

## THE CLAYEY FISSURAL FILLINGS ASSOCIATED WITH N100°-110°E FRACTURES AT THE EL BERROCAL URANIUM MINE (SIERRA DE GREDOS, SPAIN): CHARACTERIZATION, GENESIS AND RETENTION CAPACITY OF RADIOACTIVE AND OTHER ELEMENTS

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### RESUMEN

En relación con los procesos de migración/retención de los radionucleidos naturales en un medio granítico fisurado se han estudiado los rellenos fisurales arcillosos ( $< 60 \mu\text{m}$  y  $< 2 \mu\text{m}$ ) asociados con las fracturas N100°-110°E de la mina de U de El Berrocal. La fractura rellena por el filón de cuarzo mineralizado con pirita, calcopirita, esfalerita y galena; y posteriormente por pirita, pechblenda, calcita y barita, pertenece también a dicha familia de fracturas.

De acuerdo con los datos difractométricos, termogravimétricos, de energías dispersivas de rayos X acoplado a sendos microscopios electrónicos de barrido y transmisión y del análisis del complejo catiónico de cambio, los rellenos arcillosos están esencialmente constituidos por cuarzo, sericita, ilita, beidellita cálcico-magnésica, feldespato potásico, albita, apatito y ocasionalmente caolinita. La monacita, torbernita, autunita, otros fosfatos de Ca, Y, Ce, La y TR no clasificados, sulfato férrico, jarosita, yeso, barita, calcita, silicatos de Pb, oxihidróxidos de Fe, gibbsita, geles de Al y geles silicatados complejos de TR están como trazas en la fracción  $< 2 \mu\text{m}$ .

Desde el punto de vista geoquímico, la fracción  $< 2 \mu\text{m}$  de las muestras está enriquecida en U, Th, V, Cu, Zn, Sn, Ni, As, Ba, Ca y C orgánico, en relación con la fracción  $< 60 \mu\text{m}$ . Además, el Cl está presente, en concentraciones importantes, en casi todos los minerales y mineraloides de la fracción  $< 2 \mu\text{m}$ .

Estos datos sugieren que los materiales arcillosos estudiados se originaron por alteración hidrotermal de las harinas de falla, durante la fase N100°-110°E de fracturación.

De acuerdo con los datos de  $\delta^{18}\text{O}$  obtenidos del cuarzo filoniano y de la fracción  $< 2 \mu\text{m}$  de las muestras, el proceso de arcillización se produjo probablemente en dos fases. La primera, de naturaleza sericítico-ilitica, se originó por la interacción entre las harinas graníticas de falla y soluciones hidrotermales ácidas, ricas en KCl, en un rango de temperaturas comprendido entre 70-120° C. La segunda fase, de naturaleza esmectítica, se produjo probablemente durante los procesos de alteración meteórica, antiguos y/o actuales, por fuerte lixiviación del K de la sericita-ilita preexistentes. Esta fase de alteración meteórica pudo ser también la responsable de la transformación de la ilita y, probablemente, la esmectita en caolinita, en aquellas fracturas mineralizadas con sulfuros. La jarosita, los sulfatos de Fe, el yeso, la torbernita, la autunita, la gibbsita y los geles de Al se originarían probablemente también en esta última fase de alteración meteórica.

Los minerales y mineraloides accesorios neoformados juegan un papel importante en la retención, por precipitación o adsorción, de los elementos radiactivos, U y Th, y otros análogos, Y, Ce, La, REE, liberados durante la alteración hidrotermal del granito y meteórica de la mineralización uranífera. El Th está principalmente en la estructura de la monacita heredada.

La lixiviación secuencial del U indica que los oxihidróxidos de Fe y los carbonatos retienen cantidades relativamente importantes de dicho elemento, mientras que los minerales de la arcilla no parecen jugar un papel importante en la retención del U por adsorción. No obstante, pudieron actuar como una barrera físico-química para la precipitación de los fosfatos de  $\text{UO}_2^{++}$ .

El alto contenido en C orgánico de la fracción arcilla de las muestras puede explicarse por la actividad bacteriana actual observada en los rellenos fisurales, o por la presencia de

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ácidos orgánicos, transportados por las aguas percolantes desde la superficie topográfica. En este último caso, han podido formarse complejos orgánico-arcillosos.

**Palabras clave:** *Rellenos fisurales arcillosos, elementos mayores y trazas, isótopos estables, génesis, elementos radiactivos, capacidad de retención, mina de U El Berrocal, Sierra de Gredos.*

### ABSTRACT

The clayey fissural fillings (< 60  $\mu\text{m}$  and < 2  $\mu\text{m}$  fractions) associated with the N100°-110°E fractures, at the El Berrocal U mine, have been studied in relation to the natural radionuclide migration/retention processes in a fissured granitic environment. The fracture filled with pyrite, chalcopyrite, sphalerite, galena-bearing quartz, later mineralized by pyrite, pitchblende, carbonate and barite also belongs to that fracture set.

According to the data obtained by X-ray diffraction, thermal and thermogravimetric analyses, EDX coupled to both scanning and transmission electron microscopes and cation exchange methods, the clayey fissural fillings are essentially composed of quartz, sericite, illite, Ca/Mg beidellite, K-feldspar, albite, apatite and occasional kaolinite. Traces of monazite, torbernite, autunite, other unidentified Ca, Y, Ce, La and REE phosphates, ferric sulfates, jarosite, gypsum, barite, calcite, Pb silicates, Fe-oxyhydroxides, gibbsite, Al gels and REE silicate complex gels have been also detected in the < 2  $\mu\text{m}$  fraction.

From a geochemical point of view, the < 2  $\mu\text{m}$  fractions, in relation to the < 60  $\mu\text{m}$  fractions, are very positively anomalous in U, Th, V, Cu, Zn, Sn, Ni, As, Ba, Ca and organic C. Furthermore, Cl is present, in important amounts, in almost all of the essential and accessory minerals and mineraloids in the < 2  $\mu\text{m}$  fractions.

These data suggest that the clayey materials analyzed were mainly produced by hydrothermal alteration of the granitic gouges during the N100°-110°E fracturation phase. Based on the  $\delta^{18}\text{O}$  data obtained from the quartz vein and the < 2  $\mu\text{m}$  fractions, the argillitization process was probably produced by two phases. The first, of sericitic-illitic nature, was caused by the interaction between acid, KCl-rich hydrothermal solutions and the granitic fault gouges, at a temperature range between 70-120° C. The second, of smectitic nature, was probably produced during ancient and/or present weathering processes by strong K leaching of the pre-existing sericite-illite, at room temperature. During the weathering phases, illite and probably smectite were transformed to kaolinite in those fractures with sulfide mineralizations. Jarosite, ferric sulfates, gypsum, torbernite, autunite, gibbsite and Al gels were also probably formed.

The new formed accessory minerals and mineraloids play an important role, either by adsorption or precipitation, in the retention of the radioactive elements, U and Th, and other analogous elements, Y, Ce, La, REE, released during the hydrothermal alteration of the granitic fault gouges and weathering of the uraniumiferous mineralization. Th is mainly held in inherited monazite.

The U sequential leaching indicates that Fe oxyhydroxides and carbonates are important mineral phases for U retention. On the contrary, the clay minerals do not seem to play an important role in the U retention by adsorption, but they do work as a physico-chemical barrier for the  $\text{UO}_2^{++}$  phosphate precipitation.

The high organic C content in the clay fractions could be due to present biological activity in the clayey fissural filling or to organic acids transported from the topographic surface by the percolating water. In this last case, organic-clay complexes would probably be formed.

**Key words:** *Clayey fissural fillings, major and trace elements, stable isotopes, genesis, radioactive elements, retention capacity, El Berrocal U mine, Sierra de Gredos.*

### Introduction

The El Berrocal pluton is located at the central part of the Centro-Iberian Zone (Julivert *et al.*, 1972), near the contact between the Tajo River Tertiary basin and the Sierra de Gredos (fig. 1a). The main granitic facies of this pluton, the so called El Berrocal facies, is the host rock of an U mineralization, mined in the 1960's and named El Berrocal U mine (fig. 1b).

The clayey materials associated with the

N100°-110°E and N155°E fractures in this U mine have been studied in relation to the project «Characterization and validation of natural radionuclide migration processes under real conditions in a fissured granitic environment. El Berrocal experimental site». The fracture filled with pyrite, chalcopyrite, sphalerite, galena-bearing quartz, later mineralized by pyrite, pitchblende, carbonate and barite (Arribas, 1965; Pérez del Villar and Pardillo, 1992) belongs to the N100°-110°E fracture set, and it is also flanked by clayey walls (fig. 1c). Not all the fractures sampled con-

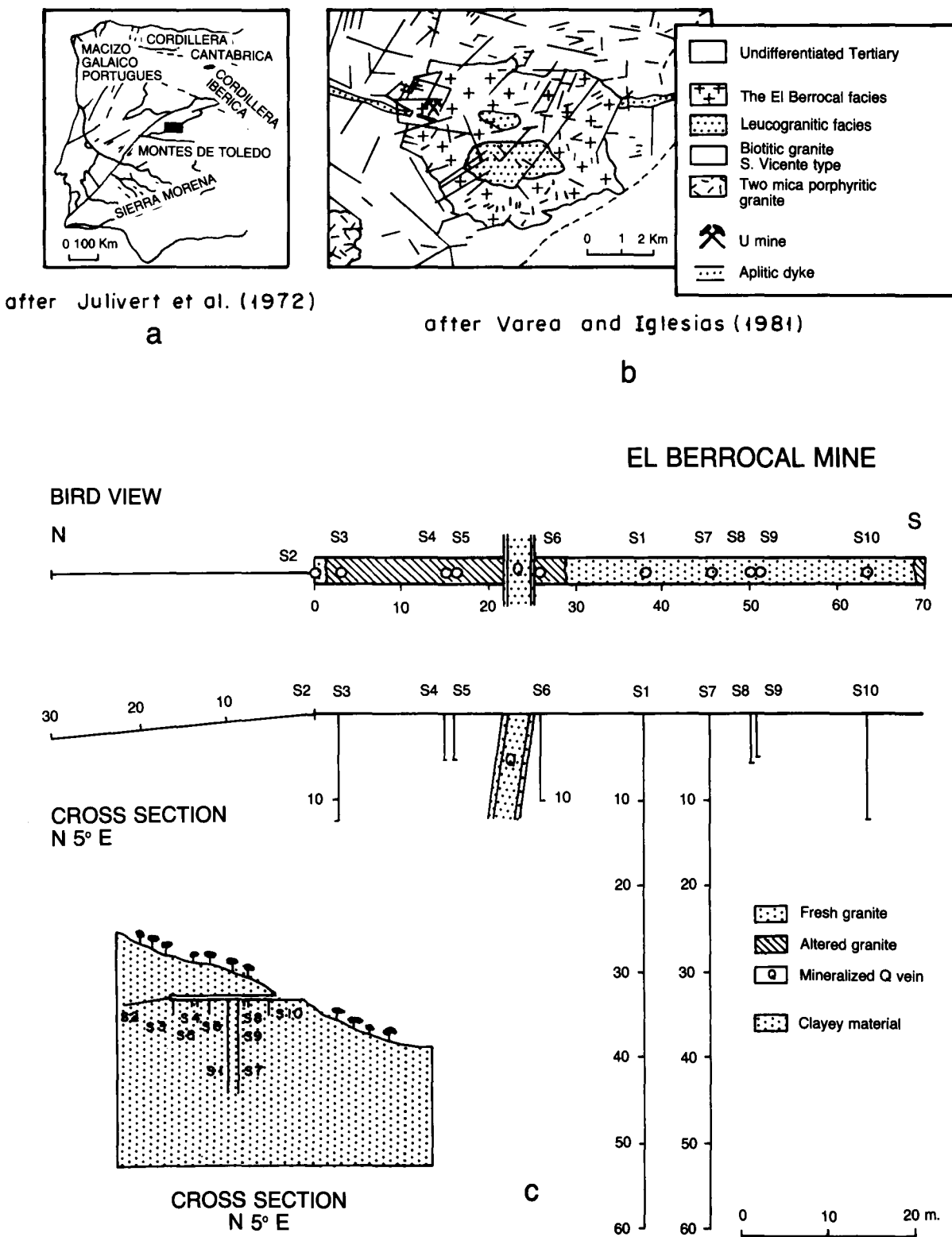


Fig. 1.—Geological situation and schematic sections of the El Berrocal uranium mine.

tain quartz veins, and carbonate minerals occur at about 40-60 m below the topographic surface, except in the mineralized vein, where they appear, in important amounts, at a greater depth.

