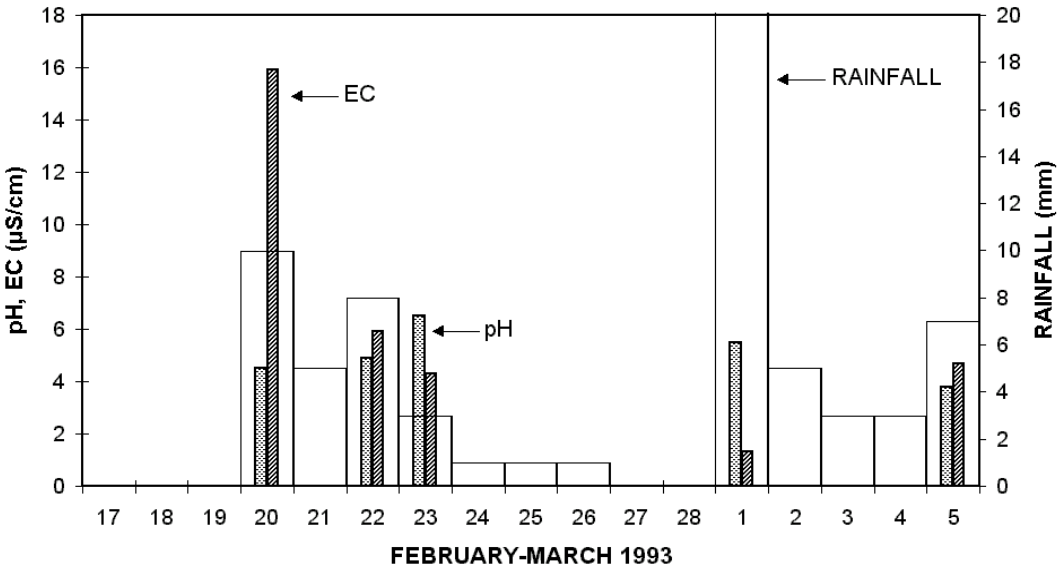

Fig. 4. Rainfall, electrical conductivity (EC) and pH of rainwater, in the period February-March

1993.

Only in one case, the pH of rainwater shows a total correspondence with the theoretical equilibrium value of pH: 5.6. One sample has a value of pH: 6.5, while three samples show middle acid values of pH: 3.8, 4.5 and 4.9; the mean pH results 5.1. Such high variation of pH is normal, because every rain event has a different history and the chemical composition of rain can change, in the time and in the space, also during a same rain event.
In the period February 23 - March 7 1996 a total precipitation of 60-70 mm was measured, almost all concentrated in a single event occurred in the February 24, when one sample of rain were analysed obtaining pH: 5.5 and EC: 6.3 µS/cm

Table 1. Field analysis of rain water (Aonda Platform)

date (m/d/y)	pH	EC µS/cm	SiO_2 mg/l
02/20/93	4.55	15.9	0
02/21/93	4.95	5.7	-
02/22/93	3.80	2.1	-
02/24/93	6.48	4.3	0
03/01/93	5.55	1.3	0
03/05/93	3.80	4.7	-
02/24/96	5.55	6.3	0

Table 2. Field analyses of water from ponds, peat bogs and solution pans. See Fig. 3 for location of sampling. ANO= Auyán-tepui Noroeste.

station	water type	date	T °C	pH	EC µS/cm	SiO_2 mg/l	discharge
14	peat	02/29/96		4.11	26.9	0.19	0.1l/s
5	peat	03/04/96		4.32	19.9	0.13	0.01l/s
13	solution pan	03/03/96		4.45	13.8	0.15	stagnant
13	solution pan	03/03/96		4.39	15.9	0.13	0.006l/s
6	solution pan	03/04/96		4.52	14.1	0.02	stagnant
12	pond	02/20/93	23.0	4.44	12.1	0.02	stagnant
12	pond	02/24/96		4.20	23.4	0?	stagnant
ANO	pond	02/21/93	18.3	3.7	26.9	0.43	stagnant
ANO	pond	02/25/93	18.1	3.6	28.9	0.43	stagnant

