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Hydrogeochemical characteristics of deep groundwaters of the Hesperian Massif (Spain)

Características hidrogeoquímicas de las aguas subterráneas profundas del Macizo Hespérico (España)

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Abstract

One of the principal tasks to evaluate the safety of a deep repository for spent nuclear fuel in crystalline rocks is to characterize the chemical composition of the groundwater and to determine the water-rock interaction processes that control it. The present work includes a synthesis of the results on the site investigations carried out in Spain on hydrogeochemical characterization of different rock types (granite and schist) up to 500 m depth. The sites investigated are ancient uranium mines located in the Central-Iberian Zone of the Hesperian Massif: (1) El Berrocal (Toledo) is a granite pluton with a high fracture density and strong hydraulic gradients conditioned by the topography, which acts as a recharge zone; (2) Los Ratones (Cáceres) is a granite pluton that acts as a discharge zone of the surrounding mountain range; and (3) Sageras–Mina Fe (Salamanca) is a highly fractured schistose rock in which the recharge comes from the infiltration in the surrounding mountains, and the discharge occurs in the Águeda and Yeltes rivers, bordering to the S-NW and the NE to the mine, respectively.

The hydrogeochemical interpretations of the three sites show that Los Ratones is the most representative of prolonged water-rock interaction processes and old groundwaters. The deep waters (500 m depth) flowing through the fracture system at Los Ratones are diluted (< 500 µS/cm) and Na-HCO$_3$ type. The pH value is about 7.8 ± 0.2 and the redox potential is reduced (-242 ± 62 mV), which minimizes the concentration of dissolved uranium (or other radioelements with similar behaviour) in the groundwater. The residence time was calculated from ^{14}C. The data indicate an "age" of 1.6 x 10^4 years and, from the measurements of the noble gases in the water, a recharge mean temperature of 2-3ºC. The main water-rock reaction processes responsible of the groundwater characteristics in the three sites consist of alteration of silicates, dissolution/precipitation of carbonates and ionic exchange. In this work, a model that accounts these processes and considers each local flow system is proposed for El Berrocal and Los Ratones areas.

The results obtained for the deep groundwaters of the Hesperian Massif are compared with the data of other lithologically similar locations of Europe, Canada and Japan.

Keywords: Central-Iberian Zone, Hesperian Massif, deep groundwater, hydrogeochemistry, geochemical modeling,

Resumen

Uno de los objetivos prioritarios para la evaluación de la seguridad de un almacenamiento geológico de residuos de alta actividad en rocas cristalinas es conocer la composición química del agua subterránea y determinar los procesos de interacción agua/roca que la controlan. Este trabajo trata de ofrecer una síntesis de los resultados de las investigaciones realizadas en España sobre caracterización hidrogeoquímica de diferentes tipos de roca (granito y esquisto) hasta una profundidad de 500 m. Las zonas sobre las que se ha investigado son antiguas minas de uranio localizadas en la Zona Centro-Ibérica del Macizo Hespérico: (1) El Berrocal (Toledo), un plutón granítico con una alta densidad de fracturación y fuertes gradientes hidráulicos condicionados en gran parte por la topografía, actúa como una zona de recarga; (2) Los Ratones (Cáceres), un plutón granítico que actúa como zona de descarga de las sierras colindantes; y (3) Sageras-Mina Fe (Salamanca), un área muy fracturada, de esquistos, donde la recarga procede de las precipitaciones en las zonas montañosas del entorno y la descarga se produce en los ríos Águeda y Yeltes, límites S-NW y NE de la mina, respectivamente.

Las interpretaciones hidrogeoquímicas realizadas en las tres zonas de estudio indican que la zona de Los Ratones es la más representativa de procesos de interacción agua-roca largos y aguas subterráneas antiguas. El agua que circula por las fracturas a 500 m de profundidad en Los Ratones es diluida (<500 µS/cm) y de tipo bicarbonatada sódica. El pH está en torno a 7,8 ± 0,2 y el potencial redox es reducido (-242 ± 62 mV), lo que implica una concentración muy baja de uranio disuelto (u otros radioelementos con comportamiento similar) en el agua subterránea. El tiempo de residencia de las aguas se calculó a partir de los análisis de ^{14}C. Los datos sugieren una edad de 1,6 x 10^4 años y, de la medida de los gases nobles en el agua, se ha calculado una temperatura de recarga de 2-3 ºC. La alteración de silicatos, la disolución y precipitación de carbonatos y el intercambio iónico son los principales procesos responsables de las características de las aguas en las tres zonas de estudio. En este trabajo se presenta un modelo de funcionamiento hidrogeoquímico de las zonas de El Berrocal y Los Ratones, que considera los procesos mencionados teniendo en cuenta el sistema de flujo local.

Los resultados obtenidos para las aguas subterráneas profundas del Macizo Hespérico se han comparado con los datos de otras localidades litológicamente similares de Europa, Canadá y Japón.

Palabras clave: Zona Centro-Ibérica, Macizo Hespérico, agua subterránea profunda, hidrogeoquímica, modelación geoquímica.

1. Introduction

Many of the countries in the world that generate high-level nuclear wastes have considered the disposal in deep geological formations as the best option to manage the wastes. Consequently, big efforts combining technical developments and scientific investigations have been made in the last decades to evaluate the behaviour and safety of the geological repositories. In Spain, the Nuclear Fuel and Waste Management Company (ENRESA), which is responsible for the disposal of nuclear wastes, has supported during decades site investigation programmes to evaluate the assessment of a final disposal.

The concept of deep geological disposal involves isolating the radioactive waste from the human environment for long periods, until it presents no significant hazard (Chapman and McCombie, 2003). The knowledge of hydrogeological and hydrogeochemical conditions prevailing underground is one of the most important issues in the safety assessment of a waste repository since radionuclides released from the repository will be transported to the biosphere exclusively by the groundwater. The chemical composition of the groundwater can affect the stability of the engineered barriers and the solubility of the radionuclides. Where and when the radionuclides will finally reach the biosphere depends on the groundwater flow directions and flow rates. When ENRESA planned its investigation programmes several years ago, nothing was known about the groundwater composition in Spain at depths of a thousand meters in low permeability rocks. On the contrary, many countries with nuclear wastes had adopted the decision of storage in fully saturated conditions in crystalline areas. They excavated underground research laboratories (at depths around 500 m), with the objective of characterising the rock properties and the groundwater. Most of the information available originated from Canadian and Scandinavian Shields (e.g. Almen *et al.*, 1986; Andrews *et al.*, 1988; Nordstrom *et al.*, 1989; Laaksoharju *et al.*, 1993; Gascoyne and Kamineni, 1994; Pitkänen *et al.*, 1992, 1996, 1999; Gascoyne, 2004), and different granitic areas from Switzerland, England and Japan (e.g. Burguess *et al.*, 1982; Edmunds and Savage, 1991; Eikenberg *et al.*, 1991; Pearson and Scholtis, 1993; Kickmaier *et al.*, 1997; Iwatsuki and Yoshida, 1999; Kunimaru and Iwatsuki, 2002). Many differences in the chemical composition of groundwaters were observed. Saline waters and brines at depths from 300 to 1000 m were determined in the Swedish and Canadian Shields (Laaksoharju, 1999; Gascoyne, 2004) and in the Carnmenellis granite (South Crofty mine) of United Kingdom (Edmunds and Savage, 1991), whereas very dilute groundwater was characterized in northern Switzerland (Pearson and Scholtis, 1993) and in the Toki granite of Japan (Iwatsuki and Yoshida, 1999).

The hydrogeochemical characteristics of groundwater evolve with time due to water-rock interactions. The nature and distribution of rock formations, the structural setting and the hydrogeological system have an important influence in the spatial distribution and geochemistry of groundwaters and the results of the previous studies show that each site investigation have their own features.

The aim of this work is to present the advances on the hydrogeochemical characterization of rocks of the Hesperian Massif, in Spain. The paper describes the hydrogeochemistry of three uranium mines located in low permeability media, where ENRESA funded national and international projects in order to characterize rock properties, hydraulic conditions and hydrogeochemical characteristics of the groundwaters in different rock types (e.g. granite and schist). The three sites selected for the investigations are located in the Centro-Iberian Zone of the Hesperian Massif. Their lithological, geological and hydrogeological properties are different each other, and have been reported by Rivas *et al.* (1997), Gómez *et al.* (1997), Escuder Viruete *et al.* (2001), Gómez (2002), Pérez del Villar *et al.* (2002), Escuder Viruete *et al.* (2003a), and Escuder Viruete *et al.* (2003b).

The data obtained are of direct relevance for investigations related to the migration of radioactive substances within the groundwater and their retention into the rock. Another purpose of this study is to expose the hydrogeochemical differences between the low permeability areas in Spain and in other similar locations in the rest of the world.

2. Description of the areas

Three uranium mines located in Spain in fractured media were selected to study the hydrogeochemical properties of groundwaters. A brief description of geological features and flow direction is made as follow.

2.1. El Berrocal site

The El Berrocal site is located 90 Km southwest of Madrid, near the small town of Nombela, in the province of Toledo (Spain), at an altitude over 960 m.a.s.l. The site forms part of a granite pluton, which is in the Central part of the Centro-Iberian Zone of the Hesperian Massif (Julivert *et al.*, 1972), close to the contact between Sierra de Gredos and the Tajo River Tertiary basin (Fig. 1A). The pluton hosts a number of uranium mineralizations, at least two of which were considered economic and were mined over a period of several years, until late 1960's. One of the larger ore-bodies was the focus of the international El Berrocal Project. This ore-body consists of a sub-vertical

2 m thick U-rich quartz vein (UQV), which belongs to the N100-110E fracture family. Nineteen boreholes were drilled down to depths of between 70 and 250 m, and one of these was subsequently deepened to 609 m. Groundwater samples come from 60 to 489 m depth. Most of the efforts presented in this work are focused at site scale ($\approx$ 100 m x 100 m), around the UQV. Details about the geology of the site can be found in Varea and Iglesias (1981), Pérez del Villar and de la Cruz (1989) and Pérez del Villar *et al.* (1992).

Groundwater flow on a regional scale follows the shape of the pluton, being radial distributed when viewed in plan. Recharge takes place mainly in areas of high altitude and discharge at lower boundaries of the system. However, flow paths are not homogeneously distributed due to the presence of faults. At the site scale, preferential flow zones are the quartz veins and the major fractures, which carry most of the water. Infiltration occurs at a rate of around 80 mm/year and takes place through the altered granite zone, which is about 10 m thick (Carrera *et al.*, 1997).

From a petrographic point of view, the main granite facies was classified as a weakly altered alkaline-feldspar granite with two micas, muscovite being dominant over biotite The accessory mineral association is very complex: ilmenite, zircon, monazite, xenotime, apatite, uraninite, cassiterite and primary sulphides (Pérez del Villar and de la Cruz, 1989). The geochemical features indicate highly evolved hypocalcic granite, enriched in silica, phosphorous and alumina. This granite is fertile in uranium and belongs to the ilmenite granite series or to the S-type granites (Pérez del Villar *et al.*, 1994). The granite adjacent to the N100-110ºE fracture system is affected by a low temperature hydrothermal alteration process that has led to the chloritisation of biotite, the sericitisation and illitisation of albite and less intensively of K-feldspars.