The fractures sampled affect the El Berrocal facies, which is an alkali feldspar quartz-granite, with muscovite > biotite. The accessory minerals are: corundum, andalusite, ilmenite (anatase), zircon, monazite, xenotime, auelite-thorite, apatite, uraninite, cassiterite, pyrite, sphalerite, galena and fluorite. From a geochemical point of view, the El Berrocal facies is rich in SiO<sub>2</sub> (75.3 %), Al<sub>2</sub>O<sub>3</sub> (13.6 %), P<sub>2</sub>O<sub>5</sub> (0.29 %), F (0.22 %), Li (200 ppm), Rb (400-500 ppm), Zn (70-90 ppm) and U (15-17 ppm) and poor in CaO (0.40-0.50 %), MgO (0.20 %), Ba (20-40 ppm), Sr (5 ppm) and Th (7-8 ppm). The Na<sub>2</sub>O/K<sub>2</sub>O varies between 0.80 and ≈ 1, the K/Rb ratio is low, like that of pegmatites, and the U/Th ratio ranges between 2.26 and 2.50, which is typical of the U-fertile granites (Pérez del Villar and De la Cruz, 1989; Pérez del Villar *et al.*, 1990).

According to Pérez del Villar *et al.* (1990) the El Berrocal facies is affected by a deuteric and/or late-magmatic alteration processes, represented by a pervasive chloritization of biotite, ilmenite-anatase transformation, muscovitization, incipient albite sericitization and interstitial albitization. When this facies is affected by the N100°-110°E fractures, a strong tectonization and a hydrothermal alteration is observed, represented by a general sericitization which releases free quartz. After the fissures were filled by this type of quartz, Mg-Fe chlorites, carbonates and minor and disseminated pitchblende were formed.

In the U mine gallery, the weathering processes affecting the hydrothermally-altered granite are represented by a general oxidation, dissolution of almost all the carbonates and formation of UO<sub>2</sub><sup>++</sup> minerals, mainly autunite and torbernite.

These hydrothermal and supergenic mineralogical transformations produce an important loss of Na<sub>2</sub>O, FeO and Zn, and a remarkable enrichment in K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, MgO, H<sub>2</sub>O<sup>+</sup>, Ba, Rb, Li, U and, less important, in Ce, Sr, Y, La and Th.

The aims of this work are: a) to determine whether the clayey materials associated with N100°-110°E fractures are fissure fillings or the hydrothermal alteration products of the granite; b) to define the later alteration processes, either hypogenic or supergenic, which could modify the original nature of the clay minerals; and c) to establish the behaviour of the clayey materials in relation to the mobilization/retention processes of natural analogue radionuclides (U and Th) and other heavy elements, analogous (La, Ce, Ti and V) or not, in the sense given by Chapman *et al.* (1984 and 1986).

Table 1.—Fractures and location of samples

Name	Distance (m)	Fracture	Direction/Dip
LAR-1 .....	43.70	F-1	N-100°/62° N
DAR-1 .....	45.00	Q vein	N-100°/75° N
DAR-2 .....	45.40	Q vein	N-100°/75° N
DAR-3 .....	46.50	Q vein	N-100°/75° N
DAR-4 .....	48.00	Q vein	N-155°/75° E
LAR-2 .....	49.00	F-2	N-100°/65° N
LAR-3 .....	50.00	F-3	N-105°/64° N
LAR-4 .....	52.50	F-4	N-108°/66° N
LAR-5 .....	54.00	F-5	N-95° /70° N
LAR-6 .....	56.60	F-6	N-87° /78° N
LAR-7 .....	61.30	F-7	N-82° /82° N
LAR-8 .....	65.60	F-8	N-90° /75° S
LAR-9 .....	68.00	F-9	N-90° /85° N

### Sampling and experimental procedures

The sampling has been carried out in the U mine gallery, between 43.7 and 68 m from the entrance. The situation and characteristics of the 13 samples studied are shown in figure 2, table 1. The most important fractures where the clayey samples were obtained are drawn in figure 3 and the flowchart used to separate the < 60 μm and < 2 μm fractions is represented in figure 4.

The granulometric control of the < 2 μm fraction has been carried out by photon spectroscopy correlation (PSC), using a Malvern 4700 system, equipped with a 3W argon ion laser. The experimental conditions were a laser angle at 90° and a laser power of 500 mW.

The mineralogical characterization of the < 60 μm and < 2 μm fractions has been carried out by X-ray diffraction (XRD), combining the powder and oriented aggregates methods. The former has been applied to both fractions, using a rotating sample holder. The latter, with ethylene glycol and sulfoside dimethyl and thermic treatments, has been only applied to the < 2 μm fraction.

To semiquantify the different mineral phases, some reflections and reflecting factors (tables 2 and 3) have been used. The applied equation is:

$$(I/RF)_1 + (I/RF)_2 + (I/RF)_3 + \dots + (I/RF)_n = 100 \quad (1)$$

where: I is the reflection intensity used to quantify each mineral and RF is the reflecting factor of each mineral for the chosen reflection. 1, ..., n are the identified and quantified minerals in the sample.

Table 2.—Reflections and reflecting factors (&lt; 60μm fraction. Powder method)

Minerals	2 θ	d (Å)	RF	Authors
Quartz .....	26.6	3.34	1.5	Barahona (1974)
K-Feldspar .....	27.5	3.24	1	Shultz (1964)
Albite .....	28	3.18	1	Shultz (1964)
Total phyllosilicates ..	19.9	4.45	0.1	Shultz (1964)

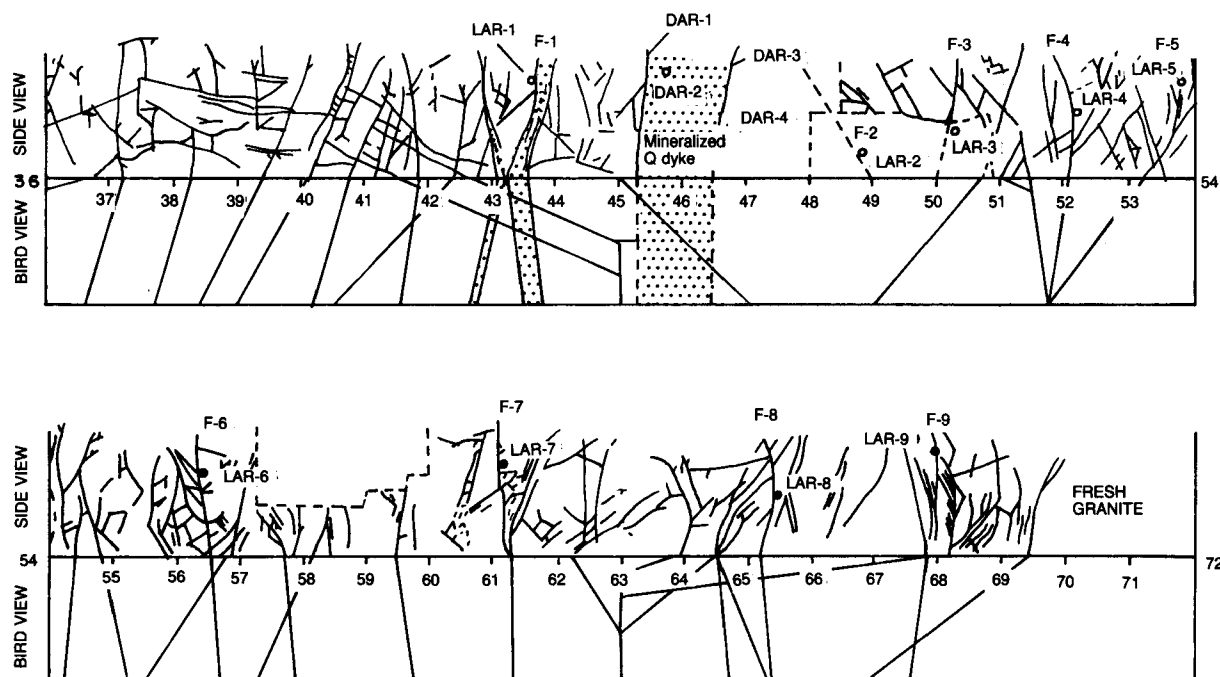


Fig. 2.—Fracture scheme of the west wall of the El Berrocal uranium mine, after Capote (1991), and location of the clayey samples.

Table 3.—Reflections and reflecting factors (< 2µm fraction. OA + EG method)

Minerals	2θ	d (Å)	RF	Authors
Smectite .....	~ 5.10	~ 17	4	Barahona (1974)
Illite .....	8.90	9.92	1	Barahona (1974)
Kaolinite .....	12.50	7.06	2	Barahona (1974)

OA + EG: Oriented aggregates + ethylene glycol.

Due to the mineralogical composition of the clay samples, the following supplementary criteria have been introduced: i) the quartz reflection intensity at 3.34Å has been obtained by subtracting the muscovite or illite reflection intensity at ≈ 10Å, since  $10\text{Å} I_{\text{Mu}} \approx 3.33\text{Å} I_{\text{Mu}}$  (Bradley and Grim, 1961); ii) in sample DAR-3, the % of apatite has been calculated by stoichiometry, assuming that the ratio  $\text{P}_2\text{O}_5/\text{CaO} = 0.73$  in the apatite of the granite (Pérez del Villar, *et al.*, 1990). The first correction has only been applied to the non-oriented powder patterns on both fractions and, only in sample DAR-3, equation (1) has been referred to 100% apatite.

For the identification of the clay and accessory minerals and mineraloids in the < 2 µm fraction, a Zeiss scanning and a Jeol transmission electron microscopes (SEM and TEM) coupled to an energy dispersive X-ray analysis system (EDX) have been used. Electron images have also been taken.

The thermal characteristics of the < 2 µm fraction have been determined using a Perkin-Elmer 1700 DTA equipment, at a scan rate of 10° C/min, under air dynamic atmosphere (40 cc/min), at temperatures between 40° and ≈ 980° C.

The chemical characterization of both fractions was determined combining the following analytical techniques: ICP spectroscopy ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{TiO}_2$ ,  $\text{CaO}$ ,  $\text{P}_2\text{O}_5$ , As, Ba, Be, Ce, Co, Cr, La, Mo, Ni, Sr, W, V, Y and Zn), X-ray spectroscopy ( $\text{SiO}_2$ , on beads, and Rb, Th and U, on powdery samples) and flame spectroscopy ( $\text{K}_2\text{O}$  and  $\text{Li}_2\text{O}$ ). Carbon and S were determined using a Leco CS-244 elemental analyzer; FeO by Sánchez de Ledesma's *et al.* (1990) method, and  $\text{F}^-$  by selective ion electrode. Soluble sulfates were determined by turbidimetry, and  $\text{H}_2\text{O}^-$  and weight loss (WL) by TGA, using a Perkin-Elmer TGS-2 equipment.

Labile  $\text{SiO}_2$  has been dissolved according to Ross and Hendrick's (1945) method and determined by spectrophotometry. Labile  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  were dissolved according to Quejido's *et al.* (1988) method and determined by ICP spectroscopy.

The cation exchange capacity (CEC) of the < 2 µm fraction has been determined by the  $\text{NH}_4\text{NO}_3$  method, according to Bolt *et al.* (1978). The U sequential leaching has been carried out according to Airey's *et al.* (1987) method.

The  $\delta^{18}\text{O}$  in clays and quartz has been determined using a Finnigan-MAT-251 mass spectrometer, following the Borthwick and Harmon's (1982) chemical method, modified by Vennemann and Smith (1990).

## Results

### Characterization of the < 60 µm fraction

**Mineralogical composition.** The semiquantitative mineralogical composition of the < 60 µm fraction (table 4) shows that the total phyllosilicates vary between 43 and 74 %, the principal components being



A



B



C



D

Fig. 3.—Pictures of the most important fractures of the El Berrocal uranium mine and associated clayey zones. A: Fracture F1 and quartz vein. Sample LAR-1. B: Southern wall of the mineralized quartz vein. Sample DAR-1. C: Fracture within the mineralized quartz vein. Sample DAR-2. D: Northern wall of the mineralized quartz vein. Sample DAR-3.

