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Factors that control the geochemical evolution of hydrothermal systems of alkaline water in granites in Central Pyrenees (Spain)

Factores de control del grado de evolución geoquímica de sistemas hidrotermales de aguas alcalinas instalados en materiales graníticos del Pirineo Central (España)

B. Buil[1*], P. Gómez[1], M.J. Turrero[1], A. Garralón[1], M. Lago[2], E. Arranz[2], B. de la Cruz[1]

[1] *Dpto. de Medioambiente, CIEMAT, Avda. Complutense 22, 28040 Madrid, Spain*
[2] *Dpto. de Ciencias de la Tierra, Facultad de Ciencias, Universidad de Zaragoza, c/ Pedro Cerbuna 12, 50009 Zaragoza, Spain*

corresponding author: belen.buil@ciemat.es,

Abstract

The geochemical evolution of the solutions from the hydrothermal systems of Caldas de Boí, Artiés, Tredós and Les (Central Pyrenees, Spain), show differences in the concentration of dissolved solids and in the presence of equilibrium or disequilibrium of the solutions in depth regarding albite.

The dating (^{14}C) of the waters belonging to the various hydrothermal systems demonstrated that the residence time is not the only factor controlling the differences in the degree of the geochemical evolution reached by each system, but other factors related to the dissolution kinetics of the minerals.

The analysis of the influence of the main factors controlling the dissolution rate of the minerals, specifically feldspars, indicates that the temperature of the solutions at depth is the variable that can justify their different geochemical evolutions, even in solutions with similar residence times.

Keywords: Hydrothermal system, granite, Pyrenees, Spain

Resumen

La evolución geoquímica de las soluciones de los sistemas hidrotermales de Caldas de Boí, Artiés, Tredós y Les, situados en el Pirineo Central (Spain), muestra diferencias reflejadas en la concentración de sólidos disueltos y en la presencia de una situación de equilibrio o desequilibrio en profundidad de las soluciones respecto a la albita.

La datación (^{14}C) de las aguas pertenecientes a los distintos sistemas hidrotermales ha puesto de manifiesto que el tiempo de residencia no es el factor de control determinante de las diferencias existentes en el grado de evolución geoquímica alcanzado por las mismas, teniendo que contemplarse otro tipo de factores relacionados con la cinética de disolución de los minerales, como responsables de estas diferencias. El análisis de la influencia de los principales factores que controlan la tasa de disolución de los minerales y, más en concreto, de los feldespatos, muestra como las diferencias de temperatura de las soluciones en profundidad son capaces de justificar el distinto grado de evolución geoquímica, incluso en soluciones con tiempos de residencia muy similares.

Palabras clave: sistema hidrotermal, granito, Pirineos, España

1. Introduction

The geothermal systems of alkaline waters in granites have been studied from different aspects: the initial evaluation of the geothermal potential in certain geographic zones (e.g. White and Williams, 1975; Suárez, 1998; Lund and Freeston, 2001; Boyd, 2002; Coolbaugh *et al.*, 2002); the characterization and geochemical modeling that allowed to define and validate the methodologies used in these systems (e.g. Michard, 1900a; Auqué, 1993); or its use as natural analogues of nuclear waste repositories (Michard *et al.*, 1991; Olsson and Gale, 1995; Wood *et al.*, 1997; van Middlesworth and Wood, 1998; Druschel and Rosemberg, 2001; Buil, 2004).

As part of the evaluation programme of radioactive waste disposal of the Spanish Nuclear Waste Managent Company (ENRESA), a multidisciplinary research in the geothermal systems developed within granitic massifs of the Spanish Central Pyrenees (1997 to 2000) was carried out. The selection of the sites for these studies was based on different aspects: first, granites are being considered in Spain, and other countries, as favourable host formations for nuclear waste disposal; second, the temperatures of deep aquifers in the thermal systems have been shown to be relatively low (from 75 to 115ºC), similar to the maximum temperatures expected in nuclear waste repositories (ENRESA, 1997); third, the water compositions are similar to groundwaters at some proposed repository sites; and fourth, the high residence time of the waters in the systems studied (from 11000 to 16000 years) allows analyzing the geochemical evolution of the groundwaters regarding time.

The aim of this work is to evaluate the influence of different parameters, such as residence time, temperature and thermodynamic equilibrium and kinetic factors, both on the composition and on the evolution degree achieved by the thermal solutions.

The set of results from these studies has improved the existing knowledge on the characteristics and geochemical evolution of the groundwaters expected in a deep geological repository of radioactive wastes, and it is of great interest for performance assessment purposes.

2. Geological and hydrogeological background

The set of hydrothermal systems considered is related to two clearly different granite units, both in the petrological and geochemical aspects: the Maladeta plutonic complex (MPC) (Charlet, 1979; Arranz, 1997; Buil *et al.*, 2002; Buil, 2004) and the leucogranite rocks appearing in the Bossòst dome core (BD) (De Sitter and Zwart, 1962; Zwart, 1962, 1963; Pouget *et al.*, 1988; Pouget, 1991; García Sansegundo, 1991; Buil *et al.*, 2002; Buil, 2004).

2.1. Maladeta plutonic complex

The Maladeta plutonic complex (MPC) is divided in two main units, separated by a ductile fracture (Fig. 1): the western unit or Aneto Unit, representing the high block of the fracture, and the eastern unit or Boí unit, representing the sunken block and the major exposed surface, where the hydrothermal systems of Caldas, Artiés and Tredós are located. This unit has two exposed massifs in its northern contact: Tredós massif (to the east) and Artiés massif (to the west). Both massifs represent small apophysis of the principal rock mass of Boí unit, with which they are probably linked in depth, as suggested by the petrological and geochemical characterization of the rock (Arranz, 1997; Arranz *et al.*, 1999; Buil *et al.*, 2002; Buil, 2004).

The sequence of lithological types in both units include a small volume of basic rocks, granodiorites or granodiorites-monzonites, which are the most representative outcrops in Boí unit and Tredós massif, as well as in a narrow band at the northern contact of the Artiés massif, and finally, sienogranites with biotite, muscovite and cordierite.

The upwellings in Caldas de Boí (southern contact of the batholite) and Tredós (northern contact of the batholite) systems outcrop in granodiorites, and none is associated with sienogranites at the surface. However, as previously mentioned, the Boí unit is the sunken block of the ductile fractured zone, and therefore, the outcrops correspond to the highest levels of the intrusive complex (Fig. 1). On the other hand, the outcrops in the Aneto unit represent the deepest levels of the complex, as evidenced by mapping and cross section (Fig. 1). The sienogranites in these levels predominate over the granodiorites. Therefore, the sienogranitic outcrops from Boí Unit are considered as small cupules or apical endings of a much greater volume of sienogranites which would constitute the core of the Boí unit (Buil, 2002, 2004) and it is considered that a significant interaction between percolating waters and sienogranites has taken place in depth.

Finally, the upwellings studied in the area of the Artiés massif outcrop in calcsilicate rocks, which are developed in the calcareous host rock (Devonian) of the Maladeta pluton. This massif is constituted by granodiorites of limited thickness (less 300 m) in the outer zone, whose characterisics are similar to the granodiorites in Boí Unit, and by sienogranites with cordierite (the most representative outcrops in Arties massif) in the inner zone further situated to the South, through which the thermal waters of
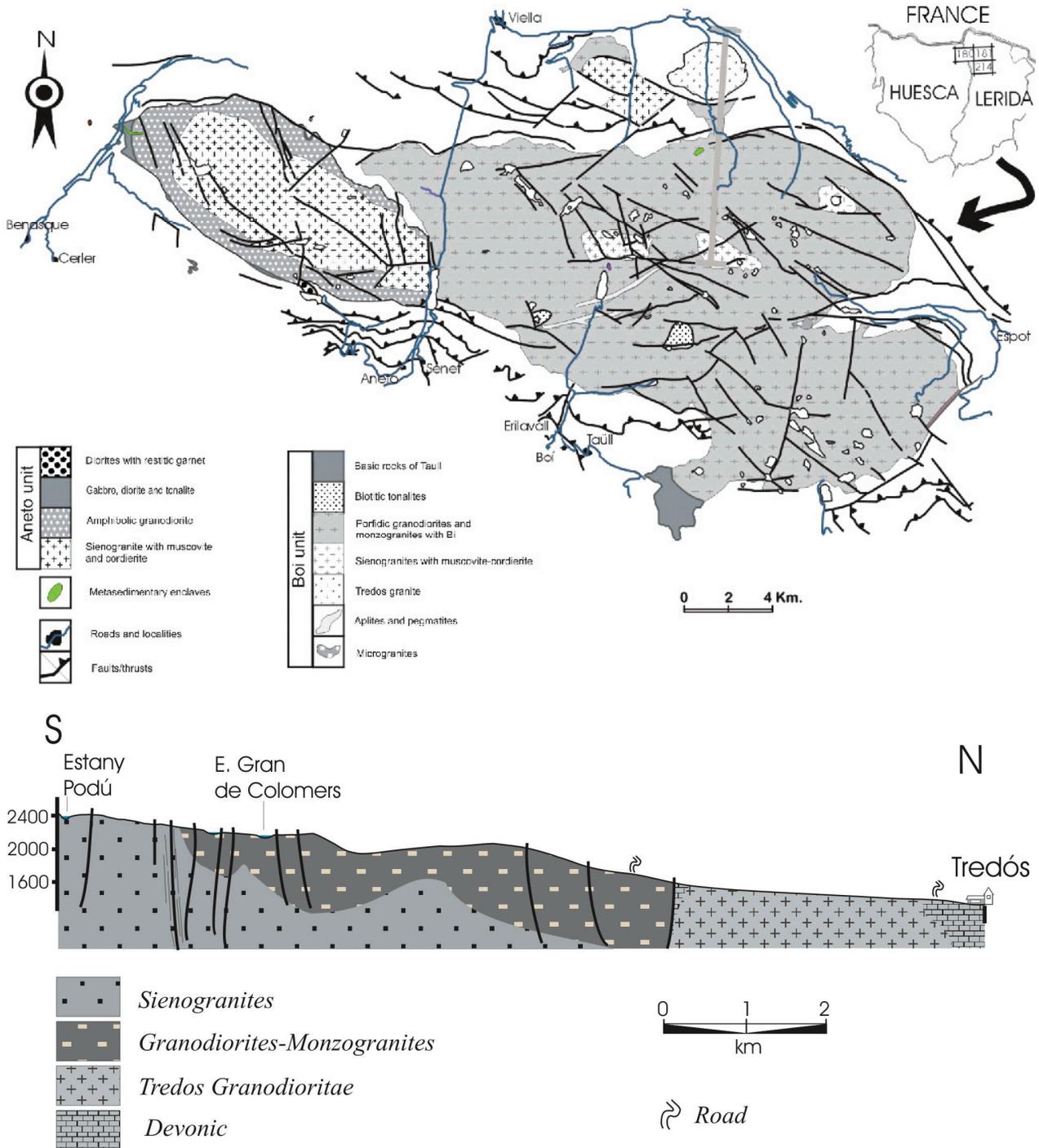
Fig. 1.- Geological map and cross section of the Maladeta plutonic complex (Arranz, 1997; Buil, 2004).