2.2. Los Ratones Mine

The Los Ratones mine is located in the Albalá Granitic Pluton (Cáceres, Spain) (Fig. 1B) in the Centro-Iberian Zone of the Hesperian Massif (Julivert *et al.*, 1972), at an altitude over 450 m.a.s.l. This pluton is a concentrically zoned body, elongated in the N-S direction, with biotitic, porphyritic granites at the rim and fine-grained two-mica leucogranites the core. Rb-Sr dating studies suggests an intrusion date of some 302±4 Ma. The uranium dyke contains tin, tungsten and phosphorous deposits genetically related to the most differentiated leucogranitic host rocks (Reguilón *et al.*, 1996). The main geological feature of this area is the North Fault, a 5-20 m-wide brittle fracture located at the northern edge. Two NNE-SSW sub-vertical
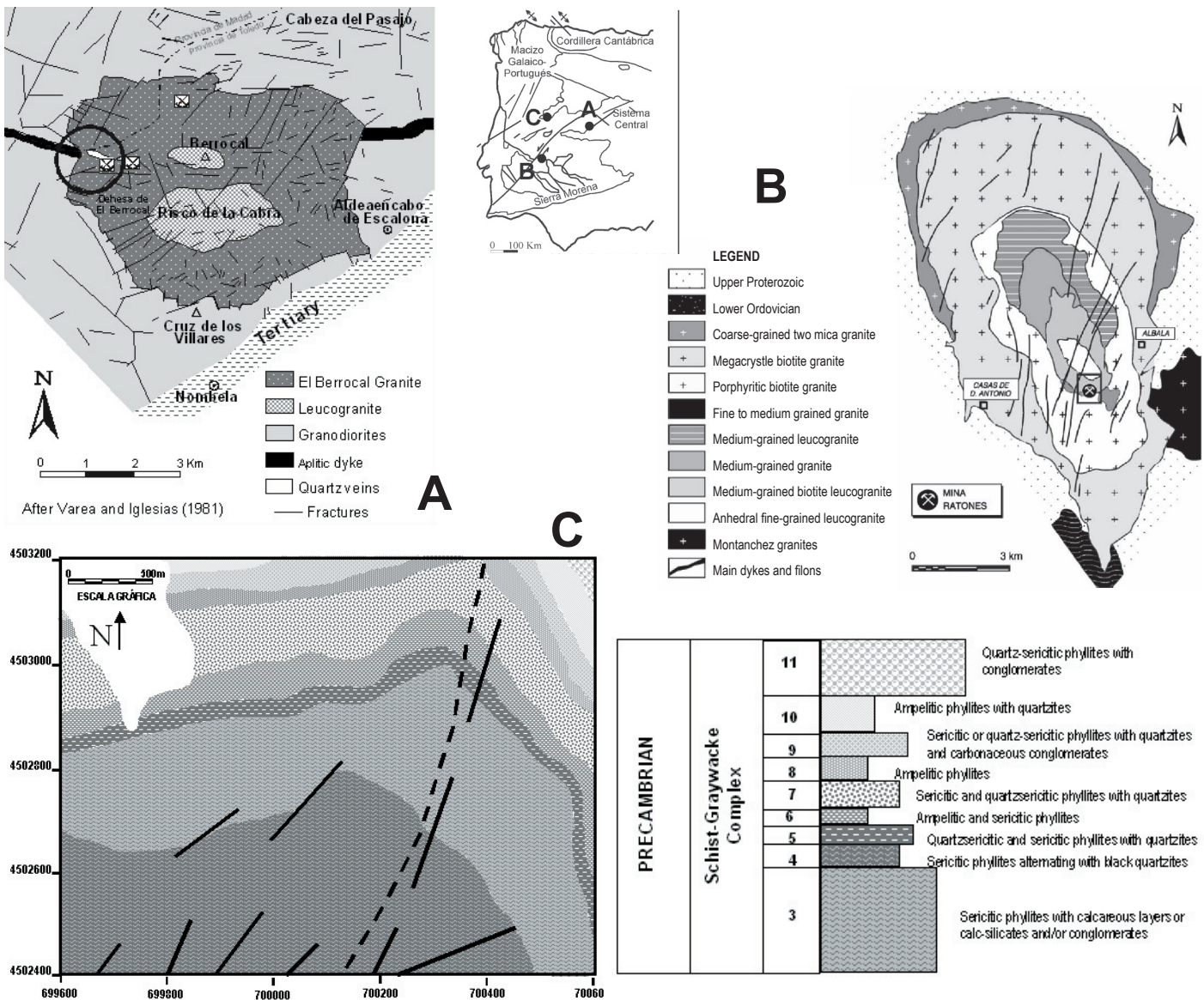
Fig. 1.- Location map of the three Spanish uranium mines. A: El Berrocal (Toledo), B: Los Ratones (Cáceres) and C: Sageras-Mina Fe (Salamanca).
Fig. 1.- Mapa de situación de las tres minas de uranio españolas. A: El Berrocal (Toledo), B: Los Ratones (Cáceres) y C: Sageras-Mina Fe (Salamanca).

trending dykes (27 and 27') intersecting the North Fault at right angles were mined between 1955 and 1975. These contain quartz and sulphide veins and are characterized by a collection of uranium minerals such as pitchblende, coffinite, uraninite and black U-oxides (parapitchblende) (Arribas, 1962), being the pitchblende usually replaced by sulphides, especially pyrite and melnikovite. SEM observations showed evidence of secondary uranium minerals such as autunite, saleeite, coffinite, phosphouraninite, and uranotile. Towards the southern edge of the study area, an inclined and broad fault zone known as the South Fault splits into three branches towards the northeast (Escuder Viruete *et al.*, 2003a).

The N-S-trending dykes and the NE-SW fractures, which intersect the mine in its northern half, form the surrounding recharge area. The groundwater gradient at

the northern zone of the mine along dyke 27 is estimated to be 0.11, while in the E-W direction the gradients are in the order of 0.03-0.06 (Ortuño *et al.*, 1999). After the sealing of the ventilation shaft through which water discharge to the surface took place, discharge began - and continues to occur - underground through dykes 27 and 27´ towards the South Fault. After passing through the weathered zone, it moves towards the Maderos stream. Since the South Fault, along which this stream flows, is deeper than the mine (Escuder Viruete *et al.*, 2003b), it has been assumed that practically all discharge, even from the deepest galleries, is drained through this structure. Good connectivity between the mine and the South Fault across the dykes has been identified (Ortuño *et al.*, 1999).

Five boreholes were drilled around the mine in order to make a comprehensive hydrogeological and hydrogeo-

chemical study of the water circulating through the main structures. Groundwater samples come from 24 to 469 m depth.

2.3. Sageras-Mina Fe

The Mina Fe uranium-ore deposit is the most important mine worked in Spain. Sageras area is located at the north part of the Mina Fe, over the same ore deposit but the uranium deposit was not mined. The mine is located 10 Km northeast of Ciudad Rodrigo (Salamanca) at an altitude over 650 m.a.s.l. The uranium mineralization is related to faults affecting the metasediments of the Upper Proterozoic to Lower Cambrian schist–graywacke complex (CEG) (Fig. 1C), located in the Centro-Iberian Zone of the Hesperian Massif (Julivert *et al.*, 1972). The CEG consist of a metamorphosed sequence of carbonaceous pelitic and fine-grained psammitic rocks. The main rock types are slates, quartzites, conglomerates, and sericitic and chloritic phyllites and schist, with some interbedded calc-silicate rocks (Martín-Izard *et al.*, 2002). The principal groups of veins strike N-S, ENE-WSW, E-W and NNE-SSW and the main uranium-bearing veins belong to these fracture families. The primary uranium minerals are uraninite and coffinite but numerous secondary uranium minerals have been formed as a result of the weathering processes: yellow gummites, autunite, metaautunite, torbernite, saleeite, uranotyle, ianthinite and uranopilite (Arribas, 1975).

The water flow at regional scale is controlled by the topography. Recharge takes place mainly in the surrounding mountains (Sierra Peña de Francia) and discharge at fluvial courses, mainly Agueda and Yeltes rivers, boundaries S-NW and NE of the area, respectively. However, at the site scale the mine is located relatively far away from the recharge zone and close to the rivers, which act as a discharge zone. Deep flows (lower than 100 m depth) should be upwards due to the river vicinity, with flow directions towards the W, NW or N. Infiltration occurs at a rate of around 100 mm/year and takes place through the slates, which are about 16 m thick (AITEMIN, 1998).

In Sageras-Mina Fe there are more than 100 boreholes drilled to investigate the mineral resources of the deposit. 35 boreholes were selected in order to analyze the chemical composition of groundwaters based on their depth and situation around the uranium ore. Groundwater samples come from 50 to 150 m depth.

Take notice of all the figures represented in this paper are expressed in meters above sea level (m.a.s.l.), so that the three field sites, with different altitudes (El Berrocal is a recharge area at an altitude over 960 m.a.s.l.; Los Ratones is a discharge area at an altitude over 450 m.a.s.l.

and Sageras-Mina Fe is an intermediate zone at an altitude over 650 m.a.s.l.), can be accurately compared. However, in the text we always refer to depth to easily locate the samples with respect to the ground level.

3. Sampling and analytical procedures

One of the main objectives of the sampling program of the groundwater was to collect representative samples with a minimum of disturbance caused by drilling works, or other types of activities. Once the drilling of the borehole is finished, the selected sections were isolated using a double packer assembly in order to avoid the mixture between groundwaters from different hydraulic heads (Fig. 2). The packers were inflated and the drilling fluid was removed from the packed-off interval and replaced by flowing groundwater. Groundwater samples were collected from the selected intervals by pumping water with an electric pump from the borehole to a flow cell isolated from the atmosphere. Inside the flow cell, pH, temperature, Eh, specific conductance and dissolved oxygen were measured. All the electrodes were connected to a multiparametric probe (Hydrolab Datasonde 4) with which physico-chemical parameters were recorded. Measurements of pH were made with a glass sensor calibrated at the sample temperature using pH 4 and pH 7 buffers. The error of pH measurements was ± 0.2 pH units. The redox potential was measured with a platinum electrode and a calomel reference electrode. ZoBell's solution (220 mV at pH = 7) was used as a standard to verify the measured values. Several days (and sometimes several weeks) of uninterrupted pumping were needed to obtain stable Eh data from each section of the boreholes. When the Pt electrode gave readings within a range of ± 5 mV, the steady state potential was regarded as having been reached and data were collected. Specific conductance measured using four graphite electrodes ranged from 0 to 100 mS/cm with a deviation lower than 0.01 mS/cm. Measurements of dissolved oxygen were made with a Clark Cell calibrated at the same atmospheric pressure and temperature as the sample point. The detection limit is 0.01 mg/L.