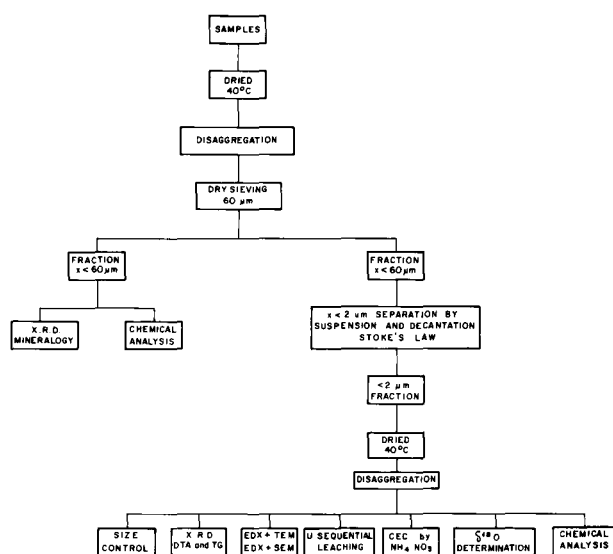


Fig. 4.—Flowchart corresponding to the separation and studies carried out in the < 60 and < 2 μm fractions.

sericite and illite and minerals belonging to the smectite subgroup. Traces of kaolinite are observed in only three samples (DAR-2, LAR-2 and LAR-3). The minerals associated with the phyllosilicates, in order of abundance, are: quartz, K-feldspar, albite and apatite.

**Chemical composition.** The chemical composition of the < 60 μm fraction has been subdivided into major (table 5a) and trace elements (table 5b).

a) **Major elements.** From all these elements, the high P<sub>2</sub>O<sub>5</sub> is remarkable in all the samples, particularly in sample DAR-3, which is also very anomalous in CaO.

The highest total SO<sub>2</sub> value is observed in sample DAR-1, and the variations observed in the rest of the major elements are due, fundamentally, to the

phyllosilicate contents of the samples. The high K<sub>2</sub>O values, in almost all the samples, indicate that sericite, illite and K-feldspar are the predominant minerals.

The H<sub>2</sub>O<sup>-</sup> has been determined at 220° C, because smectites loose their moisture in two different steps, within a temperature range from 80° C to 170° C.

b) **Trace elements.** If the values in table 5b are compared with the average values corresponding to the hydrothermally-altered and fresh granite from the mine gallery (Pérez del Villar *et al.*, 1990), the following remarks can be made:

— All the samples are very positively anomalous in Ba, compared to the altered and fresh granite, whose average concentration are 47 and 29 ppm, respectively. The samples located in the U-mineralized vein are exceptionally high in Ba, due to the existence of barite associated with the U mineralization. Furthermore, sample DAR-1, which is the most anomalous in Ba, is also anomalous in total SO<sub>2</sub>.

— Similarly, the Sr content of the clayey samples is higher than in the altered and fresh granite, whose average concentrations are 9 and 5 ppm, respectively.

— The Ce, La and Y contents of the samples are also remarkably higher than those in the altered and fresh granites, whose average concentrations, in ppm, are: 27 (Ce), 7 (La) and 7 (Y); and 22 (Ce), 6 (La) and 6 (Y), respectively. All of these elements are mainly held in monazite and xenotime in the granite. Sn follows the same trend, with contents higher than in both the altered (17 ppm) and fresh granite (17 ppm), in which Sn occurs, fundamentally, as cassiterite.

— The Zn values are also higher than in the altered and fresh granite (121 and 89 ppm, respectively). This element is found in the structures of the micas and, fundamentally, as sphalerite in the granite. The clayey samples from the mineralized quartz vein and adjacent fractures (LAR-1, LAR-2 and LAR-3) are

Table 4.—Semiquantitative mineralogical composition of the < 60 μm fraction

Min. (%)	Samples												
	LAR-1	DAR-1	DAR-2	DAR-3	DAR-4	LAR-2	LAR-3	LAR-4	LAR-5	LAR-6	LAR-7	LAR-8	LAR-9
Q.....	55	22	25	50	46	34	24	30	25	30	23	27	41
Ab.....	1	3	—	3	4	traces	7	4	3	—	3	4	4
K-Fd.....	—	—	—	—	—	7	15	8	9	8	7	8	—
Ap.....	traces	traces	traces	5	traces	traces	traces	traces	traces	traces	traces	traces	traces
T. Ph.....	43	74	74	44	50	59	54	58	63	62	66	60	54
Ser.....	xxx	xxx	xx	xxx	xxx	xx	xx	xx	xx	xx	xx	xxx	xxx
Smc.....	xx	xx	xxx	xx	xx	xx	xxx	xx	xxx	xxx	xx	xx	xx
Kao.....	—	—	x	—	—	x	x	—	—	—	—	—	—

Q: quartz; Ab: albite; K-Fd: K-feldspar; Ap: apatite (determined by stoichiometry); T. Ph.: total phyllosilicates; Ser.: sericite; Smc.: smectite; Kao.: kaolinite.

Table 5a.—Chemical composition on the &lt; 60 µm fraction (major elements)

Oxides (%)	LAR-1	DAR-1	DAR-2	DAR-3	DAR-4	LAR-2	LAR-3	LAR-4	LAR-5	LAR-6	LAR-7	LAR-8	LAR-9
SiO <sub>2</sub> .....	80.39	64.58	68.17	69.34	65.60	68.07	68.54	68.24	66.10	69.90	65.77	68.32	74.77
Al <sub>2</sub> O <sub>3</sub> .....	11.45	21.27	18.16	15.93	20.70	16.22	15.53	17.25	17.60	16.80	16.92	17.72	15.24
Fe <sub>2</sub> O <sub>3</sub> .....	0.80	1.43	1.14	1.39	1.81	1.12	0.93	1.91	2.93	0.99	2.19	1.47	0.99
FeO.....	0.10	0.20	0.37	0.23	0.17	0.66	0.74	0.22	0.24	0.19	0.19	0.19	0.07
MgO.....	0.58	1.16	1.36	0.56	0.69	1.46	1.26	0.98	0.98	1.30	1.25	1.00	0.46
MnO.....	0.05	0.05	0.05	0.05	0.25	0.05	0.05	0.05	0.09	0.06	0.05	0.09	0.06
CaO.....	0.40	0.65	0.64	2.62	0.92	0.83	0.92	0.73	0.82	0.74	0.86	0.80	0.42
K <sub>2</sub> O.....	0.81	5.05	1.46	4.37	5.10	5.24	4.95	5.78	6.10	6.20	5.58	5.94	4.08
Na <sub>2</sub> O.....	0.09	0.24	0.12	0.16	0.13	0.20	0.41	0.21	0.22	0.21	0.29	0.53	0.20
P <sub>2</sub> O <sub>5</sub> .....	0.31	0.65	0.45	2.13	0.60	0.45	0.44	0.43	0.53	0.41	0.43	0.51	0.25
TiO <sub>2</sub> .....	0.10	0.22	0.05	0.12	0.21	0.14	0.16	0.17	0.19	0.17	0.15	0.19	0.11
CO <sub>2min</sub> .....	0.03	0.02	0.04	0.10	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.02
CO <sub>2org</sub> .....	0.09	0.14	0.15	0.09	0.10	0.12	0.09	0.08	0.10	0.08	0.08	0.09	0.09
H <sub>2</sub> O <sup>-</sup> 220° C.....	1.23	2.26	4.26	1.45	1.58	3.47	3.75	2.07	2.20	2.12	3.78	1.49	0.80
H <sub>2</sub> O <sup>+</sup> .....	1.65	2.82	4.45	2.19	2.62	2.42	2.18	2.36	2.55	2.41	2.68	2.65	3.14
SO <sub>2total</sub> .....	0.06	0.15	0.04	<0.02	<0.02	0.06	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
SO <sub>4sol</sub> .....	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
F.....	0.06	0.09	0.06	0.16	0.09	0.09	0.09	0.14	0.15	0.15	0.18	0.16	0.06
F ≡ 0.....	0.02	0.04	0.02	0.07	0.04	0.04	0.04	0.06	0.06	0.06	0.08	0.07	0.08
Total.....	100.18	100.93	100.95	100.82	100.55	100.58	100.02	100.58	100.76	101.78	100.23	101.29	100.74

Table 5b.—Chemical composition of the &lt; 60 µm fraction (trace elements)

Elements (ppm)	LAR-1	DAR-1	DAR-2	DAR-3	DAR-4	LAR-2	LAR-3	LAR-4	LAR-5	LAR-6	LAR-7	LAR-8	LAR-9
Li.....	140	150	140	90	100	120	180	120	100	150	110	150	60
As.....	29	105	69	<25	<25	2025	495	<25	41	<25	<25	<25	<25
Ba.....	190	2550	500	190	555	220	295	195	215	145	235	180	155
Be.....	<5	8.2	5.5	8.1	6.3	<5	5.7	5.6	6.4	<5	7	5.4	6.2
Ce.....	25	56	40	12	48	27	41	38	40	54	35	35	19
Co.....	20	12	9.8	<5	15	<5	8.4	<5	<5	<5	<5	<5	<5
Cr.....	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Cu.....	46	465	1550	475	150	85	19	<5	6.9	<5	<5	19	34
La.....	12	27	20	26	26	31	22	26	22	31	21	18	5.6
Mo.....	19	14	<5	<5	<5	<5	6.5	<5	<5	<5	<5	<5	<5
Ni.....	5.3	<5	8	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Sn.....	34	50	38	59	40	37	45	39	40	36	37	34	57
Sr.....	8.3	17	51	20	29	32	27	24	26	33	31	20	<5
V.....	6.8	8.4	6.3	11	11	5.1	5.2	6.8	6.7	6.0	5.6	7.7	14
W.....	<25	<25	<25	29	<25	<25	<25	<25	<25	<25	<25	<25	<25
Y.....	9	18	10	24	16	16	21	16	15	13	15	14	11
Zn.....	395	355	825	280	355	760	1125	275	220	115	215	205	87
U.....	16	53	24.5	231.5	249	60	103	40	115	27	57	155	9.5
Th.....	7	14	4.5	8	13	12	10	9.5	12	11	8	12	12

positively anomalous in Zn and Cu. It should be reminded that the quartz vein is also mineralized by pyrite, chalcopyrite and sphalerite.

— The As is, in general, below the detection limit of the ICP spectroscopy, except in some samples from the quartz vein and adjacent fractures, mainly DAR-1, LAR-2 and LAR-3.

— The < 60 µm fractions are, in general, enriched

in U and Th in relation to the altered (22 and 9 ppm, respectively) and fresh (17 and 8 ppm, respectively) granite. In the former, U occurs mainly as UO<sub>2</sub><sup>++</sup> phosphates, and in the fresh granite U is fundamentally present as uraninite and Th as thorite and held in monazite.

— The highest U contents are found in samples located in the U mineralized quartz vein (DAR-3 and



DAR-4), in adjacent fractures (LAR-3) and in farther ones (LAR-5 and LAR-8). The two last samples were obtained from fractures that intersect the hydrothermally-altered granite, which is also enriched in U.

#### Characterization of the < 2 $\mu\text{m}$ fraction

**Size Control.** The granulometric distribution has been obtained for only three samples (fig. 5), which present unimodal distribution plots, with average particle sizes of  $\approx 1$ , 0.78 and 0.43  $\mu\text{m}$ .

**Mineralogical Composition.** According to the semi-quantitative mineralogical composition of the < 2  $\mu\text{m}$  fraction (table 6), all the samples are composed of illite, smectite, quartz, K-feldspar and apatite. Significant amounts of kaolinite have only been identified in sample DAR-2, located in the mineralized quartz vein. In samples LAR-1, DAR-1, DAR-4, LAR-2 and LAR-3, kaolinite occurs as traces or in very low percentages. None of the XRD patterns shows evidences of illite-smectite interstratifications. The identification of the type of smectite by DTA analysis is doubtful, because the samples are clay mixtures.

**Transmission and Scanning Electron Microscopy.** The chemical analyses obtained by TEM + EDX and the structural formula of the clay minerals (tables 7a, b, c, d) are given. The data in table 7a correspond to dioctahedral clay micas, sericite, hydromuscovite and illite, and the most numerous chemical data of the clays (table 7b) correspond to randomly-interstratified illite-smectite. However, the absence of any evidence of interstratification by XRD suggests that these last data correspond to physical mixtures of illite and smectite, and the calculation of their structural formula is, therefore, pointless. The data corresponding to the aluminian dioctahedral smectite, specifically beidellite, and the chemical composition of kaolinite (table 7c and d) complete the analytical results of the clay minerals.