Peat and surface water

The central part of the Aonda platform is widely covered by brushes, grass-carpets and peat deposits (about 50% of the surface). The peat deposits occur in the depressions, in correspondence of non fractured bedrock, with a thickness ranging from 30 cm to 2 m. In 1993 and 1996 no researches concerning peat and vegetation were carried on, but we can assume that the situation on the Auyán-tepui should be similar to that described by BRICEÑO & SCHUBERT (1992), BRICEÑO & PAOLINI (1992) and BARRETO (1992) for the Chimantá-tepui.
The runoff water, flowing through peat deposit gets enriched with organic matter derived from decomposition of vegetation. The organic solution load is responsible for the characteristic amber colour of water on the surface and into the caves, with the exception of cave dripping waters that are completely transparent.
Nine samples of stagnant waters were collected: 4 samples in small ponds, 2 samples from peat deposits and 3 samples from solution pans. The results of chemical analysis are reported in table 2. All the samples show a pH ranging from 3.6 to 4.5, with an acidity sensible upper than the rainwater. The EC ranges from 12 to 29 µS/cm. Silica concentration is very variable, ranging from about 0 to 0.43 mg/l. SiO_2 derives entirely from the solution of rock with a concentration that is

related with the time of water/rock contact and with the evaporation rate.

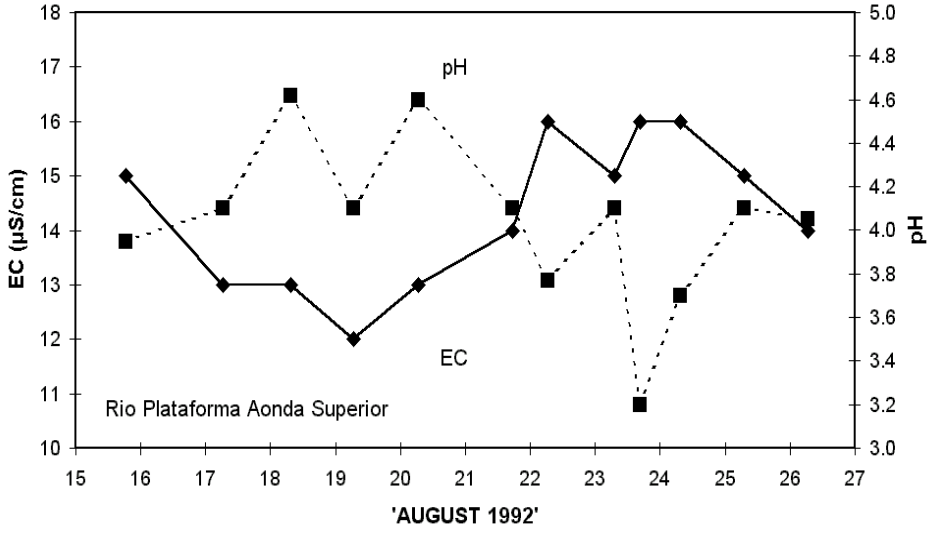

Fig. 5. Variations of electrical conductivity (EC) and pH in the Río Superior stream (station 3, Fig. 3) (BELLOMO *et al*. 1994: 36).

Surface and underground stream water

The relationships between pH and EC of the runoff water are presented in Fig. 5 and Fig. 6. The former concerns the Río Superior (data from BELLOMO *et al.* 1994 and GORI *et al*. 1993), the latter refers to a stream investigated in the north side of the Auyán-tepui in 1993 (Río Auyán-tepui Norte). In both, growing the EC (always <20 µS/cm), the pH falls.