All the samples were filtered through 0.45 µm filters, and pumped into a glove box inside a mobile laboratory (Fig. 2), to preserve the anoxic conditions of the samples and for in situ chemical characterization of the most sensitive parameters to alteration. Preservation of samples for further analysis in the laboratory was undertaken according to the constituents under analysis. Ultrapure hydrochloric acid was used to bring the water samples to pH <1.5 for determinations of Fe(II) and Fe(III). Major cations and trace elements were determined after bringing the samples to pH <1.5 with ultrapure nitric acid. Non-acidified
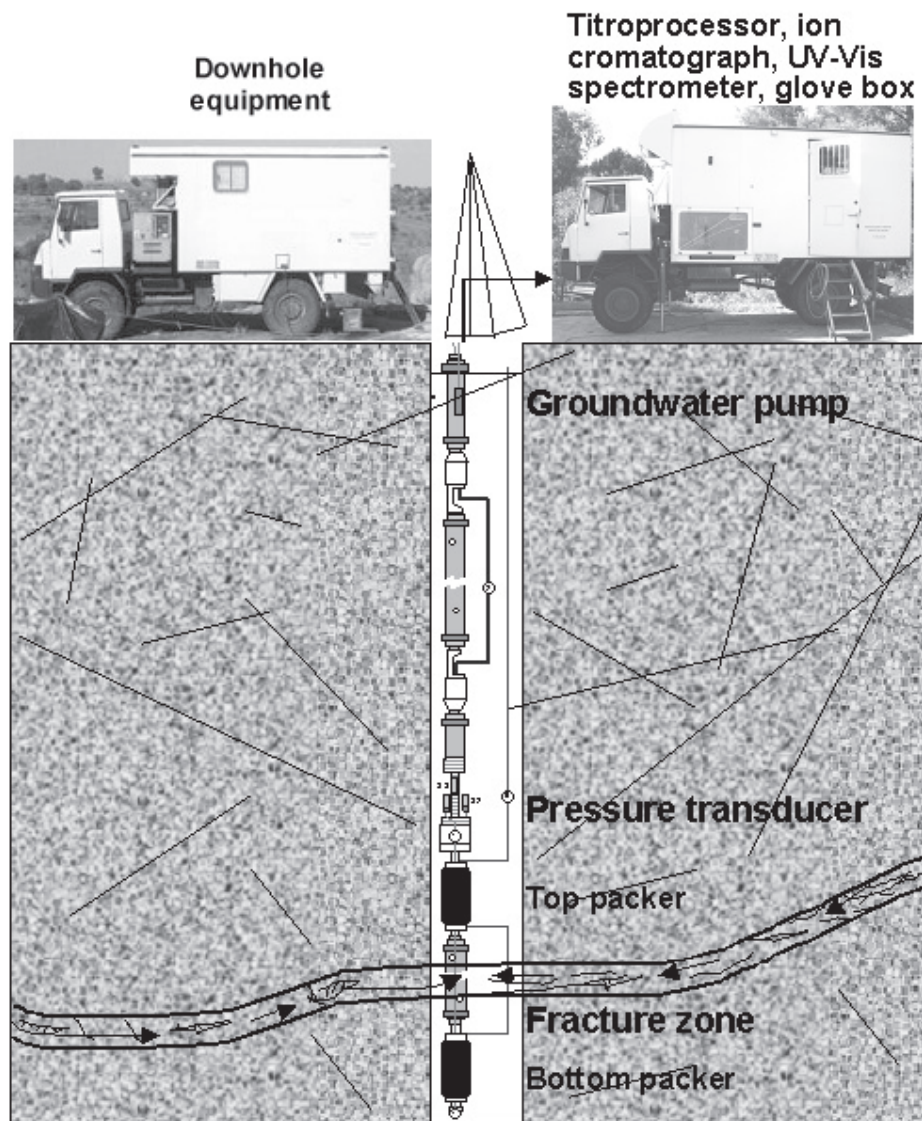
Fig. 2.- Schematic picture showing the groundwater sampling procedure and mobile hydrogeochemical labotarory.
Fig. 2.- Esquema del procedimiento de muestreo de agua subterránea y del laboratorio de la unidad móvil de caracterización hidrogeoquímica.

samples were used to determine anion and silica concentrations. The samples were transported to the laboratories in a thermostatic box at 4 ºC.

The mobile laboratory was developed in the framework of the El Berrocal project (1994) and represents state of the art for sampling and in situ characterization of groundwaters. Since 1994, the mobile laboratory has been used in all international and national projects where ENRESA and CIEMAT have been involved. The equipment of the mobile laboratory has been described in Gómez *et al.* (1994) and the major chemical parameters of the waters and many trace elements can be determined in situ.

Common anions (Cl^-, Br^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}) were analyzed by ion chromatography (U.S. EPA Method 300.1). Na, Li and K were determined by flame emission spectroscopy. The main cations and some trace elements were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Trace and ultratrace elements were determined using a Finnigan MAT SOLA quadrupole ICP-MS apparatus. Fluoride and ammonia were determined by a potentiometric method, with Ion Selective Electrodes. The alkalinity of the waters was determined in the field inside the glove box at the mobile laboratory by a potentiometric Titroprocessor Methrom 670 with inflection point detection. Total silica was determined by the ammonium molybdate colorimetric method, whereas Fe(II) and total Fe were analysed by the Ferrozine colorimetric method (ASTM, 1981).

Data quality was assessed using charge balance calculations, replicate samples and sample blanks. The charge balance calculation was used to check the data quality as explained in Freeze and Cherry (1979). According this convention, the error in the charge balance should be <10%.
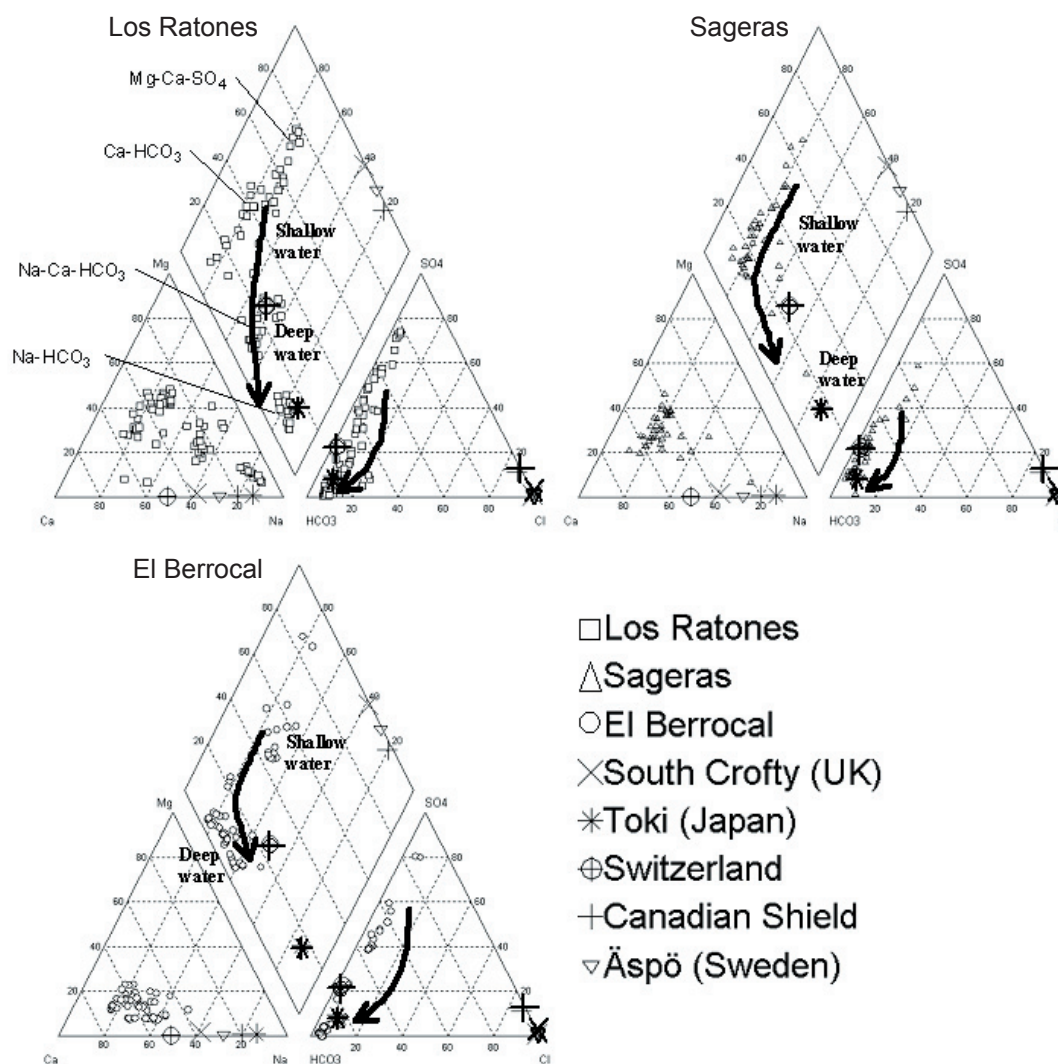
Fig. 3.- Piper triangular diagrams representing the composition of groundwaters from Los Ratones granite (Gómez, 2002), El Berrocal granite (Gómez *et al.*, 1997), Sageras-Mina Fe (Gómez *et al.*, 2003), South Crofty mine (United Kingdom) (Edmunds and Savage, 1991), Toki granite (Japan) (Iwatsuki and Yoshida, 1999), Grimsel granite (Switzerland) (Pearson and Scholtis, 1993; Garralón *et al.*, 2004), Canadian Shield (Gascoyne, 2004), and Äspö (Sweden) (Laaksoharju, 1999).

Fig. 3.- Diagramas triangulares de Piper representando la composición química de las aguas subterráneas del granito de Los Ratones (Gómez, 2002), del granito de El Berrocal (Gómez *et al.*, 1997), de Sageras-Mina Fe (Gómez *et al.*, 2003), de la mina South Crofty (Reino Unido) (Edmunds and Savage, 1991), del granito de Toki (Japón) (Iwatsuki and Yoshida, 1999), del granito de Grimsel (Suiza) (Pearson and Scholtis, 1993; Garralón *et al.*, 2004), del Escudo Canadiense (Gascoyne, 2004), y de Äspö (Suecia) (Laaksoharju, 1999).

4. Results and discussion

4.1. Compositional variations of major ions

Groundwaters were sampled from 19 boreholes in El Berrocal, 5 boreholes in Los Ratones mine and in 35 boreholes in Sageras-Mina Fe area. A number of 178 intervals were analyzed. Only the results with acceptable charge balance and lack of tracers used during drilling activities were included in the final data set. The analytical results

of the groundwaters in Tables 1 to 3 are represented in the Piper diagrams of figure 3, where the chemical evolution trend along the flow paths are indicated by arrows.

In general, the chemical composition of waters is consistent with the local flow paths based on the hydraulic head values in each site. The water quality changes in the three areas from Ca-HCO$_3$ type near the surface via Na-Ca-HCO$_3$ type at medium depth to Na-HCO$_3$ type at 465m depth. Another type of water was detected in some boreholes that intersect the uranium mineralization ex-