Similarly, the semi-quantitative chemical composition of the accessory minerals and mineraloids associated with the clay minerals has been obtained by EDX + SEM and the data are given in table 8. The Fe compounds and minerals (Fe oxyhydroxides,  $\text{Fe}^{3+}$  sulfates and jarosite) occur either as coatings on the clay particles or as single grains. Something similar occurs with the Al oxyhydroxide gels. Gibbsite, calcite, gypsum, barite, apatite, monazite, torbernite and complex aluminosilicates generally appear as single euhedral to anhedral grains, some of them reaching up to 20  $\mu\text{m}$ . According to the electron images of these minerals and mineraloids (fig. 6), the REE

silicates and K-Al-Si-Cl complexes are gels trapped by the clay minerals.

Chlorine is present in almost all the minerals and mineraloids, sometimes in important concentrations. This anion could be a tracer of the hydrothermal so-

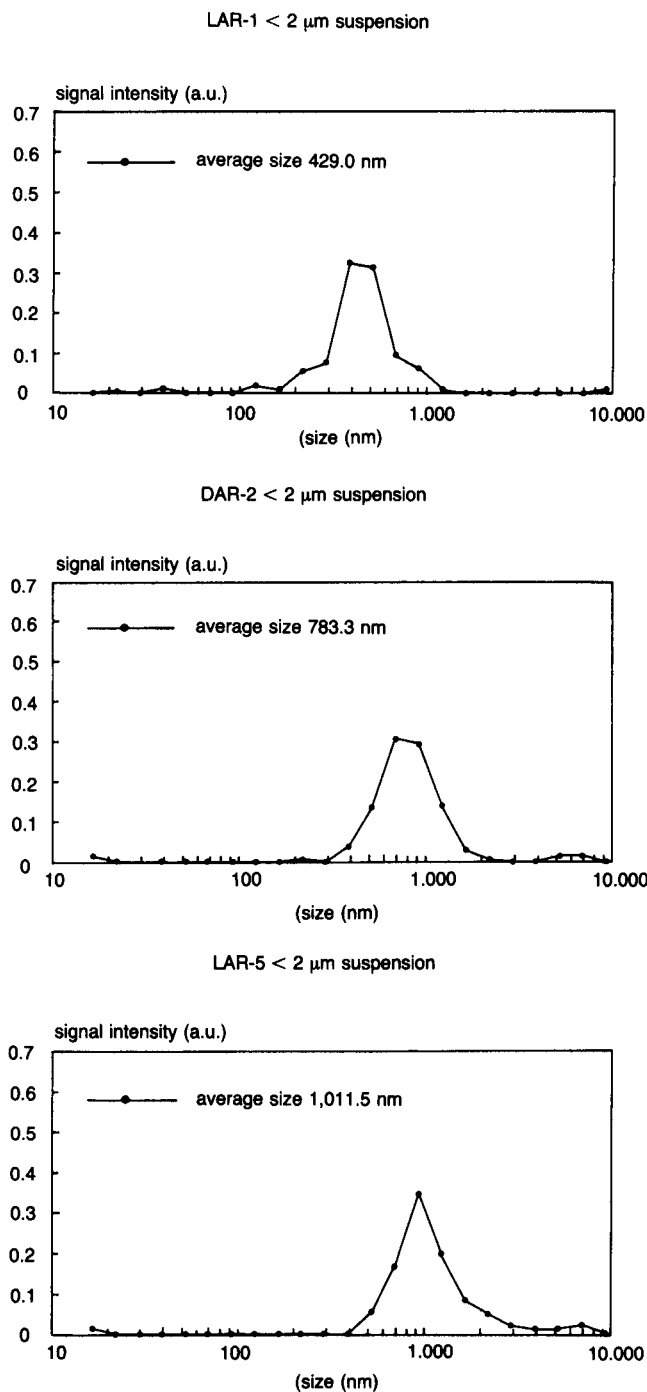


Fig. 5.—Size distribution plots obtained for three < 2  $\mu\text{m}$  fractions.

Table 6.—Semiquantitative mineralogical composition of the &lt; 2 μm fraction

P.M.	LAR-1 %	DAR-1 %	DAR-2 %	DAR-3 %	DAR-4 %	LAR-2 %	LAR-3 %	LAR-4 %	LAR-5 %	LAR-6 %	LAR-7 %	LAR-8 %	LAR-9 %
T.Cl. ....	81	91	84	80	70	68	60	71	72	74	65	81	71
Q. ....	19	9	16	13	11	18	17	18	17	14	18	14	12
K-Fd ....	traces	traces	—	traces	18	14	23	10	11	12	16	5	17
Ap. ....	traces	traces	traces	7	traces	traces	traces	traces	traces	traces	traces	traces	traces
OA + EG													
Illite ....	50	64	27	48	42	31	21	35	32	32	31	43	45
Smc. ....	30	26	48	32	28	35	38	36	40	42	34	38	26
Kao. ....	—	—	9	—	traces	2	1	—	—	—	—	—	—
Q. ....	19	9	16	13	11	18	17	18	17	14	18	14	12
K-Fd ....	traces	traces	—	traces	18	14	23	10	11	12	16	57	17
Ap. ....	traces	traces	traces	7	traces	traces	traces	traces	traces	traces	traces	traces	traces
Total .....	99	99	100	100	99	100	100	99	100	100	99	100	100

T.Cl.: total clay; P.M.: Powder method; OA + EG: oriented aggregates + ethylene glycol; Smc.: smectite; Kao.: kaolinite; Ap.: apatite (by stoichiometry).

Table 7a.—Chemical composition and structural formula of sericite-illite s. str. with &lt; 5 % of expanding layers

Samples	DAR-3	DAR-4	DAR-3	LAR-1	DAR-3	DAR-3
Oxides (%)	(1)	(2)	(3)	(4)	(5)	(6)
SiO <sub>2</sub> .....	50.63	48.90	49.62	49.15	51.03	51.29
Al <sub>2</sub> O <sub>3</sub> .....	32.92	32.53	36.83	38.23	36.54	36.54
Cr <sub>2</sub> O <sub>3</sub> .....	—	—	—	—	—	—
Fe <sub>2</sub> O <sub>3</sub> .....	4.62	6.87	2.53	2.03	1.14	2.08
MgO.....	—	—	—	—	—	—
CaO.....	—	—	—	—	0.96	—
K <sub>2</sub> O.....	11.83	11.71	11.02	10.59	10.32	10.09
Total.....	100	100	100	100	99.99	100
Si <sup>4+</sup> .....	6.467	6.308	6.265	6.180	6.395	6.413
Al <sup>3+</sup> .....	1.533	1.692	1.735	1.820	1.605	1.587
Total.....	8.000	8.000	8.000	8.000	8.000	8.000
Al <sup>3+</sup> .....	3.424	3.254	3.747	3.850	3.792	3.797
Fe <sup>3+</sup> .....	0.444	0.667	0.240	0.190	0.110	0.200
Cr <sup>3+</sup> .....	—	—	—	—	—	—
Mg <sup>2+</sup> .....	—	—	—	—	—	—
Total.....	3.868	3.921	3.987	4.040	3.902	3.997
K <sup>+</sup> .....	1.927	1.927	1.775	1.700	1.651	1.610
Ca <sup>2+</sup> .....	—	—	—	—	—	—
Mg <sup>2+</sup> .....	—	—	—	—	—	—
Total.....	1.927	1.927	1.775	1.700	1.781	1.610
Δ.....	-1.533	-1.692	-1.735	-1.820	-1.605	-1.587
◇.....	-0.396	-0.237	-0.039	0.120	-0.294	-0.009
=.....	1.929	1.929	1.774	1.700	1.899	1.596
Si/Al.....	1.304	1.275	1.142	1.089	1.184	1.191
%.....	79.47	87.71	97.80	100	84.52	99.43

Δ : Tetrahedral charge.

◇ : Octahedral charge.

= : Interlayer charge.

% : Percentage of tetrahedral charge.

lutions responsible of the alteration processes. Sulphur, P and heavy metals, especially Cu and Zn, are also detected in these minerals and mineraloids. Even Cr and Ni occasionally appear in the Fe oxyhydroxides.

Uranium has been identified in sample DAR-3 as a 20μm euhedral torbernite crystal; Th has been detected in monazite, and both elements in an unidentified Th-U-REE-Si-Al-P mineral.

#### Chemical Composition:

a) *Major elements.* The analytical results of the major elements, including free SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> (table 9) show that:

— As in the < 60 μm fraction, high P<sub>2</sub>O<sub>5</sub> contents are also present in the clay fractions, principally in those corresponding to the samples from the mineralized dyke. Among them, sample DAR-3, which is rich in apatite, is very anomalous both in P<sub>2</sub>O<sub>5</sub> and CaO.

The variations observed in the K<sub>2</sub>O contents are related to the (illite + K-feldspar)/smectite ratio.

— All the samples show high free SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> contents. The former is associated with Al gels, and the latter occurs as Fe oxyhydroxides, as confirmed by EDX + SEM analyses. The free Al<sub>2</sub>O<sub>3</sub> values are lower than expected, according to the data obtained by the abovementioned techniques. However, this can be explained if most of the free Al oxyhydroxides occurred as gibbsite, which is insoluble by the partial dissolution method used.

— The high organic CO<sub>2</sub> content is remarkable in all the samples, particularly in samples LAR-1, DAR-2, LAR-2 and LAR-5.

b) *Trace elements.* As for the major elements, the trace elements in the < 2 μm fraction (table 10) are

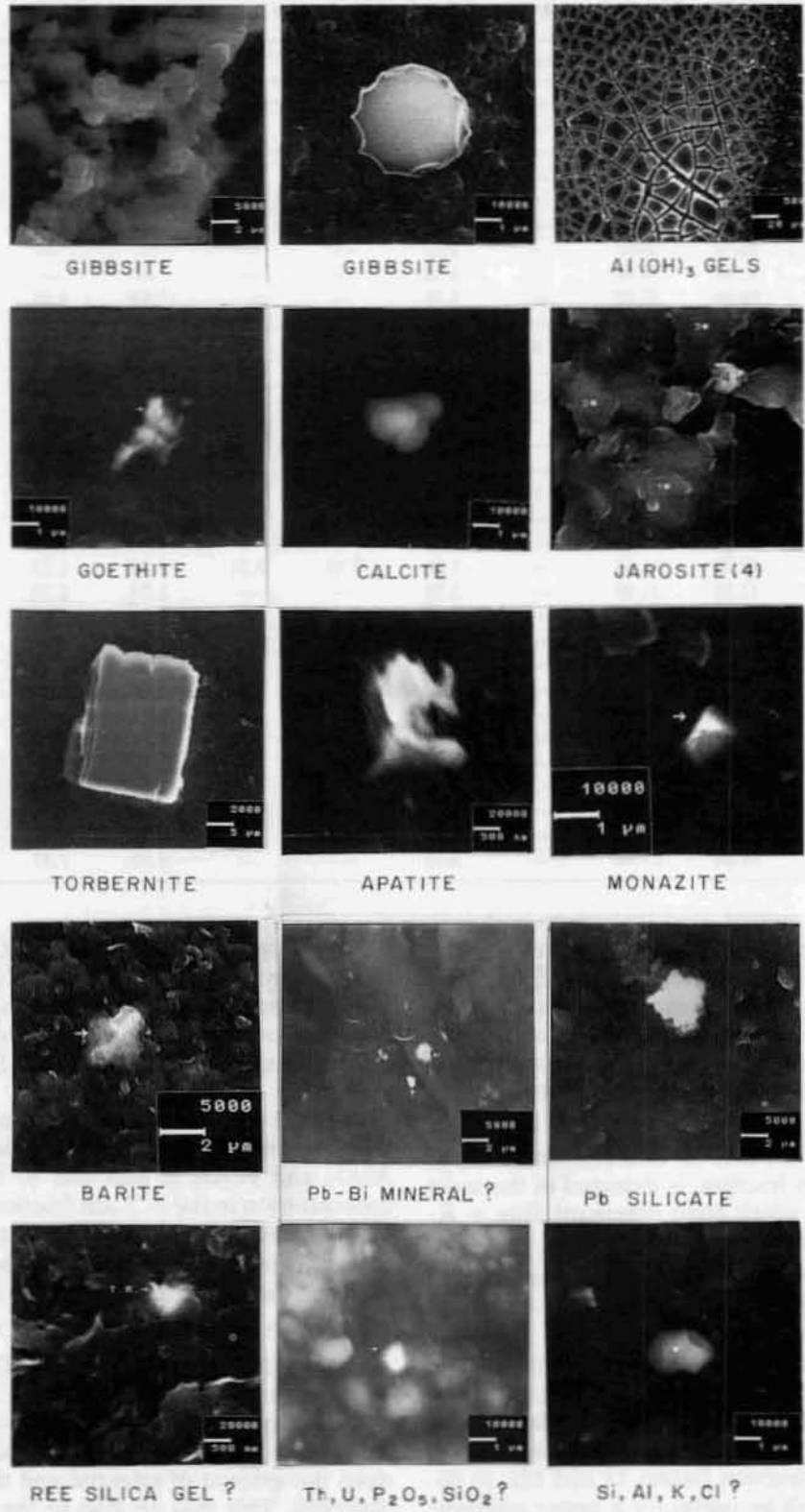


Fig. 6.—SEM images of the most important minerals and mineraloids associated with the clay minerals.