The analysis of all the samples collected during 1993 and 1996 (Tab. 3 and Tab. 4) displays a typical pattern with the maximum of EC in correspondence of pH: 4 (Fig. 7), the same relationship can be observed in the cave dripping water (Fig. 8). Figures 7 and 8 display also the concentration of SiO_2. The relationship with pH has an opposite pattern in respect with the EC, and a better correlation index with pH (R^2: 0.82 for stream water, R^2: 0.96 for cave dripping water). Comparing

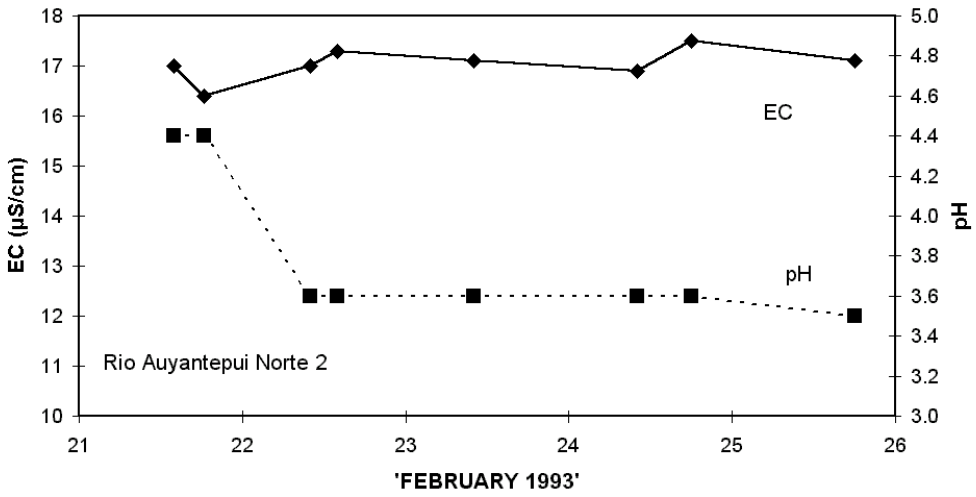

Fig. 6. Variations of electrical conductivity (EC) and pH in the Río Auyán-tepui Norte .

the data of the water sampled on tepui, and the relation between SiO_2 dissolution rate and pH, after the experimental data of BENNETT *et al.* (1988), KNAUSS & WOLERY (1988) and BRADY & WALTHER (1989) (Fig. 9), we observe many analogies, being the lowest concentration of SiO_2 and the lowest quartz dissolution rate in correspondence of the "zero point charge" (ZPC) of quartz (about pH: 3).

Table 3. Field analyses of water from rivers and cave streams.
See Figs. 3 and 10 for location of sampling. AN: Auyán-tepui Norte, ANO: Auyán-tepui Noroeste.