SAGERAS-MINA FE Sample name	Date	Zone elevation (m.a.s.l)	EC (µS/cm)	pH in situ	O2 mg/l	T (ºC)	Eh (mV)	HCO3- mg/l	F- mg/l	I- mg/l	Cl- mg/l	Br- mg/l	NO3- mg/l	SO4 mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Fe2+ ppb	Fe mg/l	SiO2 mg/l	Li mg/l	U ppb	3H T.U	As ppb	Sr ppb	Zn ppb	Mn mg/l	Charge Balance (%)
SG13	7/5/03	603.0	601	7.14	0.21	16.0	-54	343	0.46		6.0	0.02	1.88	25.1	67.0	19.0	18.0	1.90	<50	0.05		0.06	569	3.27	10	630	<50	0.07	9.6
SG16	25/6/02	668.6	104	6.22	0.60	15.5	190	47			2.1	<0.02	1.40	11.0	9.2	2.8	10.0	1.40		0.03			17			60	190	<0.03	-6.2
SG2	7/5/03	606.6	590	7.23	0.85	16.0	-136	223	0.17		6.1	0.02	0.94	87.9	45.0	18.0	39.0	2.80	152	0.48		0.04	215	2.89	31	1100	<50	0.15	3.3
SG20	6/5/03	599.5	541	7.38	0.27	15.9	-176	229	0.31		5.3	0.02	0.07	67.3	47.0	13.0	25.0	2.20	2300	2.50		0.05	1100	3.53	105	810	<50	0.17	9.5
SG22	27/6/02	630.0	315	7.10	0.18	15.7	-110	202			5.3	<0.02	0.10	17.0	35.0	11.0	19.0	2.30		0.06			33			200	70	0.06	8.0
SG24	6/5/03	611.0	651	7.02	1.25	15.7	51	329	1.24		7.2	0.04	22.85	31.2	84.0	16.0	17.0	1.40	<50	0.05		0.05	159	7.27	35	310	150	<0.03	6.7
SG26	26/6/02	613.3	670	6.70	0.66	15.9	-330	358			10.1	<0.02	0.10	36.0	56.0	31.0	29.0	3.20		0.33			60			810	<50	0.33	3.3
SG29	29/10/02	628.2	378	7.59	0.12	15.7	-135	253	0.31	0.06	16.0	<0.02	0.10	22.0	47.0	18.0	22.0	1.80	350	0.37	27.20	0.05	1000	3.14	8	609	43	0.40	5.0
SG34	8/5/03	591.0	789	7.10	0.36	15.9	-330	240	0.54		14.5	0.05	0.08	59.6	53.0	12.0	47.0	2.00	401	0.41		0.06	1100	3.26	26	490	<50	0.33	-1.9
SG38	26/6/02	623.0	370	7.24	0.08	15.5	-120	244			7.4	<0.02	0.10	21.0	40.0	22.0	22.0	1.50		0.07			1190			420	210	0.39	-3.0
SG38T1	29/10/02	607.4	352	7.35	0.93	15.7	-109	246	0.24	0.03	8.1	<0.02	0.10	21.0	45.0	14.0	21.0	1.60	<50	0.05	30.50	0.05	1200	2.76	21	534	23	0.39	8.3
SG38T2	29/10/02	630.3	331	7.37	0.50	15.3	-203	233	0.23	0.02	11.0	<0.02	0.10	14.0	36.0	13.0	22.0	2.60	240	0.24	28.60	0.04	165	3.19	7	384	12	0.30	0.2
SG40	29/10/02	615.4	376	7.43	0.09	15.6	-110	241	0.45	0.04	14.0	<0.02	0.10	39.0	51.0	15.0	21.0	2.10	1100	1.20	27.80	0.05	569	3.70	50	393	41	0.38	8.3
SG41	25/6/02	600.0	630	6.80	0.49	16.1	-140	251			8.7	<0.02	0.10	88.0	53.0	31.0	23.0	3.00		9.90			65			540	<50	0.88	-6.6
SG41BIST1	24/10/02	613.5	401	7.44	0.19	15.4	-101	274	0.36	0.03	9.7	<0.02	0.61	35.0	53.0	20.0	27.0	2.00	866	0.89	27.70	0.05	4200	3.07	25	817	179	0.46	-0.1
SG43T1	29/10/02	612.2	378	7.35	0.08	15.2	-136	240	0.51	0.03	12.0	<0.02	0.10	50.0	52.0	19.0	18.0	1.40	<50	0.06	28.70	0.04	7700	4.16	17	386	43	0.16	7.5
SG47	30/10/02	622.4	414	7.40	0.08	14.9	-127	258	0.41	0.02	15.0	<0.02	0.10	48.0	58.0	17.0	22.0	1.80	472	0.51	27.80	0.06	894	3.41	24	550	163	0.67	7.0
SG49	27/6/02	612.0	880	6.99	0.13	15.6	-106	379			26.0	<0.02	0.10	181.0	87.0	50.0	52.0	23.00		6.80			248			1100	<50	0.64	-7.3
SG5	7/5/03	606.0	419	7.09	0.21	15.9	-17	251	0.33		5.1	0.02	0.19	40.3	58.0	11.0	18.0	1.90	50	0.06			1200	4.99	16	270	<50	0.37	9.6
SG50	25/6/02	630.0	720	6.80	0.27	14.9	-70	190			36.0	<0.02	0.10	191.0	68.0	49.0	29.0	1.80		2.30			406			760	<50	0.26	-8.2
SG52T1	23/10/02	618.0	685	7.20	0.09	15.6	-151	264	0.30	<0.02	33.0	<0.02	0.10	170.0	80.0	43.0	48.0	3.50	4600	4.60	21.50	0.08	76	3.31	14	1700	20	0.80	-8.2
SG52T2	23/10/02	637.5	585	7.31	0.29	15.2	-81	229	0.28	<0.02	35.0	<0.02	0.30	128.0	70.0	36.0	38.0	2.40	261	0.28	19.40	0.07	775	3.95	3	1800	67	0.45	-9.4
SG53	23/10/02	620.3	717	7.55	0.06	14.9	-127	284	0.30	0.02	53.0	<0.02	0.10	157.0	85.0	45.0	47.0	2.80	1400	1.50	25.90	0.10	2700	2.22	57	1600	28	0.22	-6.8
SG54	23/10/02	611.0	717					374	0.24	<0.02	20.0	<0.02	0.10	95.0	88.0	39.0	32.0	2.50	298	0.30	31.90	0.07	149	5.88	2	1100	5	0.78	-3.9
SG55	27/6/02	600.0	1250	6.70	0.30	15.8	-196	656			19.0	<0.02	0.10	72.0	73.0	41.0	125.0	5.60		2.90			50			570	<50	0.53	0.9
SG58T2	8/5/03	631.0	953	6.45	0.11	15.7	-45	81	0.10		13.9		0.32	117.5	36.0	14.0	15.0	1.50	1200	1.30		0.04	63	4.57	6	320	<50	0.32	8.8
SG61	26/6/02	624.0	365	6.70	0.11	15.8	-220	225			16.0	<0.02	8.80	2.4	36.0	21.0	22.0	1.60		2.60			8			180	<50	0.94	-6.2
SG64	8/5/03	604.5	1116	6.69	0.11	15.7	-351	501	0.08		15.0		2.17	118.9	126.0	36.0	38.0	7.50	404	0.41			17	3.97	35	1300	<50	0.56	0.9
SG66	23/10/02	609.6	580	7.21	0.16	15.8	-312	359	0.29	<0.02	9.2	<0.02	0.10	76.0	76.0	34.0	31.0	2.10	300	0.32	34.80	0.05	183	3.15	28	581	6	0.94	-2.9
SG70	7/5/03	622.0	369	6.61	0.27	14.3	-64	155	0.45		5.7		11.47	47.0	35.0	12.0	14.0	1.20	2800	2.80		0.04	99	3.85	8	210	60	0.34	9.0
SG73	24/10/02	618.3	626	7.49	0.12	15.4	-117	463	4.10	0.02	14.0	<0.02	0.10	59.0	44.0	8.1	170.0	8.40	6800	7.00	18.10	0.05	90	1.56	11	402	24	0.77	-9.8
SG9	7/5/03	602.0	510	7.22	0.34	16.0	-74	279	0.30		4.5	0.02	0.43	29.4	59.0	14.0	21.0	1.90	66	0.08		0.05	2800	2.94	47	620	<50	0.24	5.7

Table 1. Analytical data for groundwaters in Sageras-Mina Fe.
Tabla 1. Datos analíticos de las aguas subterráneas de Sageras-Mina Fe.

ploited during the mining time. The percolation of the rainwater through the mineralized dykes produces the oxidation of sulphides present in the dykes such as pyrite and arsenopyrite, since the recharge water contains approximately 6 mg/L of dissolved oxygen. These waters are sampled at different depth and the chemical composition is Mg-Ca-SO_4 type water. The neutral conditions of the water (pH = 6.8-7.5) show that their origin are not influenced by the mining works or by the typical acid drainage caused by the leaching of the tailings.

In general, the waters sampled in Los Ratones and in El Berrocal sites are dilute ranging from 100 to 700 µS/cm. In Sageras-Mina Fe area the electric conductivity of the water is higher than in the other two sites investigated, being up to 1250 µS/cm.

Shallow and intermediate groundwaters are neutral (pH = 7.0-7.4) in the three uranium mines. The distinctive composition of the groundwaters sampled from most of the boreholes of El Berrocal (60 to 489 m depth) and Sageras-Mina Fe (up to 100 m depth) is Ca-HCO_3 type.

Ca-HCO_3 type waters evolve to Na-Ca-HCO_3 type groundwaters, which represent the intermediate to deep zone (100-150 m) at Sageras-Mina Fe and Los Ratones (100-200 m depth). At 450 m depth the waters are Na-HCO_3 type, as those sampled at Los Ratones. It must be also pointed out that Cl in all type of waters is not a significant component.

In figure 3 five-groundwater compositions from granitic locations of Europe, Canada and Japan are included. All of them were sampled at depths ranged between 480-

LOS RATONES Sample name	Date	zone elevation (m.a.s.l)	EC (µS/cm)	pH in situ	O2 mg/l	T (ºC)	Eh (mV)	HCO3- mg/l	F- mg/l	I- mg/l	Cl- mg/l	Br- mg/l	NO3- mg/l	SO4 mg/l	S2- mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Fe2+ ppb	Fe mg/l	SiO2 mg/l	Li mg/l	U ppb	3H T.U	As ppb	Sr ppb	Zn ppb	Mn mg/l	Charge Balance (%)
Shaft	9/5/01	464.8	343	6.96		17.8	-83	118	1.50	<0.02	11.0	<0.02	0.16	48.0	1.9	29.7	11.0	14.0	3.53	14167	15.30	31.27	0.09	13	3.85	1533	74	12	2.57	1.1
Main Shaft	3/4/01	476.6	377	6.60	0.20	19.3	-120	96	1.40	0.02	11.0	<0.02	<0.1	58.3	2.5	29.3	11.7	15.3	3.63	16667	18.90	33.20	0.09	4	3.62	1100	76	22	2.10	10.7
SR1-T1	21/3/01	419.0	485	7.00	0.10	16.0	-200	243	1.67	0.03	7.9	<0.02	<0.1	41.7	2.	35.0	26.3	21.0	2.80	13600	16.13	34.57	0.16	18	4.03	2600	70	33	2.63	0.6
SR1-T2	21/9/00	440.5	530	7.05	0.00		-200	87	0.33	<0.02	9.0	<0.02	2.60	210.0		30.0	30.0	35.0	2.70	312	2.50	36.50	0.23	6	6.89	65	123	8	0.91	-8.1
SR1-T3	28/3/01	462.2	590	7.30	0.12	15.5	-160	99	0.40	<0.02	11.3	<0.02	10.13	180.0	1.5	36.7	31.7	33.0	3.87	3600	4.10	32.20	0.24	6	6.14	93	120	334	1.90	5.8
SR2-T1	3/4/01	441.8	152	7.75	0.10	16.0	-190	64	0.42	<0.02	5.4	<0.02	<0.1	13.7	1.5	3.3	5.9	21.0	1.10	411	0.63	60.43	0.22	<1	10.97	125	8	474	0.31	6.1
SR3-T1	29/3/01	332.0	300	8.40	0.10	14.5	-275	163	0.26	<0.02	8.5	<0.02	<0.1	16.3	1.5	16.0	8.2	39.0	1.80	649	0.67	22.43	0.29	1	3.50	152	89	38	0.16	-1.1
SR4-T1	13/3/01	388.6	710	6.70	0.10	17.0	-200	225	0.32	0.02	7.2	0.50	<0.1	173.0	1.3	44.0	37.3	50.0	2.77	4933	5.07	47.23	0.42	44	4.75	219	112	32	0.77	1.3
SR4-T2	15/3/01	423.3	650	7.50	0.10	17.0	-225	168	0.48	0.02	7.6	0.22	<0.1	174.3	1.3	39.0	35.3	45.7	2.00	2000	2.30	47.57	0.36	45	4.65	241	96	138	1.10	4.5
SR4-T3	20/3/01	459.3	690	8.05	0.10	17.8	-310	178	0.54	0.02	7.8	0.20	<0.1	170.3	0.8	36.0	34.3	43.7	2.20	15500	15.77	25.37	0.36	43	5.62	51	90	66	1.40	2.2
SR5-T1	8/5/01	-2.3	528	7.94	0.00	29.5	-300	314	0.34	<0.02	18.0	0.38	1.40	1.6	<0.3	7.0	5.0	110.0	2.90	19	0.09	26.00	0.73	1	0.00	46	61	11	<0.03	-1.6
SR5-T2	8/5/01	38.7	578	7.75	0.00	28.0	-280	321	0.37	<0.02	26.0	0.21	2.80	8.9	<0.3	7.2	7.2	115.0	2.80	27	0.13	23.10	0.77	2	0.00	35	66	23	<0.03	-2.8
SR5-T3	9/5/01	253.2	460	7.93	0.00	23.4	-280	273	0.71	<0.02	13.0	0.84	1.10	2.1	<0.3	9.3	6.9	88.0	2.40	44	0.06	23.10	0.63	2	0.00	35	46	35	0.04	0.0
SR5-T4	9/5/01	317.7	340	7.70	0.00	21.3	-130	186	0.44	<0.02	11.0	0.27	3.50	9.0	<0.3	16.0	9.9	39.0	3.70	5	<0.03	30.10	0.31	46	0.00	137	41	152	0.19	-4.5
SR5-T5	8/5/01	395.2	311	7.05	0.00	19.5	-38	178	0.51	<0.02	11.0	0.37	6.20	1.6	<0.3	13.0	7.9	40.0	3.80	787	0.90	24.20	0.37	2	0.00	138	33	50	0.15	-4.2

Table 2. Analytical data for groundwaters in Los Ratones mine.
Tabla 2. Datos analíticos de las aguas subterráneas de mina Los Ratones.