Table 7b.—Chemical composition of the physical mixtures between illite and beidellite

Samples	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	TiO <sub>2</sub>	MgO	CaO	K <sub>2</sub> O	Total
DAR-3 (7).....	52.05	35.49	—	2.67	—	—	—	—	9.78	99.99
DAR-3 (8).....	47.63	39.74	—	3.31	—	—	—	—	9.32	100
DAR-3 (9).....	51.81	36.94	—	2.01	—	—	—	—	9.24	100
DAR-3 (10).....	46.49	37.90	—	2.73	—	—	3.68	—	9.20	100
DAR-4 (11).....	49.76	33.20	—	3.43	—	—	3.41	1.30	8.89	100
LAR-1 (12).....	51.95	37.78	—	1.70	—	—	—	—	8.57	100
DAR-3 (13).....	52.73	35.57	—	3.22	—	—	—	—	8.48	100
DAR-2 (14).....	52.01	34.90	—	4.70	—	—	—	—	8.39	100
DAR-4 (15).....	50.26	32.42	—	3.76	—	—	3.69	1.61	8.26	100
DAR-4 (16).....	50.06	32.54	—	3.51	—	—	4.06	1.61	8.22	100
DAR-2 (17).....	52.29	34.65	2.98	1.93	—	—	—	—	8.15	100
DAR-4 (18).....	48.71	34.23	—	3.98	—	—	3.82	1.30	7.95	100
DAR-4 (19).....	47.82	31.73	0.55	4.93	—	—	4.66	2.48	7.84	100
DAR-3 (20).....	52.74	37.17	—	2.29	—	—	—	—	7.80	100
DAR-4 (21).....	51.29	31.76	—	3.77	—	—	3.26	2.28	7.64	100
LAR-1 (22).....	55.31	35.39	—	1.82	—	—	—	—	7.49	100
LAR-1 (23).....	58.07	32.24	0.84	1.37	—	—	—	—	7.48	100
LAR-1 (24).....	51.77	34.41	—	1.12	—	—	5.24	—	7.46	100
DAR-4 (25).....	52.22	30.70	—	4.14	—	—	4.69	1.12	7.13	100
DAR-4 (26).....	49.92	31.61	—	3.86	0.95	0.21	5.36	1.15	6.93	100
DAR-4 (27).....	52.35	31.99	—	3.92	—	—	2.74	2.70	6.30	100
LAR-2 (28).....	56.42	27.75	—	3.67	—	—	3.97	2.15	6.04	100
LAR-2 (29).....	53.76	30.67	—	3.24	—	0.50	4.58	1.34	5.91	100
LAR-2 (30).....	57.65	28.16	—	2.78	—	—	4.66	0.91	5.84	100
LAR-2 (31).....	57.00	29.04	—	1.52	—	—	5.80	1.43	5.21	100
LAR-2 (32).....	55.90	26.93	—	4.36	—	—	6.13	1.52	5.16	100
DAR-3 (33).....	47.31	31.36	—	7.91	—	—	6.71	1.61	5.10	100
DAR-2 (34).....	55.61	29.13	—	3.92	—	—	3.90	2.45	4.98	100
DAR-4 (35).....	62.61	25.11	—	3.14	—	—	2.10	2.23	4.81	100
LAR-2 (36).....	56.12	28.36	—	2.63	—	—	6.56	1.60	4.73	100
DAR-2 (37).....	55.74	29.62	—	4.19	—	—	4.60	1.42	4.44	100
LAR-2 (38).....	58.84	27.46	—	3.73	—	—	4.35	1.47	4.12	100

in agreement with the contents observed in the < 60  $\mu\text{m}$  fraction. Thus, As, Ba, Cu and Zn positive anomalies are detected in the same samples as for the < 60  $\mu\text{m}$  fraction, though enhanced. Cerium, La and Y are also present in important amounts, though generally in slightly lower concentrations than in the < 60  $\mu\text{m}$  fraction.

The highest level of Rb, an element not determined in the < 60  $\mu\text{m}$  fraction, is detected in the most K<sub>2</sub>O-rich samples, which have dominant illite + K-feldspar over smectite.

The same U and Th anomalies observed in the < 60  $\mu\text{m}$  fraction are also detected in the clay fraction, though generally enhanced.

The ratio between the chemical composition of the < 2 and < 60  $\mu\text{m}$  fractions has been calculated to obtain the chemical enrichment or impoverishment factor reached during the separation of the clay fraction from the < 60  $\mu\text{m}$  fraction (tables 11 and 12). In general, this factor will be useful for a better interpretation of the retention capacity of the clays for light and heavy elements, either by adsorption or precipi-

tation. Thus, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, mineral CO<sub>2</sub>, organic CO<sub>2</sub>, As, Ba, Be, Cu, Ni, Sn, V, Zn, U and Th are generally enriched in the < 2  $\mu\text{m}$  fraction. However, Ce, Y, Sr and P are only enriched in certain samples, usually belonging to the mineralized vein zone.

The first four oxides are fundamentally related to the clay mineral enrichment. The enrichment in Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> is also due to the oxyhydroxide concentration in the < 2  $\mu\text{m}$  fraction, and the enrichment in CaO and mineral CO<sub>2</sub> is related to the calcite enrichment in this fraction. The enrichment observed in the trace elements will be discussed in another section.

*Cation Exchange Capacity.* The CEC of the < 2  $\mu\text{m}$  fractions, expressed in mEq/100 gr (table 13), shows that: i) the smectite-rich samples have the highest CEC. However, a good correlation between the amount of smectite and these values is not observed. This may be due to the semiquantitative mineralogical composition of the < 2  $\mu\text{m}$  fractions, and ii) except in sample LAR-1, the most important

Table 7c.—Chemical composition and structural formula of beidellitic smectite

Samples	DAR-2	DAR-2	DAR-2
Oxides (%)	(39)	(40)	(41)
SiO <sub>2</sub> .....	55.92	61.53	58.91
Al <sub>2</sub> O <sub>3</sub> .....	33.57	29.24	36.74
Cr <sub>2</sub> O <sub>3</sub> .....	1.10	—	—
Fe <sub>2</sub> O <sub>3</sub> .....	3.18	2.86	1.87
MgO.....	3.32	3.40	—
CaO.....	1.55	0.64	1.41
K <sub>2</sub> O.....	1.38	1.25	1.07
Total.....	100.02	100.02	100.02
Si <sup>4+</sup> .....	6.700	7.290	6.928
Al <sup>3+</sup> .....	1.300	0.710	1.072
Total.....	8.000	8.000	8.000
Al <sup>3+</sup> .....	3.440	3.370	4.020
Fe <sup>3+</sup> .....	0.290	0.260	0.165
Cr <sup>3+</sup> .....	0.100	—	—
Mg <sup>2+</sup> .....	0.170?	0.370?	—
Total.....	4.000	4.000	4.185
K <sup>+</sup> .....	0.210	0.19	0.161
Ca <sup>2+</sup> .....	0.200	0.220	0.177
Mg <sup>2+</sup> .....	0.420?	0.23?	—
Total.....	0.830	0.64	0.338
Δ.....	-1.300	-0.710	1.072
◇.....	-0.170	-0.37	0.555
=.....	1.450	1.090	0.517
Si/Al.....	1.413	1.786	1.360
%.....	88.43	65.74	100

Δ : Tetrahedral charge.  
 ◇ : Octahedral charge.  
 = : Interlayer charge.  
 % : Percentage of tetrahedral charge.

exchange cations in all the samples are Ca and Mg, and Na is always dominant over K.

*U Sequential Leaching.* The data of the U sequential leaching, classified by the reagents used and by the mineral and mineraloid phases with which the U is associated are given in table 14. The percentage of readily leachable U in the samples varies from 5 to approximately 35 % of the total U. Generally, this U is fundamentally associated with the amorphous and crystalline Fe oxyhydroxides, and the carbonate phase also plays an important role in the retention of this radioelement. Furthermore, the extremely low amount of U (< 0.1 ppm) associated with the clay fraction as exchange cation should be pointed out, except in sample LAR-5 (2.9 ppm).

*δ<sup>18</sup>O in the < 2 μm Fractions and in the Quartz from the U Mineralized Vein.* The δ<sup>18</sup>O values have

Table 7d.—Chemical composition and structural formula of kaolinite

Samples	DAR-2	DAR-2	DAR-2	DAR-2	DAR-2	DAR-2
Oxides (%)	(42)	(43)	(44)	(45)	(46)	(47)
SiO <sub>2</sub> .....	54.08	52.83	52.22	53.69	54.93	52.98
Al <sub>2</sub> O <sub>3</sub> .....	43.40	46.29	45.40	46.31	44.56	45.79
Cr <sub>2</sub> O <sub>3</sub> .....	—	—	—	—	—	—
Fe <sub>2</sub> O <sub>3</sub> .....	1.46	—	1.18	—	0.51	0.83
MgO.....	—	—	—	—	—	—
CaO.....	—	—	0.67	—	—	0.40
K <sub>2</sub> O.....	1.07	0.89	0.52	—	—	—
Total.....	100.01	100.01	99.99	100.00	100.00	100.00
Si <sup>4+</sup> .....	4.045	4.060	4.000	4.040	4.060	4.013
Al <sup>3+</sup> .....	—	—	0.09	—	—	—
Total.....	4.045	4.060	4.000	4.040	4.060	4.013
Al <sup>3+</sup> .....	—	—	—	—	—	—
Fe <sup>3+</sup> .....	3.82	3.93	3.910	3.980	3.890	3.940
Cr <sup>3+</sup> .....	0.08	—	0.070	—	0.030	0.47
Mg <sup>2+</sup> .....	—	—	—	—	—	—
Total.....	3.900	3.930	3.980	3.980	3.920	3.987
K <sup>+</sup> .....	0.10	0.08	0.05	—	—	—
Ca <sup>2+</sup> .....	—	—	0.053	—	—	—
Mg <sup>2+</sup> .....	—	—	—	—	—	—
Total.....	0.10	0.08	0.156	—	—	0.064
Δ.....	0.180	0.240	-0.09	0.16	0.24	0.052
◇.....	-0.300	-0.210	-0.060	-0.060	-0.24	-0.039
=.....	0.120	0.030	0.15	0.10	0	0.013
Si/Al.....	1.06	1.03	0.98	1.01	1.04	1.018

Δ : Tetrahedral charge.  
 ◇ : Octahedral charge.  
 = : Interlayer charge.

been determined in all the < 2 μm fractions and in six quartz samples from the U mineralized vein (table 15).

Given that the < 2 μm fractions are mixtures of sericite-illite, smectite, kaolinite, quartz, feldspars and apatite, a first approach to calculate the theoretical δ<sup>18</sup>O value for illite has been done correlating the illite/smectite ratio with the experimental δ<sup>18</sup>O (fig. 7). Thus, a theoretical δ<sup>18</sup>O value = + 17.45 ‰ for pure smectite has been estimated. This value is in agreement with the theoretical δ<sup>18</sup>O value of a smectite in equilibrium with the El Berrocal meteoric water (δ<sup>18</sup>O = -8 ‰) at a T = 20° C (Reyes *et al.*, in prep. a).

From the theoretical δ<sup>18</sup>O value for smectite and the measured δ<sup>18</sup>O for quartz, the theoretical δ<sup>18</sup>O for pure illite has been determined in samples DAR-1, DAR-2 and LAR-1, in which quartz is the only accessory mineral (table 16).