Fig. 1.- Mapa geológico y corte geológico del complejo plutónico de La Maladeta (Arranz, 1997; Buil, 2004).

this system circulate toward the reservoir and the last part of its pathway (Buil *et al.*, 2002; Buil, 2004).

2.2. Bossòst dome

The Bossòst Dome (Fig. 2) belongs to a large Hercynian structure, the Garona Dome, which outcrops in the northern side of the Central Pyrenees (Spain). It is mainly constituted by Lower Paleozoic materials (Cambrian-Ordovician) and Silurian and Devonian materials form the outer cover of the structure.

From a structural point of view, this outcrop corresponds to levels of a Hercynian structure (De Sitter and Zwart, 1962), which is characterized by the development of a subhorizontal foliation and medium-high grade metamorphism. It presents a concentric metamorphic zo-
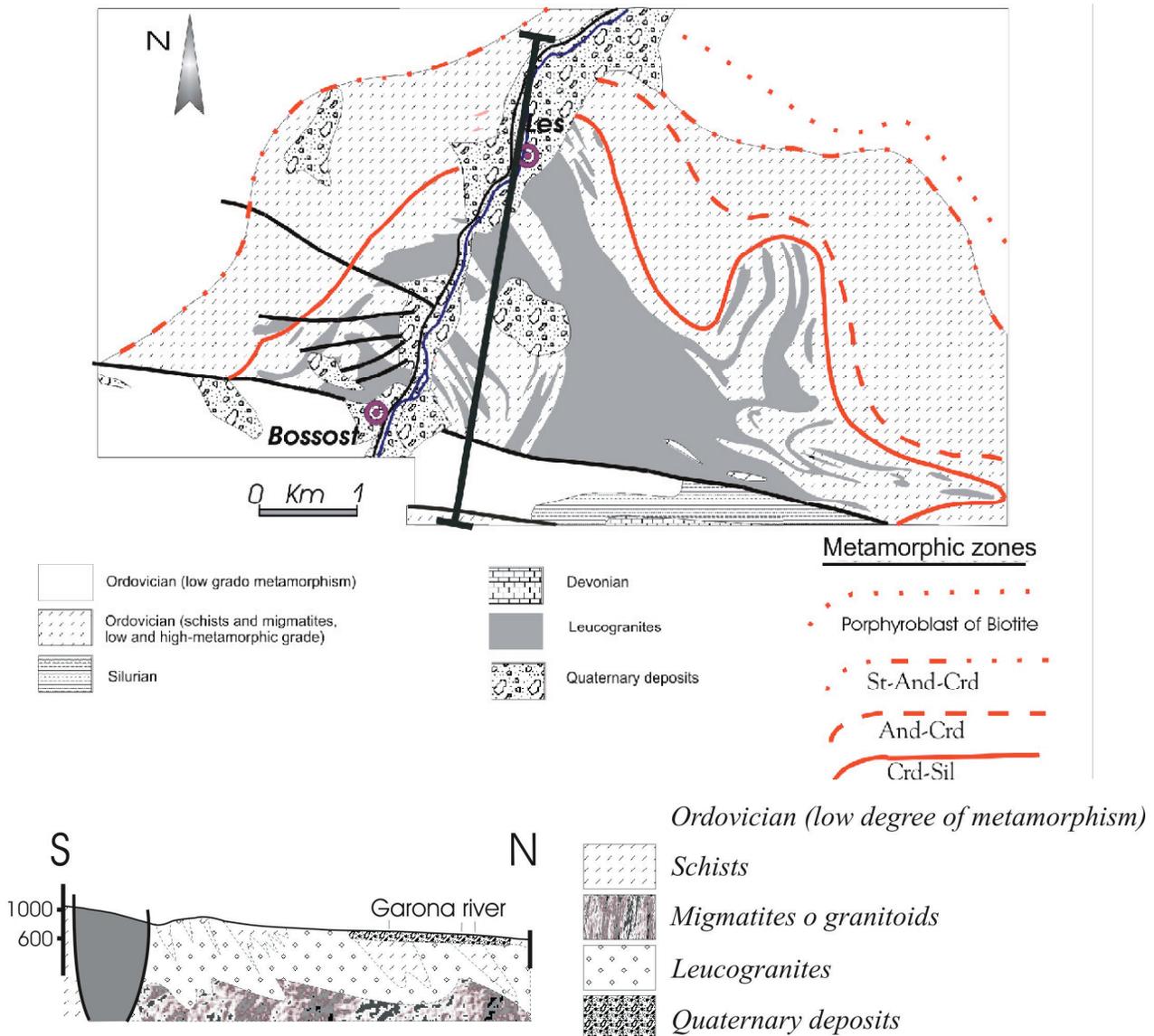
Fig. 2.- Geological map and cross section of the Bossòts dome (after Zwart, 1979; García-Sansegundo, 1992; Buil, 2004).
Fig. 2.- Mapa geológico y corte geológico del Domo de Bossòts (modificado de Zwart, 1979; García-Sansegundo, 1992; Buil, 2004).

nation, which reaches the high temperature anphibolite facies and the formation of migmatites and granitoids derived by anatexis in the central zones.

The granitoids outcrop in several zones in the Garona Dome, the zones close to the villages of Bossòst and Les (Lleida, Spain) being those with a greater development of granitic rocks. The thermal upwelling of Les is situated in leucocratic granites with K-feldspars, coarse to very coarse grain size, which can be classified as pegmatites.

2.3. Hydrogeological characteristics

From a hydrogeological point of view, the recharge waters of the hydrothermal systems studied have a meteoric origin (Buil *et al.*, 2002, 2004), and their reservoir temperatures do not exceed 150 ºC, as evidenced by the lack of variation of the $\delta^{18}O$ values (Table 1) of the thermal waters (data from IGME, 1984) compared with the values of the standard straight line for rainfall (Craig, 1961) and the regional straight line of meteoric waters defined for the French Central Pyrenees (Criaud and Vuataz, 1984; Fouillac *et al.*, 1984).

The maximum flow depth of the waters within the systems was calculated based on the geothermal gradient estimated by Fernández and Banda (1989) for the Central Pyrenees, which varies between 25 and 30 mKm^{-1}, and the temperature values reached in the reservoirs of each system. The reservoir depth estimated for each system is 4200 m for Caldas, 4000 m for Artiés, 3200 m for Tredós and 2500 m for Les (Buil *et al.*, 2002; 2004).

Name	T (ºC)	pH	Eh (mV)	Alk. (ppm)	F	Cl	SO_4^{2-}	Si	Al	Mg	Na	K	Ca	$\delta^{18}O$**	δ^2H**	^3H**
C1	52	9.1	-120.4	90.9	4110	52600	23700	34610	104	29	82206	2710	3067	-11.12	-79.5	1.4±3.8
C2	45.6	9.1	-78.4	81.1	3870	52400	37800	33180	132	86	79677	2998	3835			
C3	48.6	7.9	432.8	53.7	4040	53500	58800	33540	81	48	81145	2476	3154			
C4	33.5	8.1	-32.9	52.5	2660	29800	36400	19330	61	452	46689	1887	6878			
C5	30.5	7.6	-12.1	51.9	2670	31200	36400	17190	68	527	39444	1894	7457			
C6	27.9	7.4	393.6	46.4	2060	23300	24300	15720	90	572	32388	1646	7749			
C7	27.9	7.6	461	46.4	1520	18200	26900	14770	23	470	32265	1512	6194			
C8	43.4	9.2	-210.6	90.3	4360	52200	28300	32080	104	39	79511	2335	3184			
C9	33	9	-1.3	58	3260	48900	41700	27000	83	134	65727	2215	3727			
C10	26.4	9.1	-117.8	67.7	3860	51000	47100	30980	154	117	78389	2483	4139			
C11	23.9	7.3	495.5	41.5	2030	13100	20200	13250	98	687	27971	1298	6172			
C12	26.3	7.6	476.8	45.8	1800	18400	26900	14960	45	477	33408	1619	6229			
C13	21.4	9.6	-151.3	98.8	2940	15800	16200	27060	51	23	48926	1419	1754			
C14	30.9	9.5	-135.2	99.5	1780	14800	17500	25750	53	23	49463	1345	1748			
C15	28	9.4	-143.8	77.4	2570	32000	31000	27550	78	89	61437	1747	3608			
C16	42.8	9.1	-224.6	94	3280	53400	32300	31860	112	39	79614	2396	3222			
C17	20.3	7.6	356.5	39	760	11900	16200	10300	62	476	19753	1097	6003			
C18	20.1	7.4	390.9	37.8	760	10300	16200	10460	43	478	19578	1077	5917			
A1	35.6	9.4	-176	70.8	5540	36500	32300	33780	146	32	67553	1720	2918	-11.76	-84.9	2.1±3.8
L1	28	9.7	-182	83	1190	13400	12200	20310	63	191	35136	890	3825	-10.91	-75.02	0.3±2.6
L2	25.3	9.5	-42.3	67.1	870	82700	16200	17320	94	60	28172	950	2973			
T1	32.2	9.6	-155.2	69.6	1250	10900	12200	23880	35	20	32940	1405	2496	-10.96	-78.45	4.5±3.9
T2	33.6	9.5	-165.2	64.1	1190	10500	13500	21430	51	44	31668	1378	2862			
T3	33.8	9.5	-132.3	64.7	1080	99300	13600	22550	101	69	29493	1285	2868			
T4	26.5	9.6	-123.3	68.3	1110	11600	12200	25980	63	38	32583	1532	2731			
T5	28.1	9.6	-142.4	73.8	1220	12000	12200	28500	705	239	34333	1686	2663			