EL BERROCAL Sample name	Date	zone elevation (m.a.s.l)	EC (µS/cm)	pH in situ	O2 mg/l	T (ºC)	Eh (mV)	HCO3- mg/l	F- mg/l	I- mg/l	Cl- mg/l	Br- mg/l	NO3- mg/l	SO4 mg/l	S2- mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Fe2+ ppb	Fe mg/l	SiO2 mg/l	Li mg/l	U ppb	3H T.U	As ppb	Sr ppb	Zn ppb	Mn mg/l	Charge Balance (%)
S01050L000390	1/3/90	848.9	293	6.20	0.55	14.0	478	22	6.00	<0.02	5.1		10.50	100.0	<0.02	37.0	5.7	11.0	2.80	<50	<0.03	45.00	0.05	65		<4	50	850	1.20	-7.0
S02016O260393	26/3/93	900.9	272	7.10		14.0	154	166	1.70	<0.02	5.2	4.30	<0.1	3.9	<0.02	35.0	8.2	12.0	0.76	1882	3.00	33.70	0.08	32	6.70	9	40	2900	0.59	-0.7
S03003L120593	2/5/93	895.2	207			14.0	335	117	1.40	<0.02	5.2	1.20	<0.1	5.7	<0.02	25.0	5.2	12.0	0.81	<50	<0.03	42.60	0.07	10	8.90	12	40	220	0.58	-1.7
S04003L000392	1/3/90	896.9	130	6.33	2.64	21.0	348	70	0.58	<0.02	5.6		0.07	5.8	<0.02	12.0	3.1	13.0	0.90	364	0.26	37.60	0.05	<1		<4	<30	280	0.24	-0.2
S06005L000392	1/3/92	893.8	284	6.63	2.35	16.0	275	78	0.41	<0.02	6.2		0.16	64.0	<0.02	34.0	7.0	11.0	1.00	1132	1.40	34.30	0.04	<1		<4	<30	550	0.79	0.0
S07046O040394	4/3/94	853.0	282	6.85	8.95	14.0	100	129	2.90	0.39	5.4	0.30	<0.1	33.0		38.0	5.2	15.0	2.20	2721	1.30	28.80	0.07	2		<4	40	40	0.48	-1.7
S1/7039O151292B	15/12/92	859.8	282	6.60	1.40	14.6	150	90	2.80	<0.02	4.1	<0.02	<0.10	64.0	<0.02	35.0	4.5	15.0	1.50	955	1.50	47.10	0.05	2		<4	50	1700	1.30	-8.0
S11041O300693C	30/6/93	831.0	311			13.0	190	154	1.00	<0.02	3.7	<0.02	<0.10	25.0	<0.02	43.0	4.8	13.0	1.00	2536	2.00	37.30	0.07	9		<4	<30	2500	0.61	-0.9
S12025L000392	1/3/92	846.8	267	6.41		21.8	358	58	0.70	<0.02	4.2		2.60	75.0	<0.02	31.0	5.6	16.0	1.40	110	0.07	28.40	0.05	4		<4	120	1800	0.79	2.9
S13064O220793A	22/7/93	889.0	331			13.0	60	218	2.00	<0.02	3.4	0.74	<0.10	2.8	<0.02	54.0	6.0	15.0	0.89	181	0.20	39.60	0.10	21	3.50	15	<30	60	0.90	1.0
S1382O250594C	25/5/94	871.0	349	7.12		20.0	128	217	1.50	<0.02	4.2	0.76	<0.1	2.4	<0.02	50.0	6.0	14.0	1.40	916	1.20	32.00	0.16	60		2	52	10	1.00	-4.2
S14033O010793B	1/7/93	925.0	99	7.10		18.0	55	48	0.22	<0.02	3.8	2.10	0.67	2.3	<0.02	6.2	1.2	9.6	0.88	1051	1.30	30.70	0.03	29		<4	<30	4600	0.04	-9.7
S14093O200593B	20/5/93	865.0	167	7.67		13.0	107	96	1.50	<0.02	3.8	2.40	<0.1	2.1	<0.02	16.0	1.9	16.0	1.80	1050	1.10	44.10	0.09	105		25	40	7500	0.26	-5.3
S15096O270593C	27/5/93	840.0	220			13.0	279	121	1.10	<0.02	3.9	1.40	1.60	5.0	<0.02	28.0	4.5	11.0	1.60	<50	<0.03	31.00	0.06	109		<4	<30	420	0.81	1.4
S15120O220494A	22/4/94	816.0	213	5.38		16.0	188	133	1.10	<0.02	3.8	1.10	<0.1	4.7	<0.02	32.0	4.9	11.0	1.80	3228	3.20	28.60	0.06	301	7.51	9	<30	230	0.76	5.5
S17138O180594C	18/5/94	816.0	271	7.19		20.0	228	163	1.40	<0.02	4.0	0.20	<0.1	4.2	<0.02	38.0	2.9	18.0	1.60	500	0.51	45.90	0.51	420		7	48	40	2.22	0.8
S02016O000392	1/3/92	900.9	266	7.50	4.50	15.6	208	178	1.70	<0.02	4.7		0.27	2.0	<0.02	34.0	8.6	15.0	0.77	241	0.05	32.30	0.08	8		<4	<30	2200	0.48	-3.1
S16459O031194A	3/11/94	514.0	217	7.06		25.4	129	138	2.40	0.09	4.5	1.00	<0.1	<0.1	<0.02	25.0	2.3	19.0	1.10	3860	3.50	36.00	0.10	13		13	80	6700	0.41	-6.7
S16459O161194A	16/11/94	514.0	215	7.07		15.4	48	134	2.80	0.13	3.9	0.81	<0.1	<0.1	<0.02	23.0	1.8	19.0	1.20	3382	3.70	32.00	0.10	13		10	70	4800	0.34	-10.1

Table 3. Analytical data for groundwaters in El Berrocal mine.
Tabla 3. Datos analíticos de las aguas subterráneas de mina El Berrocal.

560 m depth.

The Spanish groundwaters have chemical compositions similar to those of the Toki granite (Japan) and Grimsel granite (Switzerland), but clearly different from Canadian or Scandinavian Shields and Carnmenellis groundwaters. The dominance of Cl and Na and the low concentration of HCO_3 and Ca in major ion composition are typical characteristics of the Scandinavian and Canadian Shields groundwaters. One of the potential sources of this salinity (Cl⁻ = 1246 mg/L) of fracture groundwaters in Canadian Shield is the presence of brines that entered the granite during Paleozoic times either from penetration of overlying seawater or laterally from influx of basinal brines of the Western Canada Sedimentary Basin (Gascoyne, 2004).
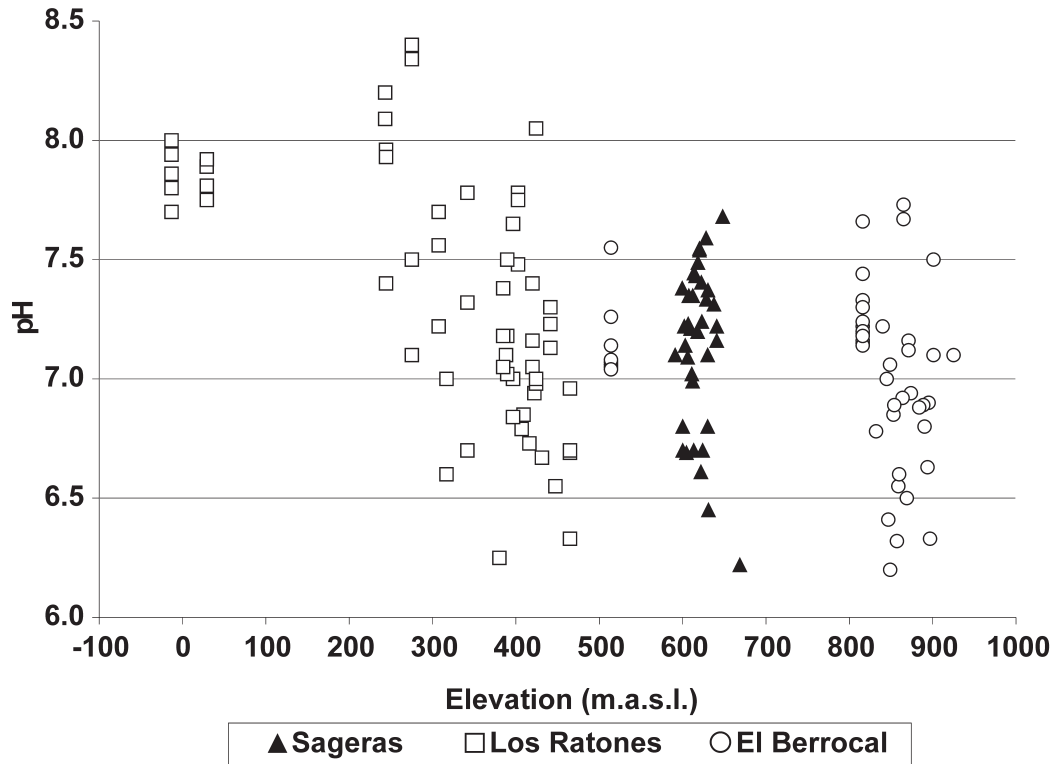
Fig. 4.- Variation of pH with elevation for the three mines studied. Elevation expresed in m.a.s.l (meters above sea level).

Fig. 4.- Variación del pH con la profundidad en las tres minas estudiadas. La profundidad está expresada como cota en m.s.n.m (metros sobre el nivel del mar).

In the Scandinavian Shield, brackish-saline groundwaters ($Cl^- = 6000$ mg/L) are the result of a mixture in varying degrees of present and ancient Baltic seawater and melt water (Laaksoharju, 1999). On the other hand, the main characteristic of the deep groundwaters within the Carnmenellis granite is their high salinity ($Cl^- = 9280$ mg/L), whose origin could be the water-rock interaction within the granite, specifically silicate mineral hydrolysis (Edmunds and Savage, 1991).

Groundwater from the Toki granite is very dilute ($Cl^- = 4.1$ mg/L) and is rich in Na^+ and HCO_3^-. The chemical evolution is mainly controlled by the dissolution of plagioclase and calcite, and by the ion exchange reaction between montmorillonite in the fractured zones and groundwaters (Iwatsuki and Yoshida, 1999).

The results of these studies indicate that the chemical composition of groundwaters is largely dependent on the geological history of each area, which determines the different chemical evolution as well. Therefore, investigations of hydrogeochemical conditions related to the safety of deep waste repositories must be performed in each country where the option to disposal the high radioactive wastes in geological formations is adopted.

4.2. pH and redox conditions

The redox condition of groundwater is an important parameter for radionuclide transport, because under reducing conditions many of the radionuclides occur in a reduced form with very low solubility. Reducing conditions are therefore a requirement on the repository site.

The Eh and the pH of the waters are measured in a flow cell thus avoiding contact with atmospheric oxygen. Figure 4 depicts the relationship between pH and elevation. The pH values ranged from neutral to mildly alkaline as a function of the elevation. The sub-surface waters in the three mines are near-neutral and buffered by dissolution of carbonates, especially calcite, in El Berrocal and Sageras-Mina Fe waters. Deeper groundwaters (Los Ratones mine) become more alkaline (pH = 8.4) due to the equilibrium of carbonates (ankerite) and the ionic exchange between Ca in solution and Na of the montmorillonite present in the fracture fillings (Gómez, 2002).