station	date (m/d/y)	time	T °C	pH	EC µS/cm	SiO_2 mg/l	discharge l/s
31	02/23/96	9.00		5.12	9.9	2.12	?
30	02/23/96	9.30		5.13	16.8	2.65	?
29	02/23/96	11.00		4.96	9.2	3.44	?
28	03/03/93	11.00		4.74	9.6	0.76	>30000
27	03/03/93	10.30	19,8	4.26	22.6	0.27	3500
9	03/01/93	15.00		3.93	21.4	0.48	150
9	03/01/93	16.30		4.53	16.4	0.38	300
9	03/04/93	17.00		4.39	19.3	0.23	800
9	02/28/96	14.00		4.21	20.5	0.19	650
9	02/29/96	14.00		4.24	21.2	0.19	800
9	03/01/96	12.00		4.22	21.4	0.17	500
9	03/04/96	15.00		4.29	19.8	0.21	200
8	03/06/96	14.00		4.30	21.5	0.25	80
4	03/03/93	10.00	17,2	4.39	18.2	0.19	2500
4	03/01/96	12.00		4.22	21.3	0.19	400 ?
4	03/02/96	16.00		4.22	21.1	0.16	400 ?
4	03/04/96	13.00		4.28	21.2	0.15	100
7	03/02/96	12.00		4.21	22.0	0.15	60
3	03/04/96	14.00		4.28	21.4	0.17	100
10	02/20/93	10.00	19,4	3.64	18.0	0.27	0.1
10	02/22/93	14.00	20,4	4.18	24.3	0.27	0.1
10	02/24/93	14.00		4.27	23.1	0.40	1
10	02/24/96	17.00		4.24	22.6	0.19	0.1
10	02/25/96	11.00		4.16	26.5	0.18	60 ?
11	02/27/93	14.00		4.66	11.7	0.92	2
AN	02/20/93	18.00	17,2	3.7	13.4	0.21	10
AN	02/21/93	14.00	19,1	4.4	17.0	0.21	4
AN	02/21/93	18.30	17,8	4.4	16.4		4
AN	02/22/93	10.00	18,2	3.6	17.0	0.21	16
AN	02/22/93	14.00	18,8	3.6	17.3		16
AN	02/23/93	10.00	17,5	3.6	17.1	0.21	50
AN	02/24/93	10.00	17,4	3.6	16.9	0.24	50
AN	02/24/93	18.00	17,8	3.6	17.5		16
AN	02/25/93	18.00	17,7	3.5	17.1		5
ANO	02/28/93		17,1	3.6	26.6		
ANO	02/28/93		17,2	3.6	18.2		
ANO	02/28/93		17,4	3.7	27.1		

Table 4. Laboratory analyses of water.
See Figs. 3 and 10 for location of sampling.

station	date (m/d/y)	time	Ca mg/l	Mg mg/l	Li mg/l	Mn mg/l	Na mg/l	K mg/l
31	02/23/96	9.00	0.6	0.16	0.16	0	0.45	0.25
30	02/23/96	9.30	0	0.12	0.02	0	0.29	0.13
29	02/23/96	11.00	0.1	0,12	0.03	0	0.38	0.19
9	03/01/96	12.00	0	0	0.04	0	0	0.01
4	03/01/96	12.00	0.9	0.02	0.01	0	0.17	0.03
22	03/03/96	16.00	0.1	0	0.03	0	0.15	0.02

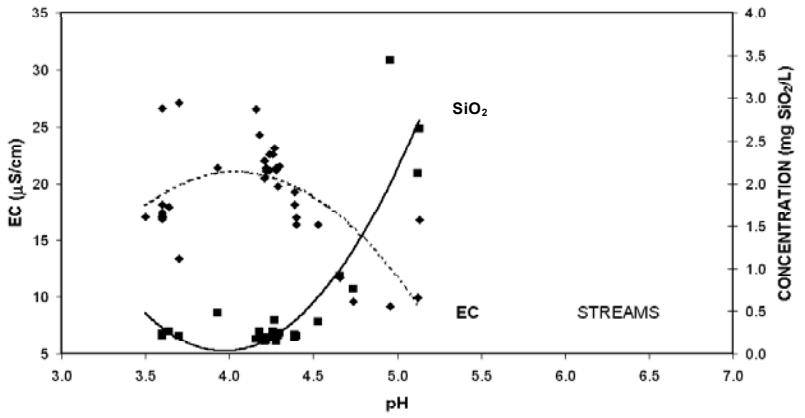

Fig. 7. Variations of electrical conductivity (EC) and pH in the stream of Sima Auyàn-tepui Norte 2.