Name	T (ºC)	pH	Eh (mV)	Alk. (ppm)	F	Cl	SO_4^{2-}	Si	Al	Mg	Na	K	Ca
T1b	32	9,6	-225	74,4	1400	8000	11000	23190	61	23	33100	1400	2467
T4b	26,6	9,6	-233	78,5	1500	8600	11000	24510	43	19	34100	1621	2516
L1b	27,2	9,8	-284	84,7	1100	7900	7000	19030	40	170	34100	859	3626
C1b	47,8	9,2	-252	93,4	3900	47800	28000	33630	134	30	78500	2343	2955
C2b	48,2	9,2	-236	89,1	3900	46200	36000	34620	215	60	81400	2524	4337
C8b	41	9,2	-265	95,2	4100	53900	27000	33440	111	33	78900	2363	2988
C9b	34,9	9	-186	62,8	3100	39300	51000	30610	96	136	70600	2276	3756
C10b	26,8	9,2	-210	73,2	3900	42600	37000	33620	111	86	77200	2423	3802
C14b	30	9,4	-195	96,4	1600	10100	20000	27410	87	26	48700	1414	1842
C15b	26,4	9,3	-198	78,7	2100	35100	31000	28970	88	88	60300	1762	3585
C16b	39,4	9,2	-286	92,7	4000	49100	29000	33770	126	39	78800	2457	3165

Table 1.- Water chemical analysis of the thermal systems of Caldas de Boí (C), Artiés (A), Tredós (T) and Les (L). The superior table corresponds to the sampling of 1997 July and the inferior table to the sampling (anoxic conditions) of 1997 September

*The analytical values of the cations and anions are expressed in μg/L (ppb).

** Data from IGME (1984) and Servei Geologic de Catalunya (1990).

Tabla 1.- Análisis químico del agua de los sistemas termales de Caldas de Boí (C), Artiés (A), Tredós (T) y Les (L). La tabla superior corresponde al muestreo realizado en Julio de 1997 y la inferior al muestreo, en condiciones anóxicas, de septiembre de 1997.

* Los resultados analíticos de los cationes y de los aniones están expresados en μg/L (ppb).

** Datos del IGME (1984) y del Servei Geologic de Catalunya (1990).

Based on these results, the hydrothermal circulation circuits are U-shaped, as proposed by Chevalier-Lemire *et al.* (1990) for the Luchon (France) system, by Soulé (1990) for the Cauterets system and by Auqué (1993) for certain systems of the Spanish Central Pyrenees. This morphology corresponds to a limited horizontal

separation of the recharge and discharge areas associated with the systems, as well as to the great depth of the reservoirs.

3. Methodology

3.1. Sampling

Three sampling campaigns were performed on July 1997 (26 thermal springs), September 1997 (11 thermal springs) and September 1998 (4 thermal springs). In 1998, the waters representing the deep conditions of each system, that is, those that have not been affected by secondary processes (like mixing with cold waters on their way up), as their ^{3}H contents (from IGME, 1984) (Table 1) and the results of the geochemical processing of the analytical data (for example the relations Na vs Cl$^-$, F, SiO$_2$, K and pH vs. Na and T (Buil *et al*., 2002)) show, were sampled to carry out the ^{14}C analyses. The sampling campaigns of September 1997 and 1998 were carried out in anoxic conditions.

All the bottles used to keep the samples were made of polyethylene and were washed with HNO$_3$, rinsed with deionised water and dried. Samples for metal determinations were filtered (through a 0.45 μm membrane) and preserved with HNO$_3$ at a minimum concentration of 2 vol%. Samples for anions and alkalinity determinations were untreated and unfiltered. Samples for S^{2-} determinations were filtered (0.45 and 0.1 μm membrane filters) and preserved with Zn acetate (20 drops approximately). At each geothermal system, 2l samples for ^{14}C, filtered (0.45 μm membrane filter) and preserved with HgCl$_2$, according to laboratory recommendations, were collected.

3.2. Field measurements

The *in situ* determination of certain parameters (T, pH, Eh, conductivity, dissolved oxygen and alkalinity) is required due to the instability of the water. This problem is particularly important in the thermal solutions due to the decrease of their temperature upon storage, which can vary the value of certain physico-chemical parameters, as well as the development of precipitation/disolution reactions and oxidation of solutions.

Upwelling temperatures, pH and Eh of the hot springs were measured with an ORION 250A digital pH/Eh/T meter equipped with a pH TRIODE L/M electrode and temperature probe (ORION 9010 TM) and Eh platinum electrode with Ag/AgCl reference electrode (ORION). The conductivity was determined using a portable conductivity meter (JENWAY 4200) and the alkalinity by ti-

tration with a potenciometric titroprocessor Methrom 670 with inflection-point detection (Table 1).

The principal anions were determined in the Laboratories of the *Centre de Recerca d'Alta Muntanya of the University of Barcelona* (Spain) before 24 hours had elapsed after the sample was taken. Fluorides and chlorides were determined by an ORION 710A ion analyzer, using in the case of chlorides, CISA (50 ml for each 50 ml of sample) and ISA (2 ml for each 50 ml of sample) as interference surpressor, and TISA III (5 ml for each 50 ml of sample) for fluorides (Table 1). Once the equipment was calibrated and the samples prepared, the analyses were carried out by direct measurement. The sulphate content was determined by a spectrophotometer (Hach 680) with a wave length of 450 nm using Sulfaver as reagent (Table 1).

The physico-chemical parameters were measured by means of a multiparametric probe (Hidrolab), located inside a chamber with inert atmosphere (full of nitrogen gas, 99.995% pure and with a O$_2$ concentration less than 200 ppm). This probe measures Eh ($\pm$5 mV), pH ($\pm$0.2), conductivity (range from 0 to 100 mS/cm, $\pm$0.001 mS/cm) and dissolved oxygen (Clark´s polographic-type sensor with a range of 0 to 20 mg/L, $\pm$0.2 mg/L). The alkalinity was measured by potenciometry with a similar methodology as the one used under atmospheric conditions (Table 1).

3.3. Analytical methods

Cations (major and trace) were analyzed in the X-RAL laboratory (Toronto, Canada) by atomic emission spectrophotometry (ICP-200) and VG-type inductively coupled plasma-mass emission spectrometry, depending on the element to be analyzed and the detection limit of the analytical technique (Table 1).

In the *Servicio Central de Análisis* of the University of Zaragoza (Spain) were analyzed the following components: (1) Aluminium was analyzed by atomic absorption spectrophotometry with graphite chamber and background correction by Zeeman effect (VARIAN SPECTRA 300/400). The detection limit is 0.0004 ppm and the standard deviation does not exceed 4%; (2) Silica and magnesium were analyzed by atomic emission spectrometry (PERKIN ELMER Mod. P40). The detection limit is 120 ppb and 1.5 ppb for Si and Mg, respectively; (3) The content of sulphides was analyzed by the iodine method (A.P.H.A., 1995). The analyses were performed with stabilized samples using Zn acetate 2N and adding 5 ml of iodine (0.025) in acid conditions. Later on, the iodine excess was assessed with a sodium tiosulphate solution (0.0251 N) using starch as indicator (Table 1).
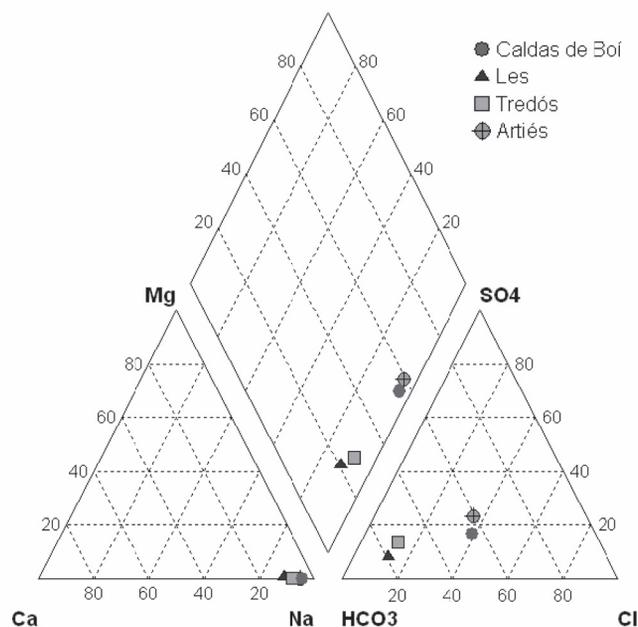
Fig. 3.- Piper diagrams of the waters from Caldas de Boí, Artiés, Tredós and Les systems. The analytical data represented in the diagrams correspond to the sampling campaigns made on July and September 1997 and July and September 1998.

Fig. 3.- Diagramas de Piper de las aguas pertenecientes a los sistemas de Caldas de Boí, Artiés, Tredós y Les. Los datos analíticos de las aguas representadas en los diagramas correspondientes a los tres sistemas proceden del muestreo de julio y septiembre de 1997 y del muestreo realizado en julio y Septiembre de 1998.

Carbon isotopic analyses were carried out in the Environmental Isotopic Laboratory of the University of Waterloo and in the Isotrace Laboratories of the Physics Department in Ontario University (Canada) by mass accelerator spectrometry (MAS), starting with 2 L of liquid sample previously stabilized with a small amount of $HgCl_2$.

$\delta^{13}C$ was determined at the University of Waterloo by mass spectrometry (VG Micromass 903).

3.4. Geochemical modeling

3.4.1. Chemical geothermometry

The temperature of the deep reservoir thermal solution was estimated by using different chemical geothermometries. The pH values of the thermal solutions in the reservoirs were calculated from the temperature values obtained, and their depth was estimated with reaction paths.