Eh and pH results measured from the waters sampled in the three uranium mines are depicted in figure 5. The
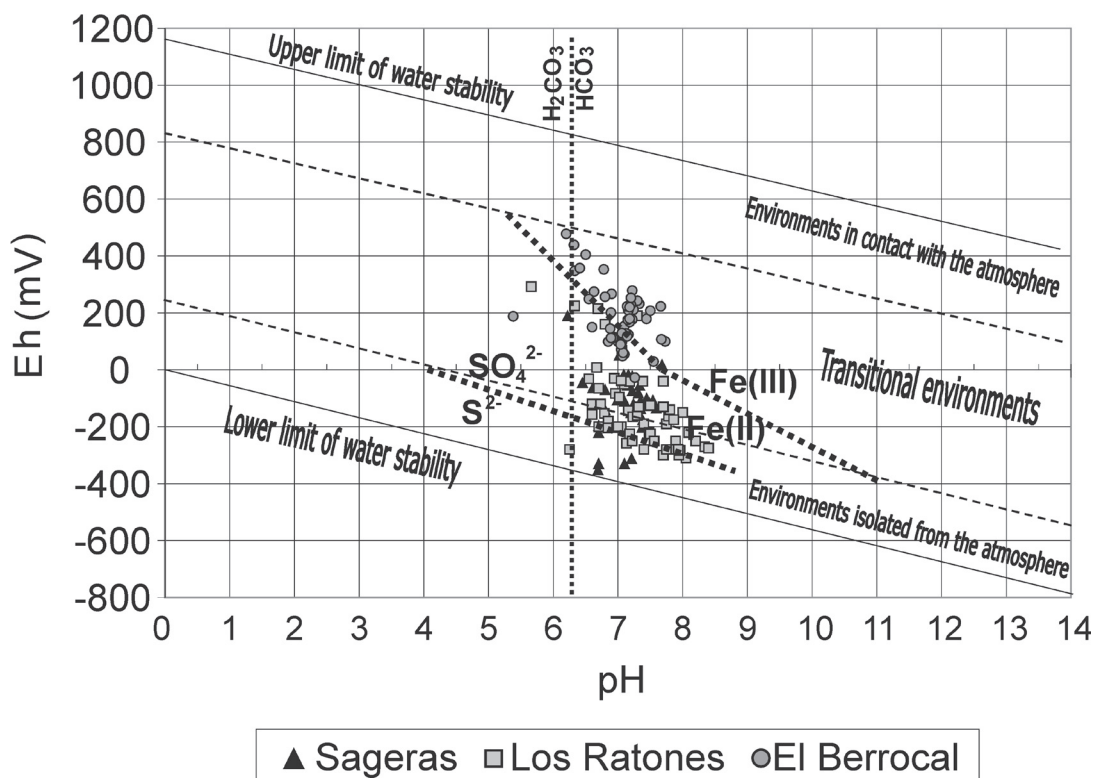
Fig. 5.- Eh-pH diagram of the groundwaters samples from Sageras-Mina Fe, Los Ratones mine and El Berrocal mine.

Fig. 5.- Diagrama de Eh-pH de las muestras de agua subterránea de Sageras-Mina Fe, mina Los Ratones y mina El Berrocal.

limits between different redox zones (environments in contact with the atmosphere, transitional environments, and environments isolated from the atmosphere) are indicated in the figure. All the waters from El Berrocal and most of the groundwaters from Sageras-Mina Fe area are in a transitional environment evolving towards environments isolated from the atmosphere but without reaching them. This is consistent with the concentration of dissolved oxygen of these waters (Tables 1 to 3). According to the hydrological model of the sites (Carrera *et al.*, 1997; Ortuño *et al.*, 2001), these waters were considered as recharging groundwater.

Deeper groundwaters of Los Ratones mine and Sageras-Mina Fe are in the field of environments isolated from the atmosphere, where carbonates are stable and the reduced species of iron and sulphur (Fe^{2+} and S^{2-}) are dominant.

Redox models performed with the EQ3/6 geochemical code (Wolery, 1992) for groundwaters related to the uranium deposit of Los Ratones, have considered that the redox control is maintained by arsenopyrite, pyrrhotite and ferrihydrite equilibrium (Gómez *et al.*, 2001). The Eh values obtained by these models are near to −164 mV, close to those measured.

4.3. Water-rock reactions

The processes related to the dissolution/precipitation of carbonates in the surroundings of the three Spanish uranium mines are evidently very important, since most of the groundwaters are bicarbonate-type waters and the presence of carbonate minerals in the fracture fillings is almost constant. In general, there is a good correlation between the bicarbonate concentration in the water and the presence of carbonate minerals (calcite, dolomite and ankerite) in the fracture fillings in the sites investigated (Pérez del Villar *et al.*, 2003; Buil, 2004).

The concentrations of bicarbonate in the groundwaters versus the concentrations of Ca^{2+}; $Ca^{2+} + Mg^{2+}$ and $Ca^{2+} + Mg^{2+} + Fe^{2+}$ are represented in figure 6. If congruent dissolution of calcite, dolomite or ankerite is assumed, these values should fit a line whose slope would be the stoichiometric relation of the ions in the corresponding mineral phase:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \text{ (calcite)}$$

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \text{ (dolomite)}$$

$$CaFe_{0.4}Mg_{0.6}(CO_3)_2 + 2CO_2 + 2H_2O \leftrightarrow Ca^{2+} + 0.6Mg^{2+} + 0.4Fe^{2+}$$
$$4HCO_3^- \text{ (ankerite)}$$
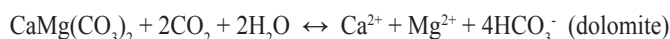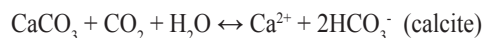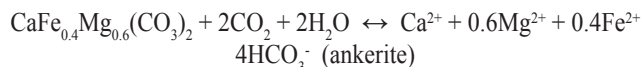
Most of the waters from the three uranium mines are close to the line with a 1:1 stoichiometry, that represents the dissolution of the mineral phases represented above. However, some of the waters have an excess of cations with respect to bicarbonate concentration if dissolution of dolomite or ankerite is assumed. These waters are sampled from the adjacent sections to the uranium dykes from Los Ratones mine and Sageras-Mina Fe. Their hydrogeochemical characteristics show a magnesium-calcium sulphate type water (Fig. 3). However, the waters are close to the line that represents the calcite dissolution.

Other groups of groundwaters are generally poor in Ca with respect to calcite dissolution and have an excess of cations in relation to the stoichiometry of the dissolution of dolomite and especially of ankerite. These groundwaters belong to Ca-HCO$_3$ type and Na-Ca-HCO$_3$ type water defined in the previous section.

As some of the waters of these groups flow towards deeper zones, the bicarbonate content increases and the decreasing in the concentration of cations is more evident, thus, its location in the figure is far away from the 1:1 line bicarbonate:cations.

In Na-HCO$_3$ type waters (deep waters from Los Ratones mine), the difference between the concentrations of cations with respect to the concentration of bicarbonate is still more evident than in waters from the others groups.

In general, the waters similar to granitic-type waters (Na-Ca-HCO$_3$ and Na-HCO$_3$) present a gradual decreasing of some cations (Ca^{2+}, Mg^{2+} and Fe^{2+}) as depth and distance from the uranium mineralization increase. This would imply that if the dissolution of carbonates is taking place in these waters, Ca, Mg and/or Fe are either precipitating or disappearing from the dissolution due to other geochemical processes.

Figure 7 shows the values of the saturation index calculated with the PHREEQC code (Parkhust and Appelo, 1999) of ankerite, calcite and siderite versus the bicarbonate content in the water from the three uranium mines. The concentrations of Fe^{2+} are expressed in Tables 1 to 3. For bicarbonate concentrations lower than 4 meq/l, ankerite and calcite are undersaturated, and tend to equilibrium as the bicarbonate concentration increases, while siderite is more frequently found as supersaturated. For bicarbonate concentrations greater than 4 meq/l, siderite is always undersaturated and ankerite and calcite are practically in equilibrium.
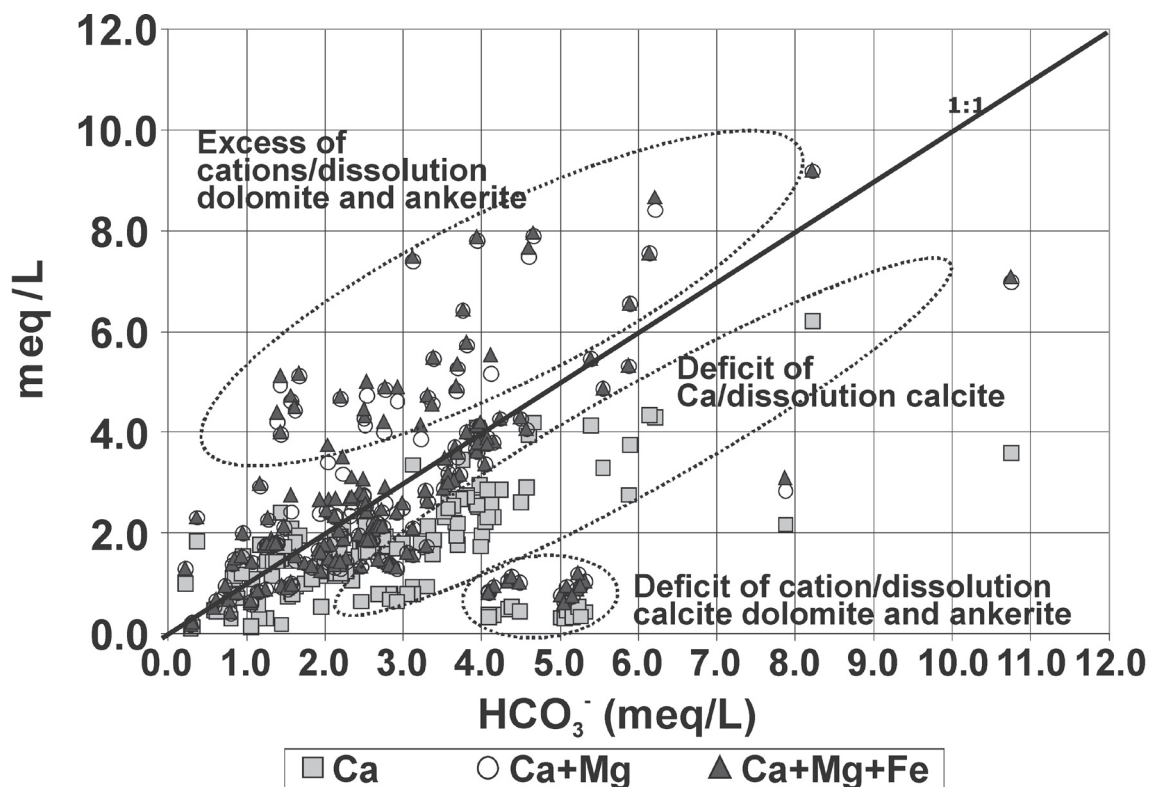