According to Savin and Lee's (1988) equation for

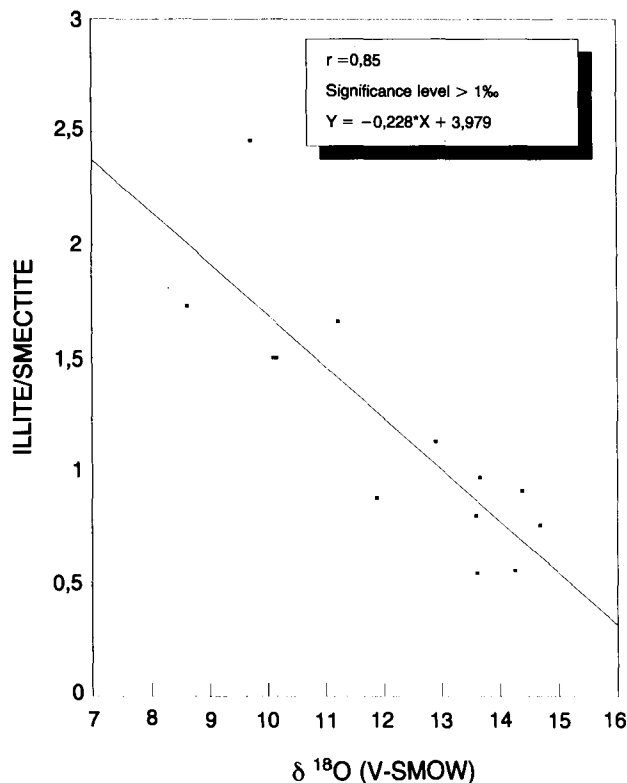


Fig. 7.—Illite/smectite ratio vs. measured  $\delta^{18}\text{O}$  for clay mixtures samples.

illite-water fractionation, illite is formed at a T range between 70-120° C (fig. 8a). Similarly, according to Clayton's *et al.* (1972) equation for quartz-water fractionation, the quartz vein is formed at a T range between 80-120° C (fig. 8b). Consequently, and as a preliminary conclusion, sericite-illite and the quartz vein are formed within the same epithermal alteration process, as had been mentioned by Pérez del Villar *et al.* (1993).

$\delta^{18}\text{O}$  are currently being measured in all the pure minerals present in the clay fraction, in order to calculate the accurate T of formation of this alteration process (Reyes *et al.*, in prep. b).

### Discussion

The mineralogical, geochemical and isotopic characteristics of the clayey materials studied suggest that these materials were formed by the interaction between the granitic fault gouges and the hydrothermal solutions originated during the tectonization process, followed by weathering. The principal clay minerals found in the samples (sericite-illite) and the presence of  $\text{Cl}^-$  in all the minerals analyzed, including the clays and some mineraloids, suggest that the hydrothermal solutions had an alkali chloride nature, with an undetermined Na/K ratio. However, this ratio was possibly controlled by the  $\text{Ab/KFd} = 1.7$

Table 8.—Semiquantitative chemical composition of the accessory minerals and mineraloids associated with clay minerals

Min.	Oxides %	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	Samples analyzed
Gibbsite	SiO <sub>2</sub> .....	0.90	—	1.81	1.17	13.40	5.27	DAR-2
	Al <sub>2</sub> O <sub>3</sub> .....	98.53	86.52	93.70	97.40	81.04	94.73	LAR-1
	Fe <sub>2</sub> O <sub>3</sub> .....	—	7.17	1.60	—	3.39	—	LAR-2
	Na <sub>2</sub> O .....	—	—	1.19	—	—	—	LAR-5
	SO .....	—	—	0.60	—	—	—	LAR-6
Al(OH) <sub>3</sub> Gels	SiO <sub>2</sub> .....	98.23	0.82	1.16	1.11	11.97	—	DAR-2
	Al <sub>2</sub> O <sub>3</sub> .....	—	91.69	97.35	97.33	79.24	—	LAR-1
	Fe <sub>2</sub> O <sub>3</sub> .....	—	—	—	—	4.67	—	—
	SO .....	0.62	0.54	—	—	—	—	—
	ClO <sub>2</sub> .....	—	6.27	0.85	0.99	—	—	—
	CuO .....	—	—	—	—	4.15	—	—
Goethite	Fe <sub>2</sub> O <sub>3</sub> .....	98.11	71.02	96.42	92.65	94.27	92.79	DAR-4
	Al <sub>2</sub> O <sub>3</sub> .....	—	7.68	1.56	2.82	2.15	3.35	LAR-5
	Na <sub>2</sub> O .....	—	3.18	—	—	—	—	LAR-6
	P <sub>2</sub> O <sub>5</sub> .....	—	6.33	—	—	—	—	—
	K <sub>2</sub> O .....	—	0.55	—	—	—	—	—
	CuO .....	—	1.58	—	—	1.18	—	1.24
	SiO <sub>2</sub> .....	—	6.41	1.12	2.32	—	—	2.18
	NiO .....	—	—	0.74	—	—	—	—
	Cr <sub>2</sub> O <sub>3</sub> .....	—	—	—	2.00	—	—	—

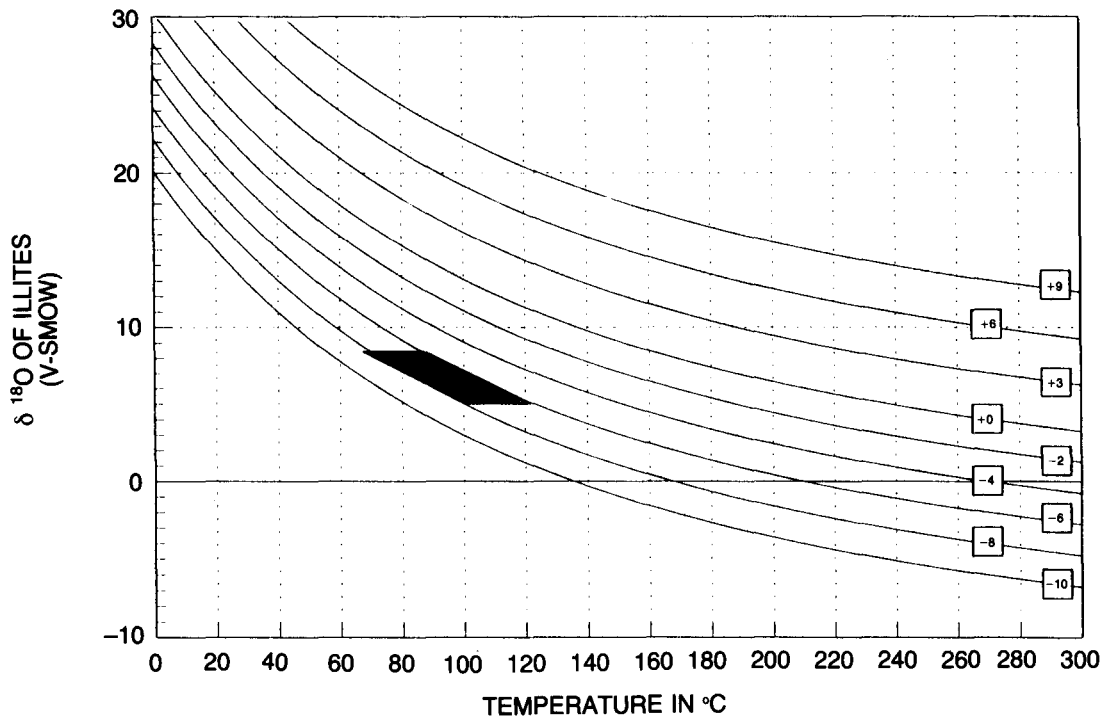
Table 8.—(Continued)

Min	Oxides %	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	Samples analyzed	
Calcite	CaO .....	74.04						LAR-1	
	SiO <sub>2</sub> .....	10.34							
	Al <sub>2</sub> O <sub>3</sub> .....	4.90							
	K <sub>2</sub> O .....	2.13							
	SO .....	1.92							
	ClO <sub>2</sub> .....	2.07							
	P <sub>2</sub> O <sub>5</sub> .....	0.87							
	MgO .....	2.18							
	Fe <sub>2</sub> O <sub>3</sub> .....	1.56							
Gypsum	Al <sub>2</sub> O <sub>3</sub> .....	0.61	1.59					DAR-4	
	MgO .....	1.03	—						
	SO <sub>3</sub> .....	22.26	50.34						
	CaO .....	47.41	40.05						
	Fe <sub>2</sub> O <sub>3</sub> .....	1.57	0.76						
	CO <sub>2</sub> .....	25.07	—						
	SiO <sub>2</sub> .....	—	3.95						
	ClO <sub>2</sub> .....	—	0.69						
Jarosite	K <sub>2</sub> O .....	9.51	6.86					LAR-1	
	Fe <sub>2</sub> O <sub>3</sub> .....	48.61	39.17						
	MgO .....	3.67	—						
	P <sub>2</sub> O <sub>5</sub> .....	5.36	3.53						
	SO <sub>3</sub> .....	32.84	24.72						
	Al <sub>2</sub> O <sub>3</sub> .....	—	10.27						
	CuO .....	—	1.10						
	SiO <sub>2</sub> .....	—	12.57						
	BaO .....	—	1.78						
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	SO <sub>3</sub> .....	40.20						LAR-5	
	Fe <sub>2</sub> O <sub>3</sub> .....	59.27							
Barite	Na <sub>2</sub> O .....	—	3.31	2.39	2.48	1.41	1.63	DAR-2	
	MgO .....	—	1.20	0.59	0.75	0.90	0.88	LAR-1	
	BaO .....	28.31	31.20	29.94	34.66	33.15	29.34		
	SO <sub>3</sub> .....	19.94	29.72	27.65	31.21	27.70	25.74		
	SiO <sub>2</sub> .....	29.63	16.15	19.54	14.75	18.30	21.79		
	Al <sub>2</sub> O <sub>3</sub> .....	14.64	8.81	11.85	7.59	9.58	12.39		
	CaO .....	3.88	5.55	3.86	5.15	5.00	3.87		
	K <sub>2</sub> O .....	0.95	2.51	2.67	2.34	2.53	3.20		
	Fe <sub>2</sub> O <sub>3</sub> .....	—	0.97	0.63	0.59	0.88	0.70		
	CuO .....	—	0.58	0.65	—	0.58	0.45		
	Apatite	P <sub>2</sub> O <sub>5</sub> .....	39.44	39.45	42.24	43.55	37.80	30.01	DAR-3
		CaO .....	41.25	42.47	42.21	43.84	41.63	32.11	DAR-4
SiO <sub>2</sub> .....		7.39	7.10	8.96	9.19	10.42	20.67		
Al <sub>2</sub> O <sub>3</sub> .....		7.23	7.26	2.24	2.31	6.62	12.38		
MgO .....		1.23	—	—	—	—	—		
K <sub>2</sub> O .....		0.61	—	—	—	1.22	2.66		
MnO .....		—	—	1.06	1.10	—	—		
Na <sub>2</sub> O .....		—	—	3.28	—	—	—		
Fe <sub>2</sub> O <sub>3</sub> .....		—	—	—	—	1.40	1.60		
CuO .....		—	—	—	—	0.91	0.57		
Monazite		Al <sub>2</sub> O <sub>3</sub> .....	15.18	22.58	7.21				LAR-6
		K <sub>2</sub> O .....	1.45	2.17	0.61				
	SiO <sub>2</sub> .....	19.11	34.72	12.47					
	P <sub>2</sub> O <sub>5</sub> .....	28.49	17.15	29.29					
	CaO .....	1.56	0.77	2.96					
	La <sub>2</sub> O <sub>3</sub> .....	8.93	6.42	12.19					
	CeO <sub>2</sub> .....	25.28	16.19	32.00					
	MgO .....	—	—	1.49					
	ThO <sub>2</sub> .....	—	—	1.77					