The geothermometers and the selected calibrated geothermometries, which were satisfactorily applied to similar systems in the Pyrennes (Spain), are the following:

i) Geothermometry based on the SiO_2-Quartz equilibrium, imposed by the characteristics of these geothermal systems. The studies carried out by others authors (for example Michard, 1990) in this type of systems shown that the waters with calculated temperatures below 80 ºC appear equilibrated with chalcedony and the waters with calculated temperatures around or upper 100 ºC with quartz. Therefore, we will use the SiO_2(aq)-Q geothermometer and, specifically, the calibration proposed by Fournier (1977) due to the similarity of the rest of existing calibrates; ii) Geothermometries based on the Na/K ratio: Empirical calibration proposed by Ellis (1970) or Anorsson (1983), theoretical calibration calculated from thermodynamic data for albite and K-feldspar proposed by Michard (1983) and empirical calibration proposed by Michard (1990), since give the more consistent results with the proposed temperature by the geothermometers based on the dissolved silica; iii) Geothermometry based on the Na-K-Ca relation: Empirical calibration proposed by Fournier and Truesdell (1973). In these type of alkaline water systems, this geothermometer provides consistent results with the rest of geothermometric techniques utilized (e.g. Michard et al., 1986) considering $\beta = 4/3$, even though the deep temperature exceeds the 100 ºC; and iv) Geothermometry based on the K-Ca relation: Empirical calibration proposed by Michard (1990).

3.4.2. Geochemical codes and calculations

WATEQ4F (Ball and Nordstrom, 1991), PHREEQE (Parkhurst et al., 1990) and SUPCRT98 (updated version of Johnson et al., 1992) were selected to obtain the speciation and solubility models and the reaction paths.

The calculations for the geochemical modeling in this study include: 1) Speciation-solubility calculations, and 2) Calculations for geothermometric modeling in order to determine the equilibrium, temperature and pH in the reservoir from the chemical and physico-chemical data of the upwelling waters. This type of modelling was performed with the data coming from the upwellings that best represented the conditions in depth.

4. Results

4.1. Hydrogeochemistry of the thermal waters

The geochemical characteristics of the solutions of the hydrothermal systems studied are similar to the type of alkaline waters of thermal solutions related to granitic materials (i.e. San Juan et al, 1988; Michard, 1990). These geochemical characteristics can be summarized as low mineralized waters ($<10^{-2}$ M), low content of dissolved salts (< 340 mg/L), high pH, negative redox potentials,

Na is the dominating cation, absence of a clear predominating anion, sulphur present with release of H_2S in upwelling conditions and low Mg contents in solution.

The thermal waters in the geothermal systems studied are classified as bicarbonate-chloride-sodium waters, in the case of Caldas de Boí and Artiés systems (Group 1), and bicarbonate-sodium waters, in the case of Lés and Tredós systems (Group 2) (Fig. 3).

The solutions belonging to Group 1 are more evolved from a geochemical point of view, as evidenced by a higher concentration of Cl and Na (Table 1) and by the total dissolved solids (around 330 ppm for Caldas and 290 for Artiés) in comparison with the solutions from the second group (around 180 ppm).

4.2. Deep physicochemical conditions (T and pH) of solutions

The geothermometric modeling was carried out with two geothermometric techniques: 1) Geothermometric simulation calculations, and 2) Classic geothermometry (chemical geothermometry).

A comparison study of the results obtained by both techniques was done. This enabled establishing the causes of the coincidences and discrepancies between the calculated temperatures, thus increasing the reliability of the estimation.

4.2.1. Geothermometric modeling

Inverse modeling which was satisfactorily validated in similar systems of alkaline waters flowing through granites (Michard, 1983; Michard, 1990; Arnorsson et al., 1983; Fournier and Truesdell, 1973; Fournier, 1977) was applied in this study.

The simulation was done considering an open system with respect to kaolinite, taking into account the thermodynamic data included by Michard (1983). This type of simulation was proposed by Michard´s group for similar hydrothermal systems of the French Pyrennees (Michard et al., 1979; Michard and Fouillac, 1980) and, later on, Auqué (1993) made a comprehensive study of the thermodynamic data used in the geothermometric modelling in an open system with respect to kaolinite, as well as the calculation hypothesis itself, obtaining quite consistent results.

As working assumption it has been considered the application of a geothermometric modeling to open systems based on the determination of the temperatures to which the saturation curves of the mineral phases that reach equilibrium in each system converge. These temperatures correspond to the temperature reached by the thermal solutions in the reservoir.

In figure 4 and table 2 are shown the saturation indices of the mineral phases and the temperatures of equilibrium. As observed in the figure, there are two different groups of systems as a function of the water-rock equilibrium conditions in depth. On one side, the hydrothermal systems of Caldas de Boí and Artiés, whose equilibrium condition in depth is constituted by albite, microcline, quartz, kaolinite, a laumontite-type calcium aluminosilicate and calcite. The base temperature of the system (reservoir) is 115ºC as estimated from the microcline-albite-quartz equilibrium, for Caldas de Boí and 110ºC for Artiés. In these two systems, the temperature estimated from the thermal solution-zoisite equilibrium was not considered, because this equilibrium condition was probably attained during the rise of the solutions and does not correspond to the base temperature of the system (Fig. 4) (Buil et al., 2002).

The second group is formed by Tredós and Les systems, whose equilibrium condition in depth includes kaolinite-quartz-microcline-calcite and epidote-zoisite-(Buil et al., 2002), showing a disequilibrium with respect to albite and with a base temperature of the system, calculated from the convergence situation of the microcline-quartz-zoisite, around 90ºC for Tredós system and 72ºC for Les.

The pH values corresponding to these temperatures, obtained by interpolation of the pH-T straight lines calculated with PHREEQE, are 8.4 for Caldas de Boí, 8.5 for Artiés, 8.8 for Tredós and 9.1 for Les (Fig. 5).

4.2.2. Classic geothermometry

The results obtained when applying the different chemical geothermometry (cfr. section 2.3.1.) to the most representative upwelling of each system are shown in table 3.

	Micro-cline	Albite	Quartz	Zoisite-type Alumino-silicate
Caldas de Boí	115 ºC	118 ºC	115 ºC	95 ºC
Artiés	107 ºC	113 ºC	113 ºC	92 ºC
Tredós	90 ºC	-----	90 ºC	87 ºC
Les	75 ºC	-----	72 ºC	70 ºC

Table 2.- Reservoir temperature values (ºC) in the studied geothermal systems, deduced from the mineral phases defining an equilibrium with depth.

Tabla 2.- Valores de temperatura (ºC) en el reservorio de los distintos sistemas hidrotermales objeto de estudio, deducido para las fases minerales que definen una situación de equilibrio en profundidad.
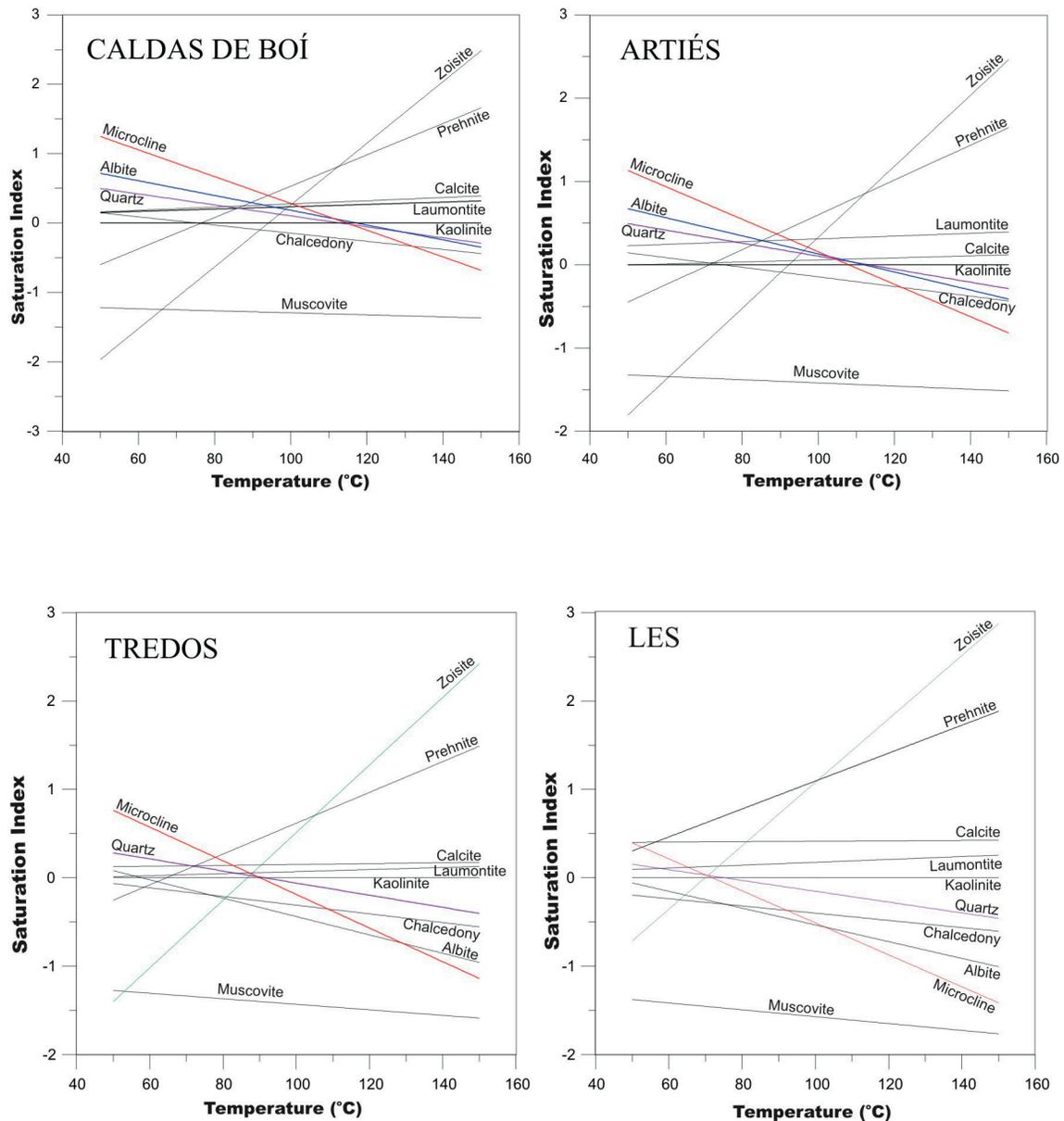
Fig. 4.- Results of the geothermometric simulation, studied as an open system for kaolinite for Caldas de Boí, Artiés, Tredós and Les.