Fig. 6.- Concentration of bicarbonates in groundwaters *versus* concentration of Ca^{2+}, Ca^{2+}+ Mg^{2+} and Ca^{2+} + Mg^{2+} + Fe^{2+}.
Fig. 6.- Concentración de bicarbonatos en las aguas *versus* la concentración de Ca^{2+}, Ca^{2+}+ Mg^{2+} y Ca^{2+} + Mg^{2+} + Fe^{2+}.
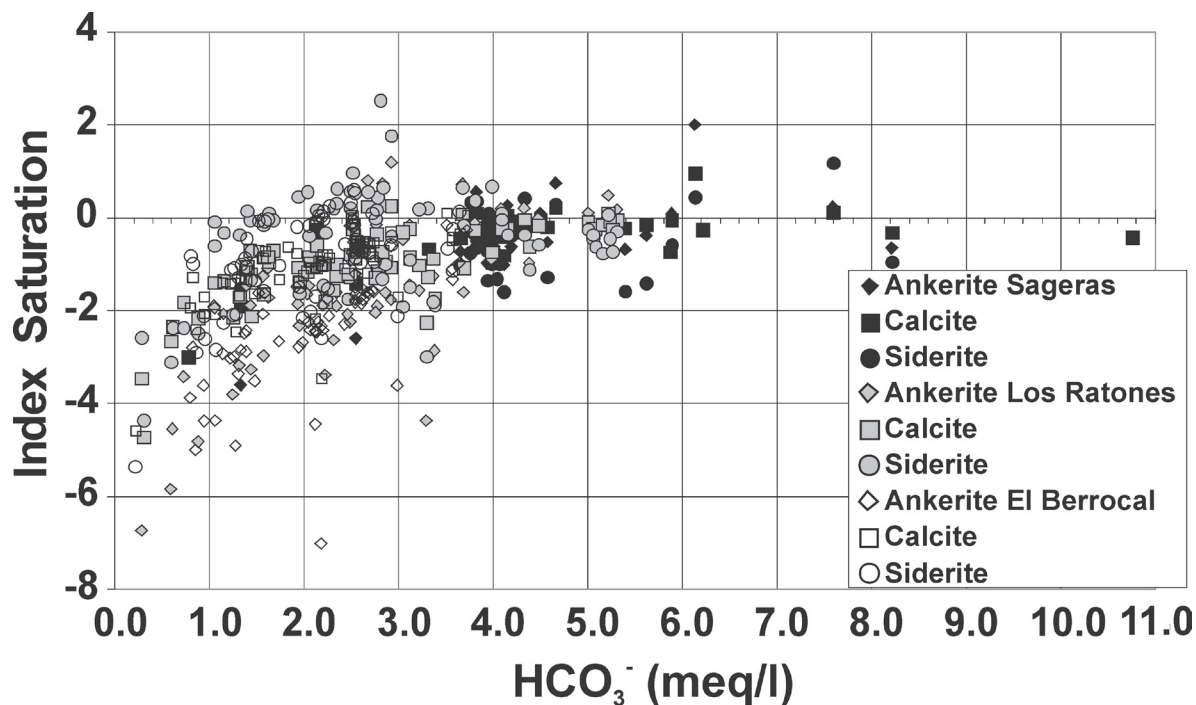
Fig. 7.- Saturation index of ankerite, calcite and siderite *versus* concentration of bicarbonates in groundwaters from Sageras-Mina Fe, Los Ratones mine and El Berrocal mine.
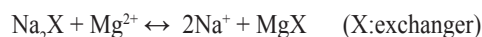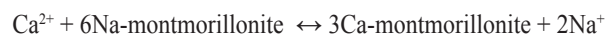
Fig. 7.- Índices de saturación de la ankerita, calcita y siderita *versus* la concentración de bicarbonatos en las aguas de Sageras-Mina Fe, mina Los Ratones y mina El Berrocal.

The precipitation of siderite can partially explain the cation excess (Ca + Mg) of the waters mainly related to the mineralization (Mg-Ca-SO$_4$ type waters), and is responsible for the decrease of dissolved bicarbonate, which comes from the dissolution of carbonates. Ca and Mg cations remain dissolved, while the bicarbonate precipitates as FeCO$_3$.

Numerous experimental and in situ data confirm that the dissolution sequence followed by the carbonate minerals is: calcite, dolomite, ankerite and finally, siderite (Blowes and Patcek, 1994; Jurjovec *et al.*, 1995). Blowes and Ptacek (1994) observed that the interstitial waters in the mine tailings are usually in equilibrium with siderite, while dolomite and ankerite are generally dissolved and do not reach equilibrium conditions. It is most likely that the saturation index of siderite indicates precipitation conditions if the oxidation of sulphides is taking place, since there is a continuous supply of Fe to the solution due to the dissolution of Fe sulphate (Dubrovsky *et al.*, 1985; Morin and Cherry, 1986; Al *et al.*, 1994; Blowes and Patcek, 1994). This process results in secondary precipitation of siderite on ankerite as was observed by Al *et al.* (1997) in samples collected from tailings.

If the variation of the concentrations of Ca^{2+} + Mg^{2+} and Na$^+$ is represented as a function of elevation (Fig. 8), groundwaters from Sageras-Mina Fe and El Berrocal do not evidence variation with depth. Nevertheless, in the groundwaters from Los Ratones mine the concentrations of these cations decrease as depth increases, while the Na$^+$ contents increase. This variation of the relative concentrations of these cations can be considered as normal, taking into account that the behaviour of Na is more conservative than Ca and Mg, since the latter two can disappear from the solution by irreversible processes (precipitation: formation of saleite, neoformation of apatites, Ca silicophosphates, etc) or by "reversible" processes such as ion exchange. The saturation indexes of the carbonate minerals do not indicate precipitation conditions. Neoformed calcite, ankerite and dolomite have not been observed in this study. Therefore, ion exchange must be the process that governs the concentration of cations:

$$Ca^{2+} + 6Na\text{-montmorillonite} \leftrightarrow 3Ca\text{-montmorillonite} + 2Na^+$$

$$Na_2X + Mg^{2+} \leftrightarrow 2Na^+ + MgX \quad (X:\text{exchanger})$$

Based on these exchange reactions, for each exchanged mol of Ca^{2+} or Mg^{2+}, 2 moles of Na$^+$ are released to the solution. The molar concentration of Na in the Na-HCO$_3$ type waters (deepest groundwater from Los Ratones) is approximately equal to the concentration of bicarbonate, which agrees with the exchange of Na by Ca and/or Mg in the exchange complex of the clay minerals. Dissolution
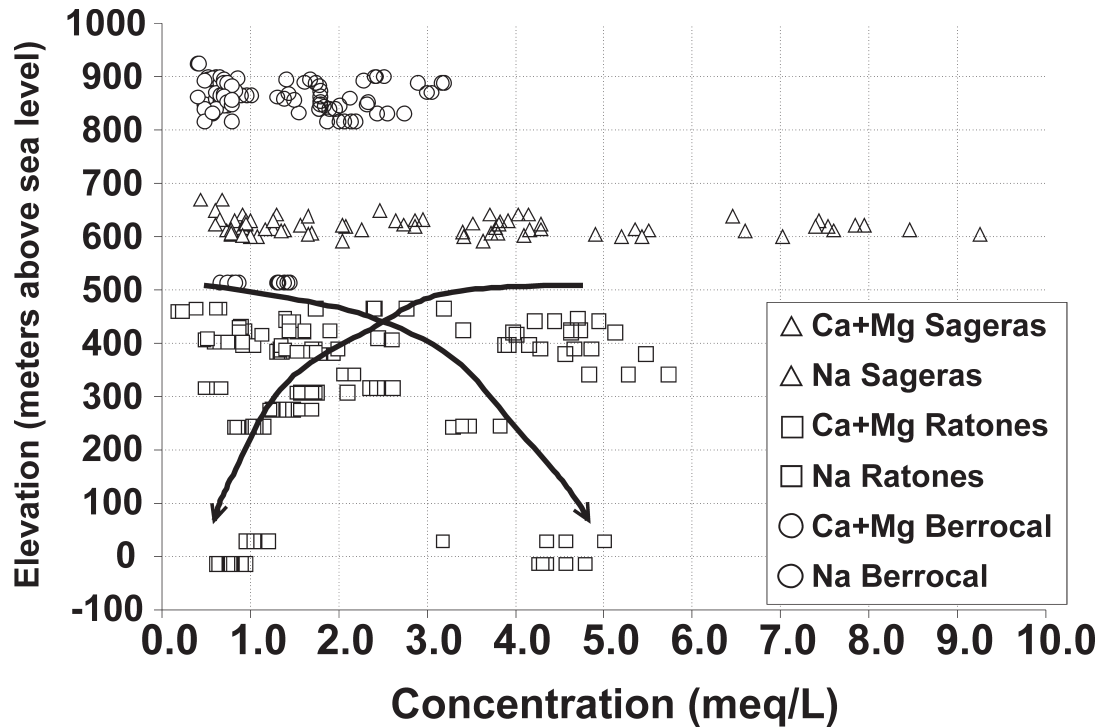
Fig. 8.- Concentration of Ca^{2+} + Mg^{2+} and Na^+ as a function of elevation in the groundwaters of the three uranium mines. Elevation expressed in m.a.s.l (meters above sea level).

Fig. 8.- Concentración de Ca^{2+} + Mg^{2+} y Na^+ en función de la profundidad en las muestras de agua de las tres minas estudiadas. La profundidad está expresada como cota en m.s.n.m (metros sobre el nivel del mar).
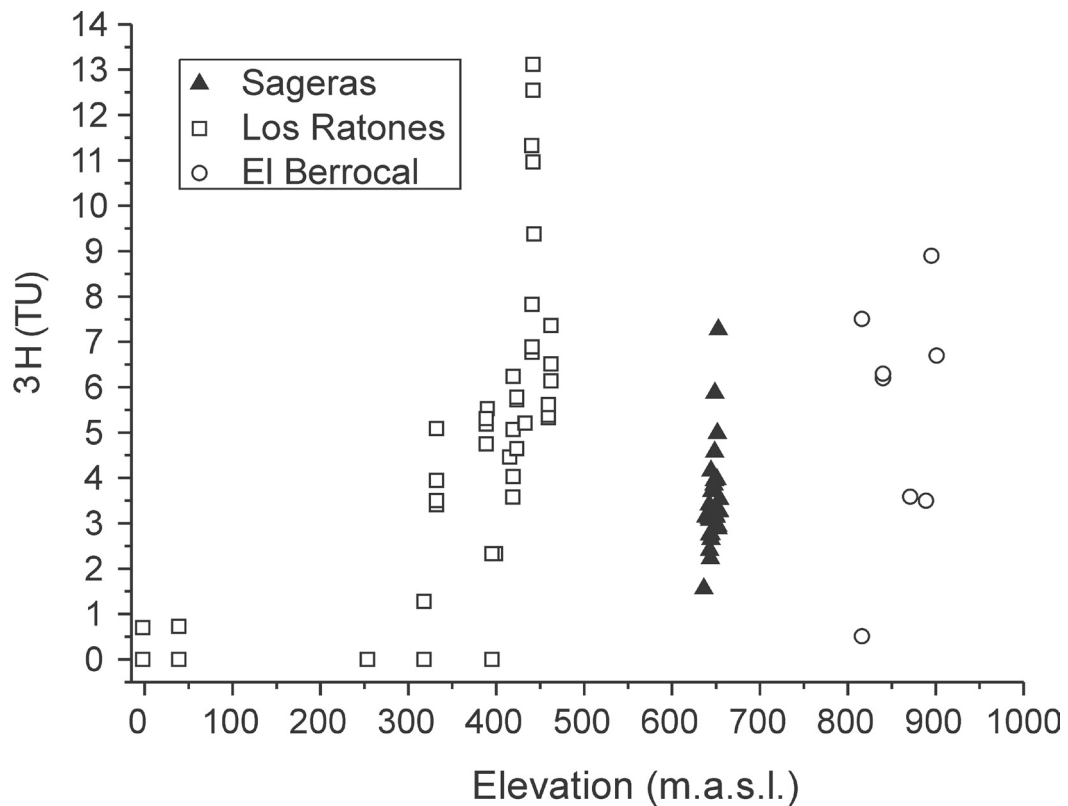

Fig. 9.- Variation of ^3H concentration with elevation for the three areas investigated. Elevation expressed in m.a.s.l (meters above sea level).