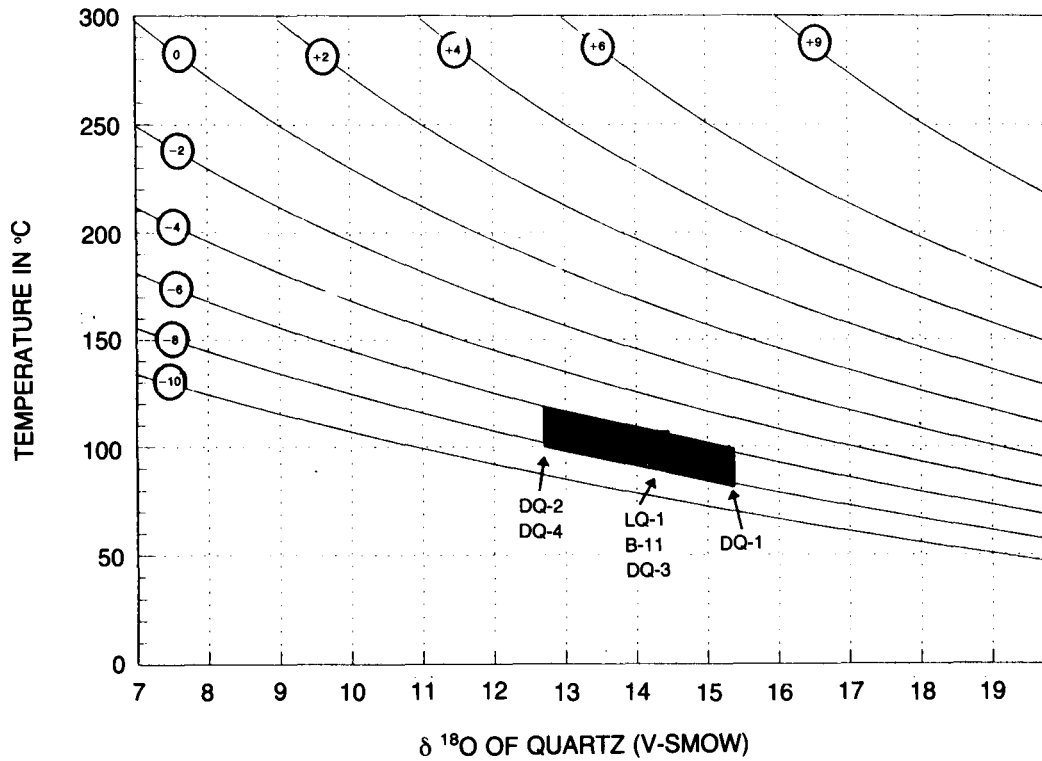
Table 8.—(Continued)

Min.	Oxides %	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	Samples analyzed
Torbernite	P <sub>2</sub> O <sub>5</sub> .....	16.70						DAR-3
	UO <sub>2</sub> .....	79.75						
	CuO.....	3.58						
Pb Silicates?	SiO <sub>2</sub> .....	37.24	45.36	49.14	51.25	48.63	50.89	DAR-3
	Al <sub>2</sub> O <sub>3</sub> .....	4.03	5.41	9.62	7.59	0.71	—	LAR-6
	Na <sub>2</sub> O.....	8.51	4.07	1.64	3.60	4.62	4.51	
	ClO <sub>2</sub> .....	1.94	—	—	—	—	0.90	
	K <sub>2</sub> O.....	8.80	6.24	6.00	5.97	5.75	6.86	
	CuO.....	1.24	—	1.36	1.08	1.28	—	
	ZnO.....	5.70	—	—	—	—	—	
	PbO.....	29.70	33.42	31.40	30.12	38.97	36.84	
Pb, Bi Minerals	SiO <sub>2</sub> .....	11.00	21.51	30.77				LAR-1
	Al <sub>2</sub> O <sub>3</sub> .....	7.22	40.10	24.92				
	K <sub>2</sub> O.....	1.50	2.90	4.41				
	CuO.....	1.56	1.76	0.91				
	Fe <sub>2</sub> O <sub>3</sub> .....	0.72	1.14	1.53				
	PbO.....	57.99	25.52	28.11				
	Bi <sub>2</sub> O <sub>3</sub> .....	20.00	6.41	8.39				
	MgO.....	—	0.66	0.95				
Ca, Y, REE, SiO <sub>4</sub> Gel	CaO.....	17.53						DAR-4
	SiO <sub>2</sub> .....	20.74						
	Y <sub>2</sub> O <sub>3</sub> .....	18.94						
	CeO <sub>2</sub> .....	14.57						
	La <sub>2</sub> O <sub>3</sub> .....	7.54						
	Na <sub>2</sub> O.....	9.22						
	SO.....	1.10						
	ClO <sub>2</sub> .....	1.87						
	TiO <sub>2</sub> .....	1.93						
Th, U, REE Minerals?	SiO <sub>2</sub> .....	40.12	42.93	38.09	22.62	31.37		LAR-1
	Al <sub>2</sub> O <sub>3</sub> .....	19.54	17.67	21.07	9.23	15.08		LAR-6
	MgO.....	—	—	1.04	1.31	0.97		
	P <sub>2</sub> O <sub>5</sub> .....	9.43	16.26	13.31	27.14	18.51		
	K <sub>2</sub> O.....	3.58	2.87	4.76	1.51	2.16		
	CaO.....	2.03	4.08	3.13	6.72	0.61		
	CeO <sub>2</sub> .....	—	—	2.16	4.88	19.59		
	La <sub>2</sub> O <sub>3</sub> .....	—	—	—	—	7.56		
	ThO <sub>2</sub> .....	15.26	1.76	9.07	15.07	2.81		
	UO <sub>2</sub> .....	5.00	11.20	—	4.49	—		
	Fe <sub>2</sub> O <sub>3</sub> .....	4.46	1.85	3.98	3.49	—		
	SO.....	—	—	0.94	1.08	—		
	Na <sub>2</sub> O.....	—	—	—	1.47	—		
	CuO.....	—	1.39	0.78	0.98	1.04		
SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , K, ClO <sub>2</sub> ?	SiO <sub>2</sub> .....	18.65						DAR-4
	Al <sub>2</sub> O <sub>3</sub> .....	10.26						
	MgO.....	8.28						
	CaO.....	5.77						
	Na <sub>2</sub> O.....	4.87						
	K <sub>2</sub> O.....	21.68						
	ClO <sub>2</sub> .....	26.95						
	P <sub>2</sub> O <sub>5</sub> .....	0.66						
	SO.....	0.70						
	Fe <sub>2</sub> O <sub>3</sub> .....	1.30						
	CuO.....	0.87						





a



b

Fig. 8.—a) Plot of Savin and Lee's (1988) equation for different  $\delta^{18}\text{O}$  of water. The shaded area corresponds to the theoretical  $\delta^{18}\text{O}$  values for pure illite. b) Plot of Clayton's *et al.* (1972) equation for different  $\delta^{18}\text{O}$  of water. The shaded area corresponds to the measured  $\delta^{18}\text{O}$  for quartz samples. Both plots consider that the  $\delta^{18}\text{O}$  for El Berrocal meteoric water is ranging from  $-6\text{‰}$  to  $-8\text{‰}$ .

Table 9.—Chemical composition on the < 2 µm fraction  
(major elements)

Oxides (%)	LAR-1	DAR-1	DAR-2	DAR-3	DAR-4	LAR-2	LAR-3	LAR-4	LAR-5	LAR-6	LAR-7	LAR-8	LAR-9
SiO <sub>2</sub> .....	53.98	52.65	53.36	53.02	53.96	56.80	59.36	55.83	54.51	55.28	56.48	55.80	52.82
SiO <sub>2L</sub> .....	0.27	0.22	0.30	0.18	0.33	0.33	0.34	0.31	0.27	0.26	0.26	0.26	0.18
Al <sub>2</sub> O <sub>3</sub> .....	25.79	26.97	22.76	19.43	24.08	20.82	20.26	22.38	21.31	22.44	20.24	23.00	26.79
Al <sub>2</sub> O <sub>3L</sub> .....	0.15	0.26	0.21	0.17	0.13	0.15	0.13	0.09	0.15	0.13	0.15	0.18	0.11
Fe <sub>2</sub> O <sub>3</sub> .....	1.47	1.53	1.79	2.01	2.47	1.26	1.52	2.46	2.83	1.42	2.59	2.23	2.23
Fe <sub>2</sub> O <sub>3L</sub> .....	0.40	0.46	0.12	0.27	0.29	0.17	0.08	0.26	0.95	0.21	0.30	0.25	0.06
FeO.....	0.28	0.26	0.37	0.20	0.16	0.57	0.69	0.14	0.21	0.14	0.14	0.13	0.10
MgO.....	1.60	1.68	1.95	1.00	1.37	2.55	2.28	1.98	1.96	2.67	2.06	1.74	0.96
MnO.....	0.05	0.04	0.04	0.05	0.15	0.04	0.04	0.04	0.05	0.04	0.04	0.07	0.08
CaO.....	0.55	0.56	0.91	4.00	1.18	1.08	1.29	0.91	0.96	1.00	1.08	0.75	0.58
K <sub>2</sub> O.....	5.70	6.14	1.86	6.20	5.98	3.82	3.86	5.25	4.70	4.45	4.51	5.04	7.30
Na <sub>2</sub> O.....	0.36	0.35	0.32	0.44	0.27	0.26	0.26	0.21	0.29	0.20	0.22	0.23	0.24
P <sub>2</sub> O <sub>5</sub> .....	0.35	0.60	0.62	3.80	0.48	0.30	0.32	0.22	0.31	0.22	0.27	0.20	0.21
TiO <sub>2</sub> .....	0.10	0.11	0.04	0.10	0.13	0.06	0.08	0.08	0.10	0.06	0.08	0.11	0.19
CO <sub>2min</sub> .....	0.03	0.04	0.03	0.14	0.11	0.07	0.04	0.01	0.04	0.04	0.03	0.04	0.03
CO <sub>2org</sub> .....	1.02	0.61	0.85	0.37	0.58	0.90	0.62	0.33	1.25	0.65	0.58	0.64	0.37
H <sub>2</sub> O <sup>-220° C</sup> .....	5.27	4.16	7.79	4.22	5.19	7.73	5.78	5.85	6.63	6.89	6.99	4.93	3.36
H <sub>2</sub> O <sup>+</sup> .....	3.50	4.01	6.16	3.39	3.57	3.92	3.61	3.98	3.71	4.48	4.04	4.34	3.81
SO <sub>2total</sub> .....	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
SO <sub>4sol</sub> <sup>=</sup> .....	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
F.....	0.12	0.15	0.10	0.15	0.09	0.16	0.17	0.15	0.10	0.11	0.14	0.12	0.04
F = 0.....	0.05	0.06	0.04	0.06	0.04	0.07	0.07	0.06	0.04	0.05	0.06	0.05	0.02
Total.....	100.94	100.74	99.57	99.08	100.48	100.92	100.66	100.34	100.29	100.64	100.14	100.01	99.40

L: Readily leachable oxides.