Fig. 4.- Resultados de la simulación geotermométrica, en condiciones de sistema abierto respecto a la caolinita, para los sistemas de Caldas de Boí, Artiés, Tredós y Les.

The temperatures estimated by this technique generally show higher values than those obtained by geothermometric modeling techniques, though the differences between both techniques do not exceed 25ºC, which is an uncertainty range similar to that defined for other similar systems (e.g. Michard *et al.*, 1986).

Geothermometers based on the SiO₂-Quartz equilibrium

The temperatures obtained by applying the geothermometers based on the the SiO_2(aq)-Quartz equilibrium differ from those calculated by geothermometric modeling, since there is a high percentage of dissolved ionic silica as $H_3SiO_4^-$ at the considered pH (Tredós 44%, Les 51%, Artiés 36% and Caldas 33%). The geothermometry based on dissolved silica rests upon an univariant equilibrium determined by the reaction: SiO_2 (quartz or chalcedony) + $2H_2O \rightarrow \rightarrow H_4SiO_4$. The activity of the H_4SiO_4 species can be considered the same as the total silica value analyzed in diluted solutions with pH values less than 8.5. In hydrothermal systems, however, like the ones studied now (with pH values between 9.2 and 9.8), caution must be taken when considering the temperatures obtained by this tech-
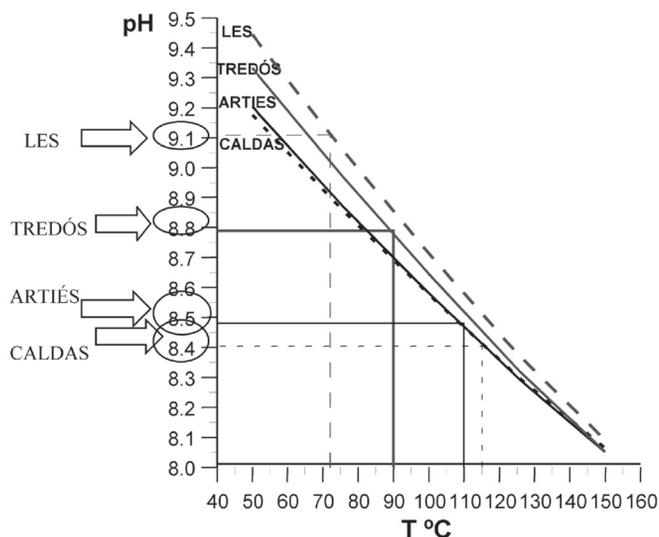
Fig. 5.- Tª-pH relationship deduced from each hydrothermal system studied.

Fig. 5.- Relaciones Tª-pH deducidas para cada uno de los sistemas geotermales objeto de estudio.

nique, since as pH increases, the ionic silica concentration ($H_3SiO_4^-$) also increases.

Nevertheless, the differences between both techniques (geothermometric modeling and SiO_2-Q geothermometry) do not exceed 25ºC (uncertainty range defined for other similar systems - e.g. Michard *et al*., 1986) being relatively low, and therefore they can be considered as acceptable temperatures for Caldas de Boí, Artiés and Tredós springs, with values which differ 7, 12 and 14ºC, respectively.

Geothermometers based on the Na/K ratio

Of all the applied geothermometric calibrations, those based on the Na-K relations are the ones that provide the best results in hydrothermal systems with alkaline waters that flow through the granites (Michard, 1983; Auqué,

1993). The reliability of this technique is based on the minerals that constitute its paths, which favor the establishment of the equilibrium relations among albite-K-feldspar-solution (Michard, 1983); and on the behaviour of the Na and K as elements controlled by an albite-K feldspar-solution equilibrium in depth, because there is no significant variations of their concentrations by reequilibrium processes during the ascent of the solutions. However, in the case of Tredós and Les upwelling, the differences between the temperatures calculated by Na-K geothermometry and geothermometric modeling are quite high, due to the lack of water-albite equilibrium in depth in both systems. The performance of an exercise to verify the equilibrium established in depth in the different hydrothermal systems using the PHREEQE code (Parkhust *et al.*, 1990), both at the temperatures obtained by geothermometric simulation and by classic geothermometry, shows that the necessary concentrations of Na, K y SiO_2 to establish equilibrium in depth among albite-microcline-quartz-kaolinite-solution are higher than those determined at upwelling conditions, around 20 % for Les and Tredós systems, and basically the same for Caldas and Artiés (Buil *et al.*, 2002; García, 2001). The thermal solution-albite disequilibrium, described in these two systems, can be attributed to the low Na and SiO_2 concentrations, which would hinder the establishment of that equilibrium at the calculated temperatures from the equilibrium established among microcline-quartz-zoisite and thermal solution.

Geothermometers based on the Na-K-Ca y K-Ca ratio

The geothermometries in which Ca is present do not seem to give coherent results either. They present significant differences with the temperatures obtained by the geothermometric calibrations and geothermometric modeling. The behavior of Ca is due to the reequilibrium processes undergone by some phases (e.g. calcite) which control this element during the rise of the thermal

	T_{eq}	SiO_2Q	Na-K	Na-K	Na-K	Na-K-Ca	**K-Ca**
		Fournier, 1977	Arnorsson, 1983	Michard, 1983	Michard, 1990	Fournier- Truesdell, 1973 ($\beta=4/3$)	Michard, 1990
CALDAS	115	122.1	98.2	110.1	95.3	90.4	93.9
ARTIES	110	122.6	87.9	101.6	87.4	78.7	82.7
LES	72	94.8	87.2	101.1	86.9	46.8	55.6
TREDÓS	90	103.8	122.8	129.8	113.9	67.8	78.0

Table 3.- Results of the SiO_2-quartz, Na-K, Na-K-Ca and K-Ca geothermometers in the thermal waters studied. The equilibrium temperatures deduced by geothermometric simulation are included.

Tabla 3.- Resultados de los geotermómetros SiO_2-cuarzo, Na-K, Na-K-Ca y K-Ca en las aguas termales estudiadas. Se incluyen las temperaturas de equilibrio deducidas mediante simulación geotermométrica para cada uno de los sistemas.

Hydrothermal Systems		Geochemical evolution	Equilb. Reservoir solution-albite	Residence time (years)	Reservoir temperature
Group I	**CALDAS DE BOÍ**		YES	$\cong$16000	115 ºC
	ARTIÉS		YES	$\cong$11700	110 ºC
Group II	**TREDÓS**		NO	$\cong$11100	90ºC
	LES		NO	$\cong$11000	72ºC
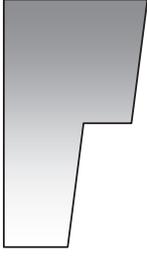
Fig. 6.- Comparison of the degree of geochemical evolution, residence time and temperature with depth for the Caldas de Boí, Artiés, Tredós and Les geothermal systems.

Fig. 6.- Comparación del grado de evolución geoquímica, tiempo de residencia y temperatura con la profundidad para los sistemas geotermales de Caldas de Boí, Artiés, Tredós y Les.

solution to the surface. Certain proximity is observed in the Tredós and Les upwelling between the temperatures obtained by the different geothermometric techniques and the calibration based on the K-Ca relation defined by Michard (1990) for this type of systems. These results could be due to an equilibrium reached in depth between a calcium aluminosilicate (which partially controls Ca in dissolution) and microcline (which controls dissolved K) (Auqué, 1993; Buil *et al.*, 2002; Buil, 2004).

4.2.3. Dating thermal solutions: Carbon isotopic analyses

In order to determine the effect of the residence time (RT) on the degree of geochemical evolution reached by the thermal solutions, as well as on the different behavior towards equilibrium with respect to albite, the thermal waters from the four systems considered were dated with ^{14}C (Table 4 – ^{14}C results were normalized to a δ^{13}C of -25‰ PDB and expressed in "percent of modern carbon"

(pMC) relative to 0.95 times the ^{14}C concentration of NBS oxalic acid (HOxI)).

Two groups of solutions were defined in terms of their RT inside the system (Fig. 6): 1) waters with RT around 16.000 years (Caldas de Boí system–16070 years-), and 2) waters with RT around 11000 years (Artiés systems –11760 years– , Tredós –11130 years– and Les –11070 years). These two groups, however, do not correspond themselves with those determined by the geothermometric modeling (Group 1: Arties and Caldas systems and Group 2: Les and Tredós systems), as a function of the degree of geochemical evolution reached by the solutions in the different systems (Fig. 6).

Thus, Tredós and Les systems, with a similar RT as Artiés (around 11000 years), are geochemically less evolved than the latter system, as evidenced by a lower concentration of dissolved solids and a disequilibrium in depth with respect to albite.

SAMPLE	CO_2 (CC STP)	δ^{13}C (‰)	^{14}C/^{12}C (pMC) (not corrected)	^{14}C/^{12}C (pMC) (corrected)	**Equivalent years (BP years)**
CALDAS DE BOÍ	5.6	-7.32	14.03 +/- 0.15	13.53 +/- 0.15	16070 +/- 90
ARTIES	7.2	-10.33	23.83 +/- 0.20	23.13 +/- 0.20	11760 +/- 70
TREDÓS	5.5	-8.44	25.89 +/- 0.21	25.03 +/- 0.21	11130 +/- 70
LES	0.7	-10.01	25.99 +/- 0.59	25.21 +/- 0.58	11070 +/- 180

Table 4.- Results of carbon isotopic analyses from the waters of the studied geothermal systems. The age of the systems is indicated on the last column.