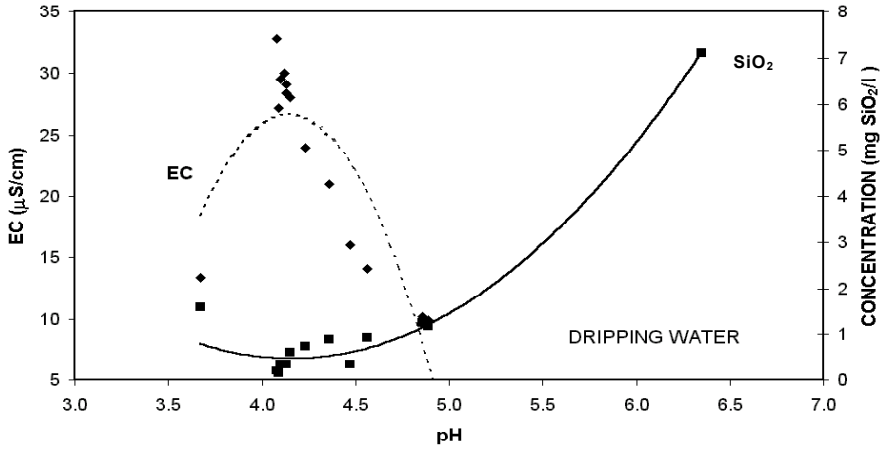

Fig. 8. Relationship between electrical conductivity (EC) (rhombuses) and dissolved SiO_2 concentrations (squares) vs. pH, in cave dripping water.

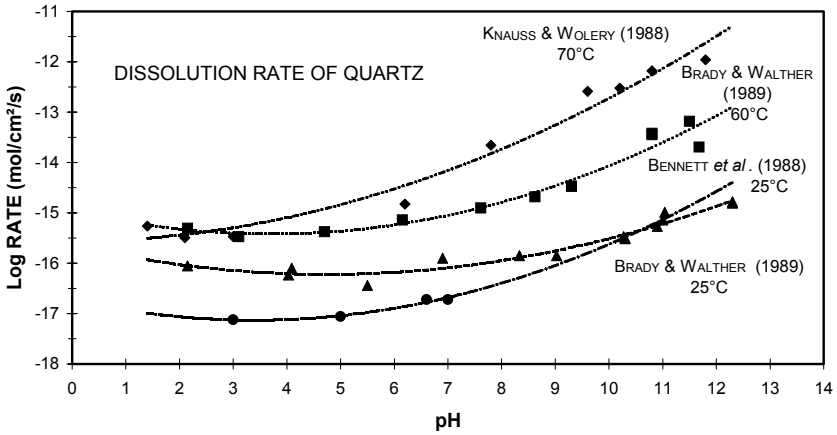

Fig. 9. Comparison of different dissolution rate of quartz vs. pH (experimental results).

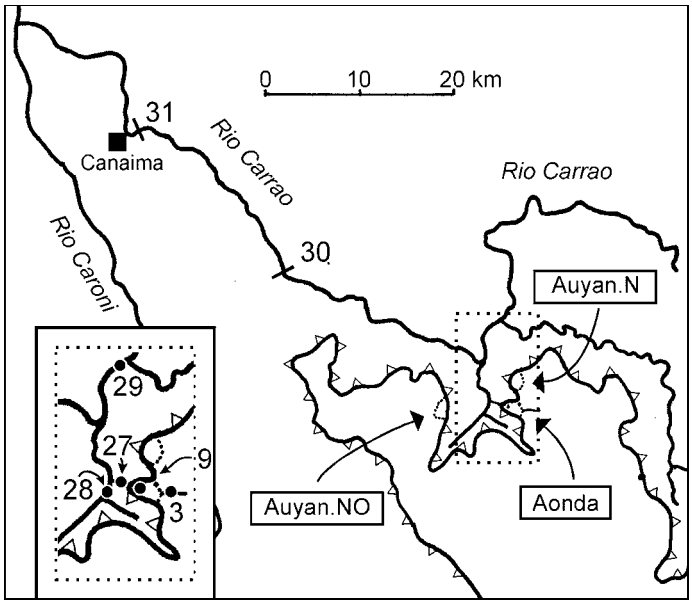

Fig. 10. Sampling stations along Aonda - Carrao river.