Fig. 9.- Variación de la concentración de ^3H con la profundidad expresada como cota en m.s.n.m (metros sobre el nivel del mar) en las tres areas estudiadas.
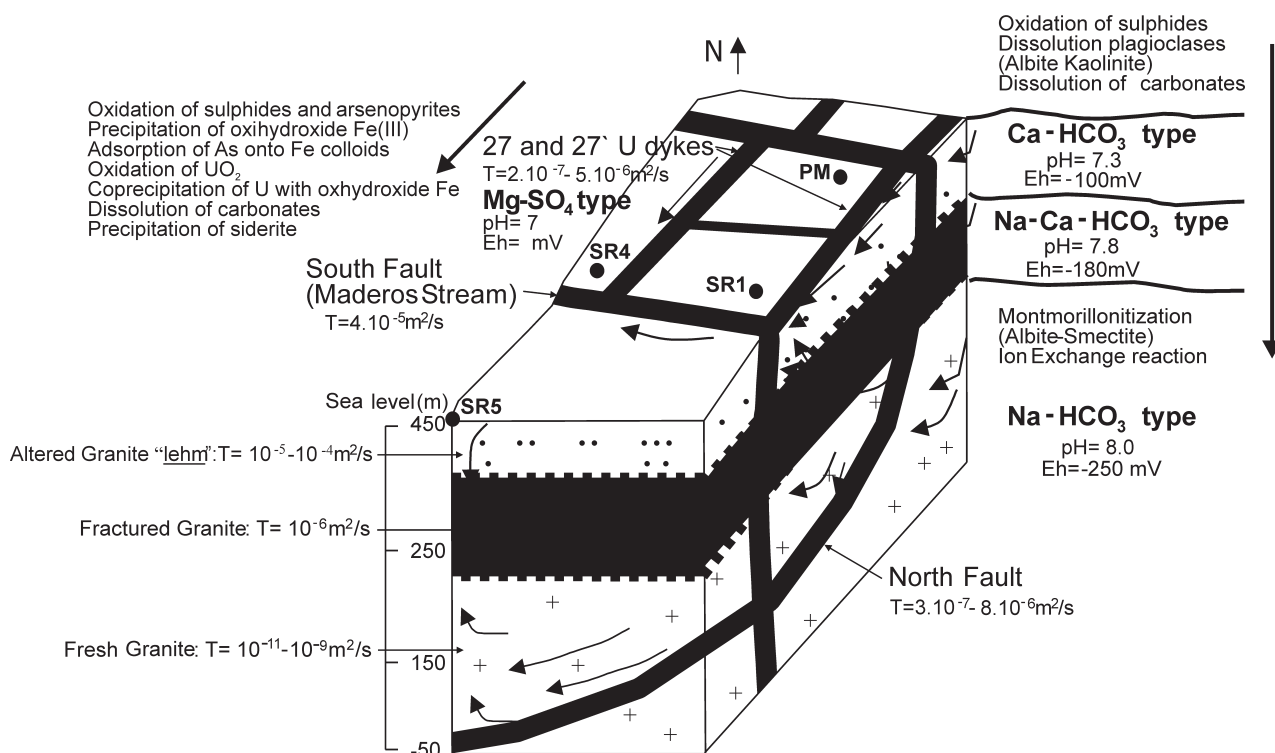
Fig. 10.- Cross-section through Los Ratones mine (Cáceres) showing variations in groundwater composition with elevation and flow direction.

Fig. 10.- Esquema de la mina Los Ratones (Cáceres) mostrando las variaciones en la composición química del agua en función de la cota y los flujos preferentes.

of Na feldspars could be a process that increases the sodium concentration in the waters, but the saturation index of the albite is in equilibrium in these waters (Gómez, 2002).

The studies performed on the alterations associated with the uranium mineralizations and fracture fillings or dykes intersected by boreholes in this work indicate that smectite is a frequent and abundant mineral in certain structures (Arribas, 1962, 1975; Buil, 2002), being calcium and magnesium (analyzed by SEM) the main cations of the exchange complex.

4.4. Groundwater residence time

The tritium content of the measured groundwater at the three sites investigated ranges from 0 to 13.1 TU (Fig. 9) (Gómez *et al.*, 1997; Gómez, 2002; Gómez *et al.*, 2003). Modern tritium content of precipitation in the Central-West sector of the Iberian Peninsula has a mean value of 4.4 ± 0.5 TU. This indicates that waters have a relatively short residence time in the flow system (i.e. they are recharge waters or a mix with water from the last 50 years). However, the waters below 200 m depth in the Los Ratones area have tritium content of <0.7 TU, indicating a residence time higher than 60 years, at least. The residence time for this deep water was calculated from

[14]C measurements. The groundwater flowing through the fractures in Los Ratones area has an "age" ranging from 1.2×10^4 years at 200 m depth to 1.6×10^4 years at 500 m depth (Gómez, 2002).

The recharge temperature was calculated from the noble gases concentration sampled in the water at different depths at Los Ratones mine (Gómez, 2002). The values range from 11.3 ºC (60 m depth) to 2.7 ºC (469 m depth), considering an altitude for the recharge of 1000 m (that of the surrounding mountains).

5. Conceptual groundwater evolution models

The conceptual groundwater evolution model adopted for Los Ratones mine is shown in figure 10, in which the main water-rock interaction processes are represented.

The most important water-rock interaction process with respect to the pH neutralization of those waters related to the mineralization is the dissolution of complex carbonates, which were identified in the fractures and dykes. Furthermore, the precipitation of siderite has a significant contribution in the regulation of Fe^{2+} and HCO_3^- in the mine waters. The relative concentrations of Ca^{2+}, Mg^{2+} and Na^+ are mainly controlled by processes of ionic exchange with smectites, studied in the fissure fillings. The
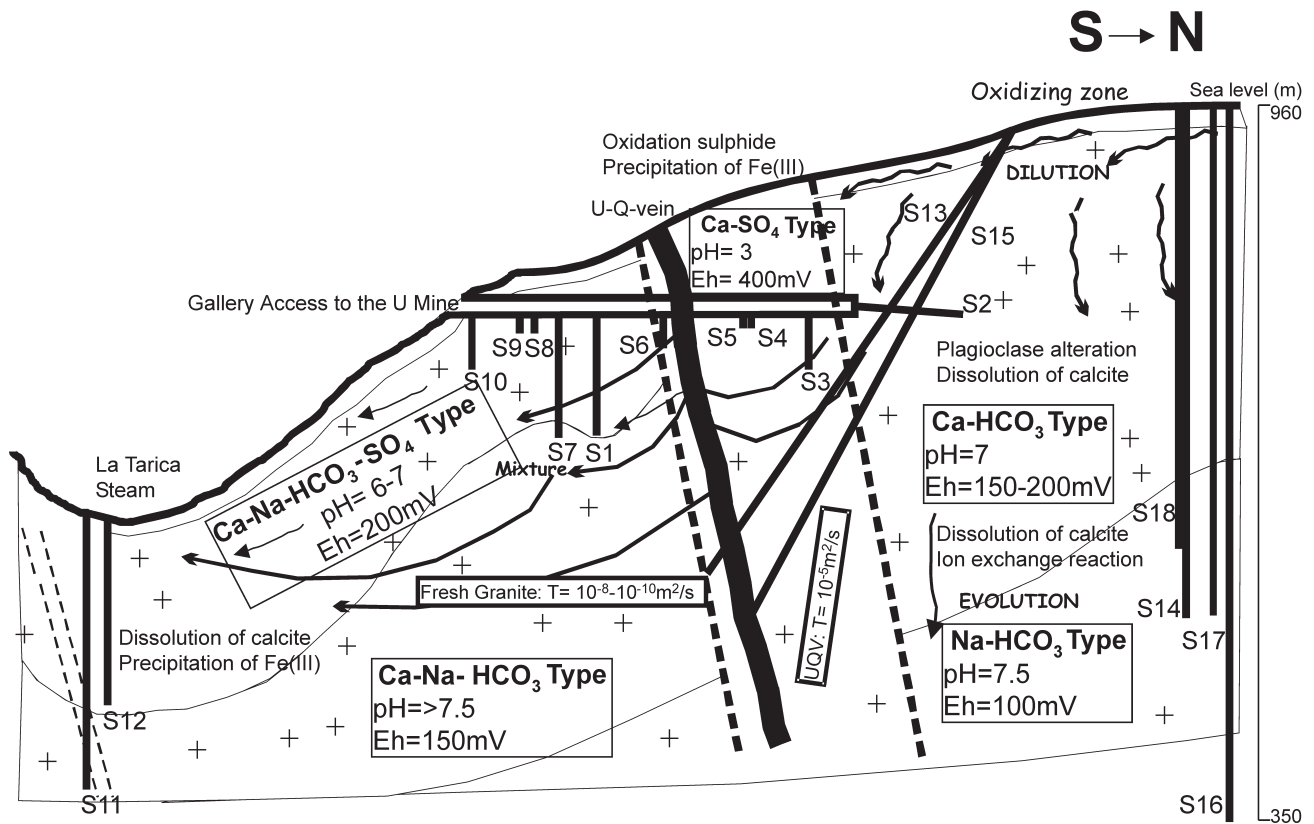
Fig. 11.- Cross-section through El Berrocal mine (Toledo) showing variations in groundwater composition with elevation and flow direction.

Fig. 11.- Esquema de la mina El Berrocal (Toledo) mostrando las variaciones en la composición química del agua en función de la cota y los flujos preferentes.

silica concentration in groundwaters seems to be controlled by the equilibrium with respect to amorphous silica (silicagel) and by the alteration of feldspars, especially albite, which are transformed to kaolinite, preferably in the superficial zones. This fact is based on petrographic and mineralogical studies, which indicate the strong alteration of feldspars, the frequent occurrence of amorphous silica, the predominance of kaolinite in the superficial zones and the abundance of smectites, especially near the mineralized zones.

The redox potential of the groundwaters in this zone is essentially controlled by the redox pairs: Fe^{2+}/Fe^{3+}, and S^{2-}/SO_4^{2-}. In the mine waters, the sulphide oxidation is the principal iron source, and, together with the precipitation of the Fe oxyhydroxides, helps to regulate the Fe concentration and the redox potential of the water.

The chemical reactions responsible for the changes in the chemical compositions of the waters of El Berrocal can be observed in figure 11. The sulphide and uranium mineralized vein is the structural and lithological heterogeneity which clearly affects the general characteristics of the waters. At a local scale, waters located to the north

of the vein are $Ca-HCO_3$ type; those located to the south of the vein and within the vein are $Ca-SO_4$ type mixed waters from both families are located to the south of the vein and evolve from $Ca-SO_4$ to $Ca-HCO_3$ as they move away from the mineralized vein.

The water chemistry is controlled by bicarbonate, sulphate and calcium ions. The dissolution and precipitation of calcite and the iron oxyhydroxides play an essential role in the water composition. Some cations, such as Mn, Fe and Zn, form double carbonates with calcium, thus, their concentration in waters is important.

Uranium dissolved in waters is controlled by the carbonate system both to the north of the vein, and in the deep zone of the discharge area to the south of the vein.

According to the hydrological model (Guimerá *et al.*, 1993) water flows from North to South, passing through the dyke in the zones of greatest permeability; as a result of this, the waters close to the dyke and located to the south have high sulphate contents originated by the oxidation of sulphides present in the dyke, whereas the waters located to the north have the chemical characteristics typical of granitic recharge zones.

6. Conclusions

The hydrochemical characteristics of the groundwaters from three uranium mines located in the Hesperian Massif have been studied. In spite of their geological and hydrogeological features, dilute Ca-HCO$_3$ type waters with modern levels of ^{3}H are located in the upper part of the three investigated sites. At greater depth and following the local flows paths the waters evolved to Na-Ca-HCO$_3$ type waters and in the deepest depth reducing and Na-HCO$_3$ type waters are the dominant.

In other parts of the world, especially the Scandinavian and Canadian Shields very saline, reducing and sodium chloride type waters are the main characteristics of the deep granitic groundwaters.

The dissolution of complex carbonates, identified in the fracture fillings and dykes, is the most important water-rock interaction process in relation to the neutralization of the pH in those waters associated with the uranium ore-deposits in veins. The dissolution of ankeritic carbonates and the precipitation of siderite significantly contribute to control the Fe^{2+} and HCO$_3^-$ concentrations in the waters of the mine. Ion exchange processes with smectites studied in the fracture fillings control the relative concentrations of Ca^{2+}, Mg^{2+} and Na$^+$ in the water.

Acknowledgments

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