Tabla 4.- Resultados de los análisis isotópicos de Carbono en aguas para los sistemas geotermales estudiados. En la última columna se indica la edad de los sistemas.
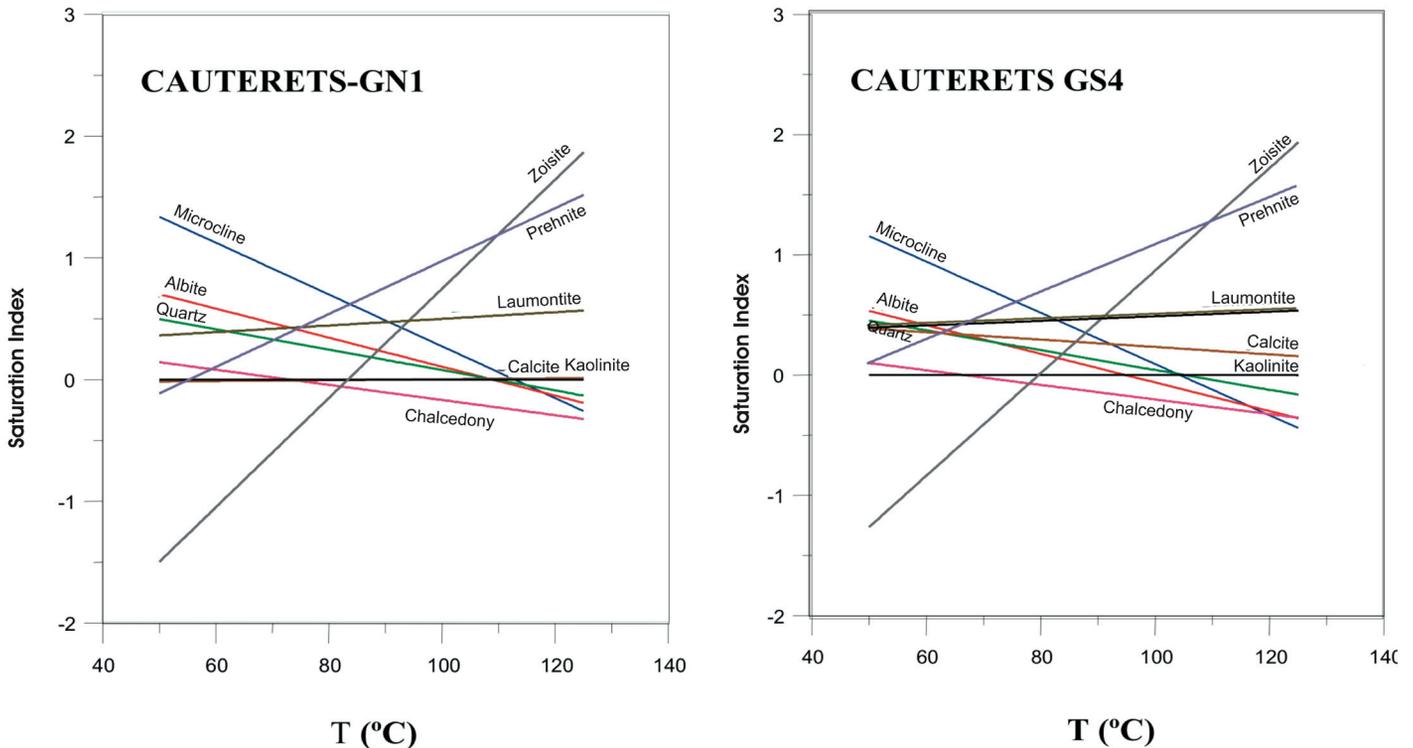
Fig. 7.- Results of the geothermometric modeling of the waters from the Cauterets system (GN1: North Group and GS4: South Group).
Fig. 7.- Resultados de la modelización geotermométrica de las aguas del sistema de Cauterets (GN1: Grupo Norte y GS4: Grupo Sur).

5. Discussion

The results obtained from the calculations made with the geothermometric modeling and dating of the thermal solutions from the four systems considered imply that the residence time is not the main control factor of the existing differences observed in the degree of geochemical evolution of the solutions of the hydrothermal systems and the equilibrium/disequilibrium conditions in depth with respect to albite.

In order to verify this statement and determine the factor(s) responsible for those differences, as well, the control performed by different factors on the final composition of the thermal solutions was evaluated.

5.1. Influence of the residence time on the geochemical evolution of the thermal waters: comparative analysis with the Cauterets geothermal system (France)

In order to evaluate the influence of the residence time on the degree of geochemical evolution reached by the solutions, a geothermometric modeling of a hydrothermal system in granites situated in the French Pyrenees was carried out. The Cauterets geothermal system has similar geological and physico-chemical characteristics to the systems studied in this paper, though with unique deep flow characteristics with respect to the residence time of the solutions present in the system. This system is formed by two groups of springs, the N group and the S group, whose physico-chemical characteristics are basically the same (Table 5), but with considerable variations concerning the residence times, 500 years for the S group and 5000 years for the N group (Soulé, 1990).

The existence of two types of springs with different residence times within the same hydrothermal system is specially interesting for the study of the physico-chemical composition of the resulting solutions and of the conditions present at depth in relation to time.

More in detail, the Cauterets system is located in the Cauterets granitoid massif and springs out in granodioritic materials, developing a U-shaped deep geothermal circuit. The thermal waters are alkaline associated with granitic materials (i.e. San Juan *et al.*, 1988; Michard, 1990a). The concentration of dissolved elements, as well as the pH, Eh, T and conductivity are very similar to the ranges found in the Caldas, Artiés, Tredós and Les hydrothermal systems.

The geothermometric models obtained (Table 5 and Fig. 7) indicate equilibrium conditions at depth for both groups of springs with albite, microcline, quartz, kaolin-

Conditions at upwelling (*)	pH	T	Na (ppm)	K (ppm)	SiO$_2$ (ppm)
Group N upwellings	9.3	46.5	2.85	0.061	1.20
Gorup S upwellings	9.2	54.8	2.26	0.047	1.10

Reservoir conditions (**)	pH	T	Na (ppm)	K (ppm)	SiO$_2$ (ppm)
Group N upwellings	8.4	(107-121)	2.82-2.87	0.051-0.064	1.22-1.50
Gorup S upwellings	8.6	(105-119)	2.23-2.34	0.041-0.052	1.20-1.51

Table 5.- Results of pH, T, Na, K and SiO$_2$ in upwelling and deep conditions (obtained by geochemical modelling) of the Cauterets system (France).
* In situ measurements made by the Water Department Laboratory of Toulousse (1985).
** Geochemical modelling of existing conditions at depth from data (*).
Tabla 5.- Resultados de pH, tª, Na, K y SiO$_2$ en condiciones de surgencia y profundidad (obtenidos mediante modelización geoquímica) del sistema de Cauterets (Francia).
*Medidas realizadas in situ en (1985) por el Laboratorio departamental del agua de Toulousse.
**Modelización geoquímica de las condiciones existentes en profundidad a partir de los datos (*).

ite and a calcium aluminosilicate, around 111ºC for the solutions belonging to group N and 100ºC for group S. Therefore, waters with very different RT (500 and 5000 years) could reach equilibrium with respect to albite, presenting a similar degree of geochemical evolution, as evidenced by their content of mobile elements and total dissolved solids. On the other hand, the solutions from the Cauterets geothermal system reach equilibrium with albite within a quite lower residence time than the Tredós and Les hydrothermal systems.

Consequently, according to the physico-chemical conditions of this type of systems situated in the Pyrenees, the required time to reach the water-albite equilibrium is lower than the residence time of the systems studied in this paper. Thus, other factors must be the ones that control the lack of albite equilibrium in depth, probably those that influence or control the water-albite equilibrium reaction kinetics.

5.2. Influence of chemical kinetics in the geochemical evolution of the thermal waters

The dissolution-precipitation of minerals represents one of the most important interaction processes, since it controls the chemical composition of the resulting solutions. The study of water-rock interaction processes requires equilibrium and kinetic models, given that the residence time of the solutions may be lower than the half life of the reactions that are generated within the system. In this case, the application of kinetic models are necessary to determine how close the reactions are to equilibrium.

In our case, in which groundwaters have very long residence times (from 11000 to 16000 years), most of the ho-
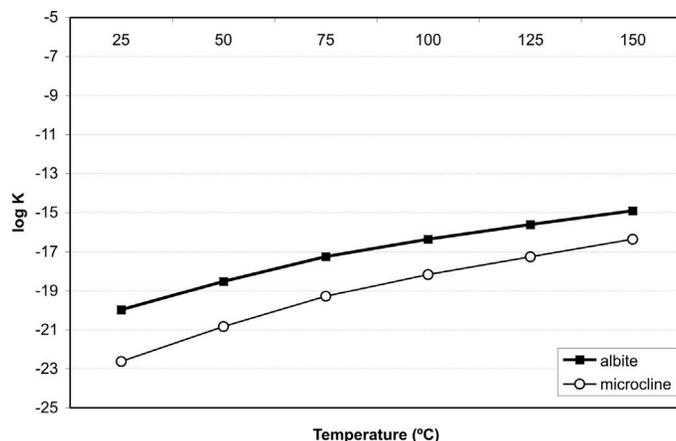
Fig. 8.- Albite and microcline stability constants (Michard, 1983).
Fig. 8.- Constantes de estabilidad de la albita y de la microclina (Michard, 1983).

mogeneous or heterogeneous chemical reactions involved are assumed to have reached equilibrium. However, in the specific case of albite dissolution, disequilibrium in depth for the Les and Tredós systems has been shown by modeling. The lack of albite equilibrium in these systems poses an important question as to which are the factors that determine the equilibrium or disequilibrium of this mineral in depth. Thus, a study related to chemical kinetic is deemed necessary.

A review of the factors that control the albite dissolution kinetics is now given, in order to explain the differences observed in these systems. An analysis of the existing differences in the thermodynamic reactions and the dissolution kinetics of alkaline feldspars was previously carried out, in order to account for the equilibrium conditions in depth with respect to microcline in all the systems, and the albite equilibrium or disequilibrium depending on the system studied.

5.3. Dissolution kinetics of alkaline feldspars

The coexistence of equilibrium and disequilibrium in the same reservoir, depending on the alkaline feldspar considered (albite or microcline) can be explained from a thermodynamic and /or kinetic point of view. Thermodynamically, the value of the equilibrium constant of the microcline dissolution reaction (KT) is lower than that for albite, at any given temperature (Fig. 8). Thus, the necessary ion concentration in solution to reach equilibrium with respect to microcline is lower than for albite. On the other hand, from a kinetic point of view, different dissolution rates of albite and microcline, under the same physico-chemical conditions of the reservoir, could account for the equilibrium/disequilibrium coexistence at depth in relation to albite and microcline.

The principal control factors of the *feldspar dissolution* are temperature, pH, Al concentration, saturation state, feldspar composition, catalytic or inhibiting effect of the organic and inorganic solutes, crystalline defects and area of surface reaction.