Table 5. Estimated drainage areas and discharges at river stations.
See Fig. 10 for location of stations.

river station	drainage areas km^2	February-March mean discharge m^3/s	measured discharge m^3/s	distance from Canaima km
3	?		2.5	57
9	?		0.8	56
27	?		3.5	55
28	35	0.63	30	55
29	7340	137		55
30	7430	139		25
31	7500	140		0

Table 6. Field analyses of water dripping from cave walls and ceiling.
See Fig. 3 for location of sampling.

station	date (m/d/y)	T °C	pH	EC µS/cm	SiO_2 mg/l	depth m	discharge
15	03/01/96		6,35		7,10	-300	1 drop/2s
16	02/23/93	17,4	3,67	13,4	1,60	-300	0.6 l/min
17	02/27/93		4,56	14,1	0,92	-300	quick dripping
18	02/27/93		4,86	10,2	1,26	-300	stagnant water
19	02/27/93		4,89	9,9	1,18	-300	stagnant water
20a	02/25/96		4,09	27,2	0,15	-80	quick dripping
20b	03/06/96		4,08	32,8	0,21	-80	quick dripping
21a	02/26/96	16.7 ?	4,47	16,0	0,34	-80	3-4 drops/s
21b	02/06(96	16.7 ?			0.32	-80	1 drop/3s
22a	03/03/96		4,13	28,4	0,35	-80	0.1-0.2 l/s
22a	03/05/96		4,13	29,1	0,35	-80	0.015 l/s
22b	03/03/96		4,15	28,0	0,60	-80	1 drop/4s
22c	03/05/96		4,36	21,0	0,90	-80	1 drop/60s
22d	03/05/96		4,10	29,5	0,35	-80	1 drop/3s
22e	03/05/96		4,12	30,0	0,35	-80	1 drop/1s
22f	03/06/96		4,23	24,0	0,74	-80	1 drop/15s

Silica concentration in the Río Aonda – Río Carrao

Fig. 10 shows the location of the sampling sections along the Río Aonda and Río Carrao from the Auyán-tepui to Canaima; Fig. 11 displays the concentration of silica, pH and EC of water in these stations. Sections 3, 27 and 28 were sampled in March 3, section 9 was sampled the day after. Sections 31, 30 and 29 were analysed in February 23. The amount of discharge had been estimated from the superficial flow rate.

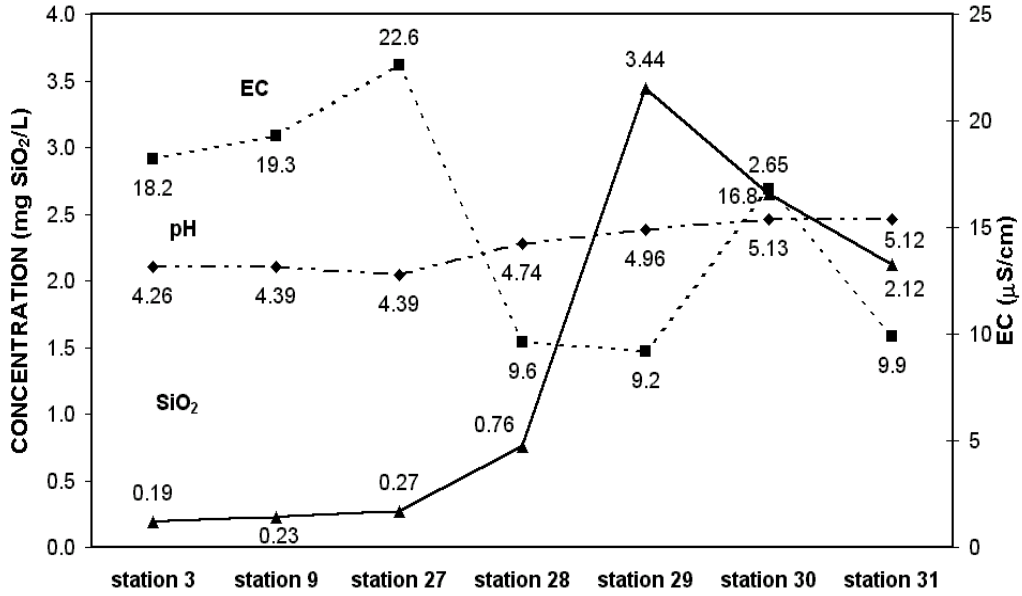

Fig. 11. Dissolved silica concentrations, pH and electrical conductivity (EC) along the Aonda – Carrao river.