It is worth mentioning that the applicability of the experimental results to natural systems still poses serious difficulties. The dissolution rates obtained experimentally are 200 to 400 times higher than the ones obtained under field conditions (Swoboda-Corlberg and Drever, 1993). This discrepancy can be accounted for by the difficulty of trying to reproduce in the laboratory such factors as interaction time, the calculated reaction surfaces, crystalline defects, the effect of all the chemical components in natural solutions, biological effects, existence of coatings, etc. According to these results, the dissolved Al concentration, temperature, pH and the saturation state of the solutions with respect to the feldspar components were chosen as the main controlling factors of the feldspars dissolution rate, since their experimental values are more easily applied to field cases, and specifically, the pH and T for their vital role on the control of the dissolution rate of the minerals (Lasaga, 1994).

5.3.1. Control of aluminium in dissolution and saturation state of solutions on the feldspars dissolution rate

The main aim of many laboratory experiences, like the ones carried out by Gautier *et al*. (1994) y Oelkers *et al*. (1994), was to improve the knowledge on the control exerted by the content of dissolved Al, as well as on the saturation state of the solutions with respect to the chemical components of the feldspars. These authors studied the variation of albite and K feldspar dissolution rate as a function of the concentration of dissolved Si and Al, at temperatures and pH similar to those present in the hydrothermal systems studied in this work (Fig. 9).

The results obtained by the two authors prove that the feldspar dissolution is produced in three consecutive phases: 1) Relatively fast exchange of alkaline cations (Na, K) from the feldspars by hydrogenions of the solution in the mineral structure, 2) Reversible exchange of water by the Al in the crystalline structure, which gives rise to an early complex, with Al-poor and Si-rich mineral surface, and 3) Release of the early complex by irreversible hydrolisis of the Si-O-Si groups. Consequently, the feldspar dissolution rate is different depending on the proximity to the equilibrium conditions (Fig. 9), in such a way that under conditions far from equilibrium (subsaturation), the alkaline feldspar dissolution rate shows an inverse dependence with respect to the contents of dissolved Al, whereas under conditions close to the solution-feldspar equilibrium, the dissolution rate is inversely controlled by the concentration in solution of the components of these minerals (Gautier *et al*., 1994).

Based on the results obtained by Gautier *et al*. (1994) y Oelkers *et al*., (1994), the feldspar dissolution cannot be held responsible for equilibrium conditions with respect to microcline and disequilibrium in relation to albite for the Tredós and Les systems. This factor only gives information of the variation of the alkaline feldspar dissolution rate as it evolves towards equilibrium with the solution (solutions close to equilibrium with feldspar, less dissolution rate; subsaturated solutions with respect to these minerals, greater dissolution rate), but it does not explain why the solution reached equilibrium with microcline and not with albite, so other factors will be considered.

5.3.2. Control of pH on the feldspars dissolution rate

pH is one of the variables that mostly controls the feldspar dissolution rate (i.e. Lasaga, 1995; Hellman, 1994). All the experiments performed with K feldspar and albite, at 25ºC and within a wide pH range, show a similar behaviour concerning the variation of the dissolution rates of both minerals at acid pH. At these pHs, the dissolution rate of both minerals undergoes a proportional decrease with respect to the decrease of acidity of the solution, a minimum value being around pH 6 to 8 (Fig. 10).

The experimental results, concerning albite specifically (Fig. 10), show that pH strongly controls the albite dissolution rate at different temperatures like 100, 200 and 300 ºC (Hellmann, 1994). Generally, there is a minimum value of the dissolution rate at these temperatures at pH close to neutral (6-8), as well as a gradual increase of the
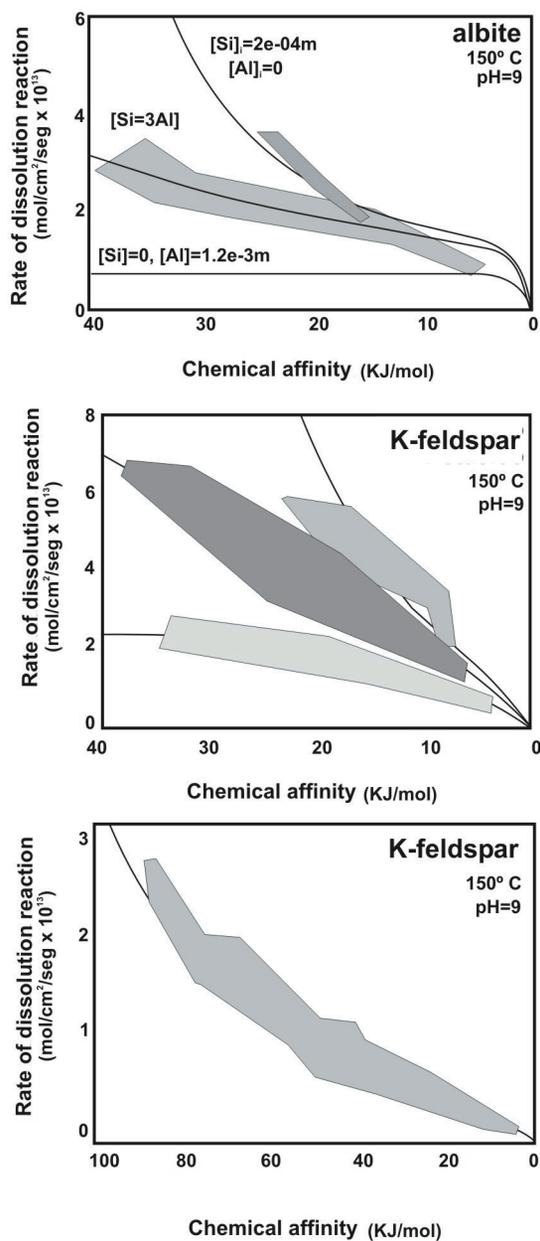
Fig. 9.- Plot showing the variation of the albite (left) and K-feldspar (right) dissolution rate as a function of the chemical affinity in solutions with variable content of Si and Al (based on Hellman, 1994).

Fig. 9.- Representación gráfica de la variación de la tasa de disolución de la albita (izquierda) y el feldespato potásico (derecha) en función de la afinidad química en soluciones con contenidos variables de Si y Al (basado en Hellman, 1994).

dissolution rate as the acidity and alkalinity of the the solutions increase.

However, the data on the variation of the K feldspar dissolution rate are more scarce in the basic regions, though the K feldspar seems to have an increase of the dissolution rate directly proportional to the alkalinity of the solutions, similar to the one undergone by albite (Blumm and Stillings, 1995).

The group of thermal solutions studied in this paper shows a slight pH variation (from 8.4 to 9.1), thus, no significant changes are expected in relation to the albite dissolution rate due to pH differences, which would explain the equilibrium/disequilibrium conditions of this mineral in the different reservoirs. Furthermore, the Tredós and Les systems present the highest pH values in depth. This would mean, according to the experimental results, that the albite dissolution rate would be greater than the one in systems that present equilibrium conditions in depth with respect to albite.

5.3.3. Control of temperature on the feldspars dissolution rate

Temperature has a significant influence on the feldspars dissolution rate. This influence is expressed by the Arrhenius equation: $K = A.e^{-Eapp/RT}$.

For any pH value, an increase of the dissolution rate with temperature is observed, though the absolute value of this increment varies depending whether it is an acid, neutral or alkaline solution. A temperature change from 50 to 100 ºC results in an increase of the albite dissolution rate, regardless of the pH of the solution with which it interacts; however, the absolute value of this increment is 2 orders of magnitude greater than for an acid solution and about 1.5 times for a basic solution (Fig. 11).

The temperature values of the solutions with residence times, in the reservoirs, of around 11000 years show significant differences, for example 110 ºC for Artiés, 90 ºC for Tredós and 72 ºC for Les. These differences can cause variations in the albite dissolution rate of up to one order of magnitude (Fig. 11). For this reason, a greater amount of albite could be dissolved in Artiés system, for the same period of time, and the Na, Si and Al concentration would be enough to reach equilibrium with albite in depth. A lower amount of albite per unit of time would be dissolved in Les and Tredós systems, where the temperatures are lower, resulting in subsaturated solutions with respect to albite in depth.

The influence of temperature on the saturation state of the thermal solutions with respect to albite is indicated in figure 12. The waters from Caldas and Artiés systems are in equilibrium with albite at the temperature present in depth (115 ºC and 110 ºC, respectively), while the solutions from Tredós and Les systems remain subsaturated with respect to albite at the temperature present at depth (90 ºC and 72 ºC, respectively), the subsaturation degree of the solutions at the springs being directly proportional to the temperature reached in the reservoir.

Finally, assuming the same conditions of temperature and pH, which are vital factors to determine the feldspar
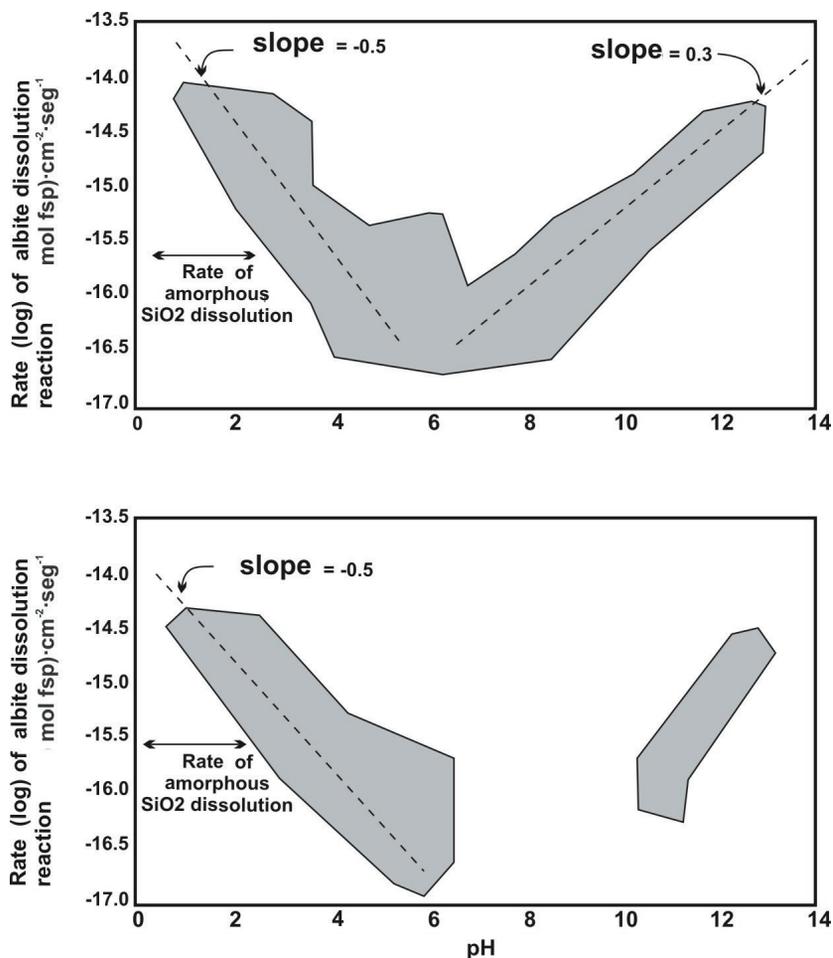
Fig. 10.- Compilation of experimental data of the albite dissolution rate as a function of pH. (based on Blumm and Stilling, 1995).