The subterranean stream that flows through the Aonda System (Río del Este) belongs to a basin where only the quartzite of the Matauí Formation outcrops (sections 3 and 9). Section 28 collects the water coming from a wider part of the Auyán-tepui, with a path of about 2 km onto the sandstone of the Uamapué Formation. Sections 29, 30 and 31 are located along the Río Carrao, where the water comes from a wide basin largely made up by sandstones, siltstones and shales of Uamapuè and Kukenam Formation.

Chemical data underline the low concentration of SiO_2 of the water from the summit plane of tepui, where runoff is enough quick. In the cave system we observe only a slight increase of SiO_2, while downstream the Resurgencia Aonda and along the Río Carrao, the silica concentration is significantly higher.

The quartz solubility, at a pressure of 10^4 Pa and a temperature of 25 °C, in pure water is about 6.6 mg/l (RIMSTIDT & BARNES 1980), but the solubility rate is very low. The runoff waters on tepui have a mean SiO_2 concentration <0,3 mg/l, and they are greatly under-saturated.

In the pediment and along the plain the streams flow on feldspathic sandstones, on which hydrolysis processes of rock weathering occur. In presence of other silicate minerals, the SiO_2 solubility can reach that of amorphous silica, that, under environmental conditions, and in pure water, is 115 mg/l (RIMSTIDT & BARNES, 1980). The higher solubility of feldspars and other silicate minerals, compared with quartz, and the longer time of contact water-rock, explain the high concentration of silica in the Río Carrao.

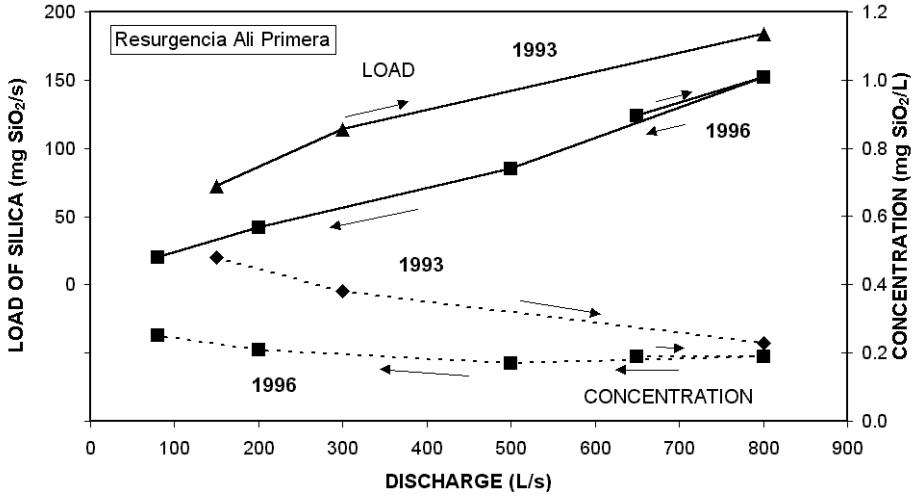

Fig. 12. Relationship between dissolved silica load and SiO_2 concentration to discharge, at Resurgencia Alí Primera.