Fig. 10.- Recopilación de valores experimentales de la variación de la tasa de disolución de la albita en función del pH de las soluciones (basado en Blumm and Stilling, 1995).

dissolution kinetics, albite presents a slower dissolution kinetics (approximately one order of magnitude lower) than that for K feldspar (Blumm and Stilling, 1995) (Fig. 11). This fact, together with a value of K(T) for albite greater than the one corresponding to microcline, could account for the presence of a subsaturated solution with respect to albite and, at the same time, in equilibrium with the K feldspar in the same reservoir.

6. Conclusions

The waters belonging to the hydrothermal systems studied are alkaline-type waters related to granitic materials, and showing similar geochemical properties, such as low mineralization (lower to 10^{-2} molal), low content of dissolved salts (< 340 mg/L), significant high pH, negative redox potential, Na as predominant cation and absence of a clearly predominant anion.

The geothermometric modeling, under open system conditions, has suggested an "equilibrium state" at depth with respect to a mineral association constituted by quartz, albite, microcline, kaolinite, a calcium aluminosilicate and calcite for temperatures around 110ºC for Artiés and 115ºC for Caldas de Boí. Likewise, for temperatures of 90ºC for Tredós system and 72ºC for Les, equilibrium in depth was reached for the same mineral association as before, except albite.

These results are coherent with those obtained by the classical SiO_2-quartz and Na-K geothermometric calibration in Caldas and Artiés, and the anomalous behavior of the Na-K geothermometric calibration has been verified in Tredós and Les, since the premise albite-water equilibrium has not been met in depth.

The presence or absence of equilibrium of the solutions in depth with respect to albite, as well as the differences in the total dissolved solid content (TDS), results in dif-
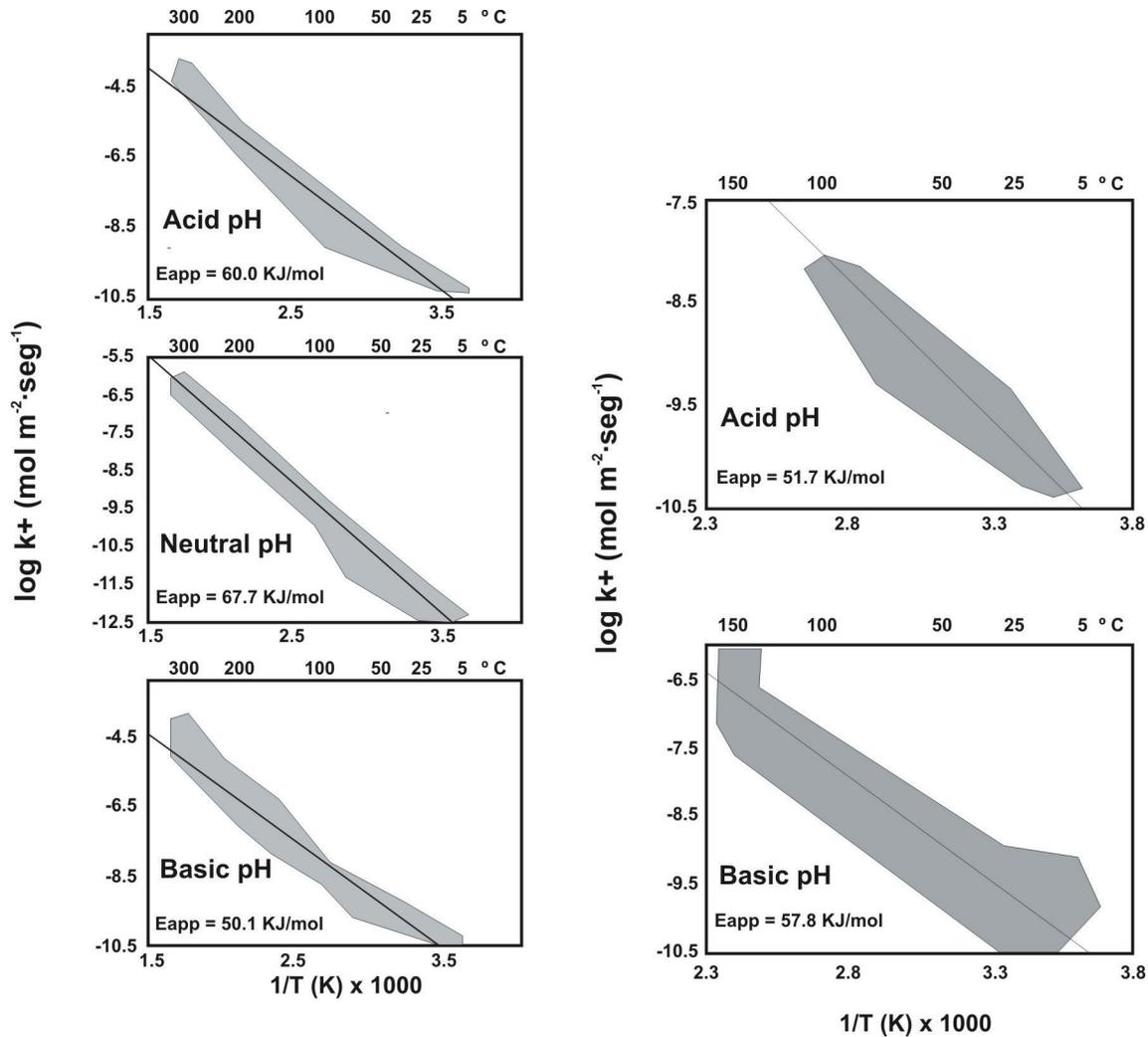
Fig. 11.- (Left): Albite dissolution rate constants (K^+) as a function of the temperature for acid, basic solutions. (Right): K-feldspar dissolution rate constants (K^+) as a function of the temperature for acid, basic solutions.

Fig. 11.- (Izquierda): Constantes de velocidad (K^+) para la disolución de la albita en función de la temperatura para soluciones ácidas, básicas. (Derecha): Constantes de velocidad (K^+) para la disolución del feldespato potásico en función de la temperatura para soluciones ácidas, básicas.
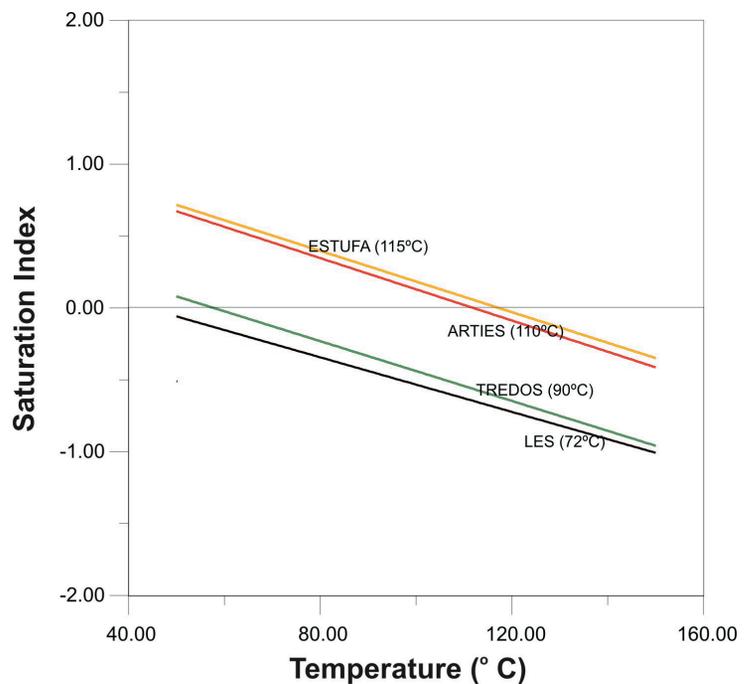
Fig. 12.- Plot of saturation state of the studied thermal solutions regarding albite, as a function of the temperature.

Fig. 12.- Representación de los estados de saturación de las soluciones termales objeto de estudio respecto a la albita, en función de la temperatura.

ferent degrees of geochemical evolution reached by the solutions in the different systems.

[14]C isotopic analyses, carried out in the thermal waters studied in this work, show that the time of residence is not responsable for the mentioned differences. This hypothesis is confirmed by the existence of systems with similar residence times (Artiés, Tredós, and Les) in which equilibrium (Artiés) and disequilibrium (Les and Tredós) states may be found in depth with respect to albite. Also, this hypothesis is further confirmed by the presence of systems, such as Cauterets, in which equilibrium in depth with albite is reached despite a much lower residence time (500 years) compared to Tredós and Les (11000 years).

The differences in temperatures reached by the thermal solutions in depth corresponding to the different systems could explain the different degrees of geochemical evolution reached even by solutions with similar residence times. A higher temperature of the solutions inside the system favors an increase of the dissolution rate of the rock-forming minerals (up to one order of magnitude for albite). This, in turn, favors an increase of the total dissolved solid concentration, which would permit the establishment of equilibrium conditions in depth with respect to certain minerals.

These results confirm the importance of the control exerted by the mineral reaction kinetics on the evolution degree of the solutions with which they interact, even in natural systems with residence times high enough to have reached equilibrium with the main minerals of the rock.

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