All these data refer to the dry season, when the discharge of streams and river is sensibly lower than during the rain season. We have no data concerning the silica concentration during wet season.
Considering a mean precipitation of 3000 mm/year over the whole basin of Río Carrao, and estimating a mean evapotraspiration of 30 % (according to the data reported by GALÁN 1992, for the Auyán-tepui and for Chimantá-tepui), we obtain a mean annual runoff of 2100 mm. In the Río Caroní the mean discharge in February and March is about 36 % of the mean annual discharge (data from EDELCA, in GALÁN 1992); assuming a constant relation between February-March mean discharge and annual mean discharge, we can estimate the mean discharge for Río Carrao. In Tab. 5 an approximate estimation of the surface of basins and of their discharge is reported.

Silica concentration in the Aonda System

SiO_2 concentration of the stream flowing through the Aonda System was measured in the Río del Este (station 8, Fig. 3) and at the Resurgencia Alí Primera (station 9, Fig. 3). The relationships discharge/concentration and discharge/solution load are shown in Fig. 12. We can observe a regular decrease of concentration with the discharge during a flood event (max. 0.48 mg/l, min. 0.17 mg/l SiO_2). Conversely, the solution silica load increases with the grow of the discharge. This can be explained because during a storm, the SiO_2 enriched water, trapped in the peat deposit, surface depressions and fractures, are washed away by rain.

Cave percolation water

Percolation and cave dripping waters differ from surface and cave stream ones because they are limpid and significantly most enriched of silica.
In the Sima del Bloque, 7 samples, collected in three different days, have SiO_2 concentration ranging from 0.35 to 0.90 mg/l. A relationship between dripping rate and concentration of silica seems to exist.
During a strong rain event, in the Sima Aonda 4 (Bo.85), at a depth of 80 m, we found the less silica enriched dripping water (0,15 mg/l SiO_2), while a second sample, collected from wall-flow water had a concentration of 0,21 mg/l SiO_2. In the Sima Aonda 2, two samples of drip-hole water had a high SiO_2 concentration (1,18 - 1,16 mg/l SiO_2), while another sample, collected from a quick dripping, displayed a concentration of 0,92 mg/l SiO_2. In the Galería de la Cascada, about 50 m

upstream the Resurgencia Alí Primera, a water falling on a drip-stone of opal resulted to have a concentration of 7,1 mg/l SiO_2, being the only sample of water over-saturated by silica.

CONCLUSIONS

Rainwater does not contain silica. On the surface of Aonda platform, the water moderately enriches with silica. Stagnant water in solution pans or peat deposit display a concentration from 0.01 to 0.19, while runoff water has a SiO_2 concentration ranging from 0.19 to 0.26 mg/l. Fracture percolation water present concentrations of 0.18-0.52 mg/l at a depth of -80 m, whereas it reaches a concentration ranging from 0.92 to 1.3 mg/l at the depth of -300 to -350 m. Only one sample, coming from an opal drip-stone, was over-saturated, with a concentration of 7.1 mg/l.
The contribution of percolation water determines a significant increase of silica concentration in the main collector of the Aonda System (Río del Este) (data of March 3-4 1993): Río Superior: 0,19 mg/l - Resurgencia Alí Primera: 0,23 mg/l - Resurgencia Aonda: 0.27 mg/l.
All these data allow an approximate computation of the dissolved silica in the Aonda platform. Being the discharge of the Resurgencia Alí Primera about 800 l/s (March 4 1993), the solution silica load results of 184 mg/s. This load is mainly due to surface solution in the basin of the Río Superior (upper platform). Since the input concentration is 0.19 mg/l SiO_2, and assuming a mean concentration of percolation water of 0.9 mg/l, we obtain that the hallogenic load is about 144 mg/s, while the silica dissolved in the Aonda System results of 40 mg/s, with a theoretical discharge of water percolation of 45 l/s.
The silica load of the Aonda System is partly from surface solution (peat, ponds, pans) and partly from underground processes. According to the data of the analysed waters we can assume that about 15% of the silica comes from surface and the 85% comes from underground solution.

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