Table 10.—Chemical composition of the < 2 µm fraction  
(trace elements)

Elements (ppm)	LAR-1	DAR-1	DAR-2	DAR-3	DAR-4	LAR-2	LAR-3	LAR-4	LAR-5	LAR-6	LAR-7	LAR-8	LAR-9
Li.....	70	90	90	60	70	100	180	100	80	100	100	120	30
Rb.....	965	1066	363	1194	1057	515	593	786	691	533	607	698	1587
As.....	63	135	150	30	<25	3875	1100	33	44	<25	<25	37	<25
Ba.....	310	540	925	295	450	290	365	285	245	155	275	170	275
Be.....	9.9	11	7.9	13	9.5	6.8	10	7.6	7.4	5.3	7.6	7.7	15
Ce.....	16	26	51	32	26	39	28	27	30	35	28	26	29
Co.....	47	13	21	<5	5.4	11	<5	<5	<5	<5	<5	<5	<5
Cr.....	8	<5	<5	<5	<5	<5	<5	<5	<5	5.6	<5	<5	<5
Cu.....	145	810	2400	740	295	200	47	5.3	15	19	<5	32	89
La.....	12	8.6	19	21	8.1	20	12	8.5	5.7	15	9.9	<5	8.7
Mo.....	23	9.6	9.6	<5	<5	16	17	<5	<5	<5	<5	<5	<5
Ni.....	18	9.3	22	5.2	5.9	16	12	<5	<5	<5	<5	<5	<5
Sn.....	42	54	63	105	42	43	44	30	40	41	42	37	95
Sr.....	11	12	89	28	26	26	31	23	23	24	26	15	9.3
V.....	18	11	11	15	12	9.9	7.1	7.3	6.3	7.9	7.5	6.4	19
W.....	34	<25	5.1	32	<25	63	72	<25	<25	<25	<25	<25	<25
Y.....	9.5	14	15	33	9.1	13	15	5.9	7.7	7.2	7.1	7.5	12
Zn.....	1250	690	1550	560	810	1850	2575	620	450	250	395	445	250
U.....	42	51	37	93	74	91	93	38	124	44	61	155	22
Th.....	15	17	12	14	25	17	15	11	18	21	11	18	25

Table 11.—Relation between the chemical compositions of the &lt; 2 μm and &lt; 60 μm fractions (major elements)

< 2 μm/<60 μm	LAR-1	DAR-1	DAR-2	DAR-3	DAR-4	LAR-2	LAR-3	LAR-4	LAR-5	LAR-6	LAR-7	LAR-8	LAR-9
[SiO <sub>2</sub> ]/[SiO <sub>2</sub> ] .....	0.67	0.82	0.79	0.77	0.83	0.84	0.87	0.82	0.83	0.79	0.86	0.82	0.71
[Al <sub>2</sub> O <sub>3</sub> ]/[Al <sub>2</sub> O <sub>3</sub> ] .....	2.26	1.28	1.26	1.23	1.17	1.29	1.31	1.30	1.22	1.34	1.20	1.31	1.76
[Fe <sub>2</sub> O <sub>3</sub> ]/[Fe <sub>2</sub> O <sub>3</sub> ] .....	2.34	1.39	1.67	1.64	1.52	1.28	1.72	1.42	1.29	1.65	1.32	1.69	2.31
[FeO]/[FeO] .....	2.80	1.30	1.00	0.87	0.90	0.86	0.93	0.64	0.87	0.74	0.74	0.68	1.43
[MgO]/[MgO] .....	2.76	1.45	1.43	1.78	1.98	1.75	1.81	2.02	2.00	2.05	1.65	1.74	2.09
[MnO]/[MnO] .....	1.00	0.80	0.80	1.00	0.60	0.80	0.80	0.80	0.55	0.66	0.80	0.78	1.33
[CaO]/[CaO] .....	1.37	0.86	1.42	1.53	1.28	1.30	1.40	1.25	1.17	1.35	1.25	0.94	1.38
[K <sub>2</sub> O]/[K <sub>2</sub> O] .....	2.03	1.21	1.27	1.42	1.17	0.73	0.78	0.89	0.77	0.72	0.81	0.85	1.79
[Na <sub>2</sub> O]/[Na <sub>2</sub> O] .....	4.00	1.46	2.66	2.75	2.07	1.30	0.63	1.00	1.32	0.95	0.76	0.43	1.20
[P <sub>2</sub> O <sub>5</sub> ]/[P <sub>2</sub> O <sub>5</sub> ] .....	1.13	0.92	1.37	1.78	0.80	0.66	0.73	0.51	0.58	0.53	0.63	0.39	0.84
[TiO <sub>2</sub> ]/[TiO <sub>2</sub> ] .....	1.00	0.50	0.80	0.83	0.62	0.43	0.50	0.43	0.52	0.35	0.53	0.58	1.73
[CO <sub>2m</sub> ]/[CO <sub>2m</sub> ] .....	1.00	2.00	1.75	1.40	5.50	3.50	2.00	0.50	2.00	4.00	3.00	4.00	1.50
[CO <sub>2org</sub> ]/[CO <sub>2org</sub> ] .....	11.33	4.36	5.76	4.11	5.80	7.50	6.89	4.12	12.50	8.12	7.25	7.11	4.11
[H <sub>2</sub> O <sup>-</sup> ]/[H <sub>2</sub> O <sup>-</sup> ] .....	4.28	1.84	1.83	2.91	3.28	2.23	1.54	2.83	3.01	3.25	1.90	3.31	4.20
[H <sub>2</sub> O <sup>+</sup> ]/[H <sub>2</sub> O <sup>+</sup> ] .....	2.12	1.42	1.38	1.55	1.36	1.62	1.65	1.69	1.45	1.86	1.51	1.64	1.21
[SO <sub>2</sub> ]/[SO <sub>2</sub> ] .....	—	—	—	—	—	—	—	—	—	—	—	—	—
[SO <sub>4</sub> ]/[SO <sub>4</sub> ] .....	—	—	—	—	—	—	—	—	—	—	—	—	—
[F]/[F] .....	2.00	1.66	1.66	0.94	1.00	1.77	1.89	1.07	0.66	0.73	0.78	0.75	0.66

[ ] Concentration.

Table 12.—Relation between the chemical compositions of the &lt; 2 μm and &lt; 60 μm fractions (trace elements)

< 2 μm/<60 μm	LAR-1	DAR-1	DAR-2	DAR-3	DAR-4	LAR-2	LAR-3	LAR-4	LAR-5	LAR-6	LAR-7	LAR-8	LAR-9
[Li]/[Li] .....	0.50	0.60	0.64	0.67	0.70	0.83	1.00	0.83	0.80	0.66	0.91	0.80	0.50
[As]/[As] .....	2.17	1.28	2.17	>1	—	1.91	2.22	>1	1.07	—	—	>1	—
[Ba]/[Ba] .....	1.63	0.21	1.85	1.55	0.82	1.32	1.24	1.46	1.14	1.07	1.17	0.94	1.77
[Be]/[Be] .....	>1	1.34	1.44	1.60	1.51	>1	1.75	1.36	1.16	>1	1.08	1.42	2.42
[Ce]/[Ce] .....	0.64	0.46	1.27	2.66	0.54	1.44	0.68	0.71	0.88	0.65	0.80	0.74	1.53
[Co]/[Co] .....	2.35	1.08	2.14	—	0.36	>1	<1	—	—	—	—	—	—
[Cr]/[Cr] .....	>1	—	—	—	—	—	—	—	—	>1	—	—	—
[Cu]/[Cu] .....	3.15	1.74	1.55	1.56	1.97	2.35	2.47	>1	2.17	>1	—	1.68	2.62
[La]/[La] .....	1.00	0.32	0.95	0.81	0.31	0.64	0.54	0.33	0.26	0.48	0.47	>1	1.55
[Mo]/[Mo] .....	1.21	0.68	>1	—	—	>1	2.61	—	—	—	—	—	—
[Ni]/[Ni] .....	3.40	>1	2.75	>1	>1	>1	>1	—	—	—	—	—	—
[Sn]/[Sn] .....	1.23	1.08	1.66	1.78	1.05	1.16	0.98	0.77	1.00	1.14	1.13	1.09	1.67
[Sr]/[Sr] .....	1.32	0.70	1.74	1.40	0.89	0.81	1.15	0.96	0.88	0.73	0.84	0.75	>1
[V]/[V] .....	2.65	1.31	1.75	1.36	1.09	1.94	1.36	1.07	0.94	1.32	1.34	0.83	1.36
[W]/[W] .....	>1	—	—	1.10	—	>1	>1	—	—	—	—	—	—
[Y]/[Y] .....	1.05	0.78	1.50	1.37	0.57	0.81	0.71	0.37	0.51	0.55	0.47	0.53	1.09
[Zn]/[Zn] .....	3.16	1.94	1.88	2.00	2.28	2.43	2.29	2.25	2.04	2.17	1.84	2.17	2.87
[U]/[U] .....	2.62	0.96	1.51	0.40	0.29	1.52	0.90	0.95	1.08	1.63	1.07	1.00	2.31
[Th]/[Th] .....	2.14	1.21	2.66	1.75	1.92	1.41	1.50	1.15	1.42	1.91	1.44	1.54	2.08

of the fresh granite and by the differential solubility of both feldspars during the hydrothermal alteration process. According to Pérez del Villar *et al.* (1990), the albitic nature of the granite and the readiness with which albite is transformed to sericite in the

hydrothermally-altered granite, as well as the low or null concentration of albite in the < 60 and < 2 μm fractions, respectively, indicate that the original solutions were enriched in K, and gradually transformed into Na-rich solutions.



Table 15.— $\delta^{18}\text{O}$  values of  $< 2 \mu\text{m}$  fraction and quartz

Samples	$\delta^{18}\text{O}_{(\text{V-SMOW})}$	Illite/Smectite
LAR-1 .....	11.21	1.66
DAR-1 .....	9.71	2.46
DAR-2 .....	14.26	0.56
DAR-3 .....	10.16	1.50
DAR-4 .....	10.10	1.50
LAR-2 .....	11.87	0.88
LAR-3 .....	13.61	0.55
LAR-4 .....	13.66	0.97
LAR-5 .....	13.60	0.80
LAR-6 .....	14.68	0.76
LAR-7 .....	14.38	0.91
LAR-8 .....	12.90	1.13
LAR-9 .....	8.62	1.73
LQ-1 (LAR-1) .....	14.21	Quartz
B-11 (LAR-1) .....	14.43	Quartz
DQ-1 (DAR-1) .....	15.35	Quartz
DQ-2 (DAR-2) .....	12.68	Quartz
DQ-3 (DAR-3) .....	14.23	Quartz
DQ-4 (DAR-4) .....	12.64	Quartz

Table 16.—Theoretical  $\delta^{18}\text{O}$  values for pure illite

Samples	$\delta^{18}\text{O}_{(\text{V-SMOW})}$	Observations
LAR-1 .....	6.26	Q as accessory mineral
DAR-1 .....	5.65	Q as accessory mineral
DAR-2 .....	8.46	Q as accessory mineral

In fact, this process has started when the quartz vein was under the oxidizing action of the meteoric water, which produced, and still produces, sulfide, pitchblende and carbonate oxidation and dissolution, acidification of the resulting solutions, and the degradation of the clay minerals to form kaolinite, gibbsite and Al gels. Jarosite has also been detected, indicating that the upper pH limit of the solutions are  $\approx 4$ . This last weathering process is in agreement with the present pH values observed in the percolating waters of the El Berrocal mine gallery, ranging from 6.8-5.8 along the gallery and  $\sim 3$  in the mineralized vein zone (Turrero and Gómez, 1990).

Concerning the geochemistry of the clay fraction, in relation to its retention capacity, several trace element groups have been established for discussion:

a) *U and Th*. The U of the clay fraction has two sources: i) directly from the uraninite of the granite and, above all, ii) from the epithermal U mineralization, mainly hosted in the principal quartz vein. The supergenic oxidation and leaching of this mineralization release  $\text{UO}_2^{++}$  to the solution, which precipitates mainly as  $\text{UO}_2$  phosphate minerals, autunite and torbernite.

According to the sequential leaching data of the  $< 2 \mu\text{m}$  fraction, practically no U is adsorbed in the clay minerals, except in one sample. The readily leachable U, approximately 25 % as an average value, is associated with carbonates and amorphous and crystalline Fe oxyhydroxides. Consequently, the rest of the U ( $\approx 75 \%$ ) is held in the accessory, inherited and refractory minerals, such as apatite and monazite, in other unidentified secondary Th-U-REE minerals (see Table 11), and mainly in secondary U minerals insoluble under the sequential leaching chemical procedure.

Thorite-auerlite and monazite from the granite are the only possible sources of the Th detected in the  $< 60 \mu\text{m}$  and  $< 2 \mu\text{m}$  fractions. The high Th content in the first fraction is due to an artificial concentration of the Th minerals during sieving or to a pre-existing natural concentration in the clayey materials due to the resistant nature of these minerals under the hydrothermal argillitization process.

The fact that the  $< 2 \mu\text{m}$  fraction is enriched in Th relative to the  $< 60 \mu\text{m}$  fraction suggests that, during the argillitization processes of the granitic fault gouge, a partial destabilization of the Th minerals took place. Consequently, the Th thus released underwent a slight remobilization and precipitated later on as unidentified Th-U-REE complex minerals (see table 11). However, Th is mainly held in fine-grained monazite, which is inherited from the granite.

b) *Zn, Cu, Ni and Sn*. Zinc would be supplied to the  $< 2 \mu\text{m}$  fraction, in part, by the destabilization of sphalerite from the granite and, principally, by the sulfides present in the mineralized quartz vein. The second source accounts for the highly anomalous Zn content of the clayey samples from the quartz vein and adjacent fractures. The anomalies of Cu and Ni are explained in the same way.

Two sources account for the Sn in the  $< 2 \mu\text{m}$  fraction: i) cassiterite from the granite and ii) sulfides in the mineralized vein, which generally contain  $\text{Sn}^{2+}$  substituting the major metallic elements. Since Sn is easily mobilized as  $\text{Sn}^{2+}$ , the second source is the most important. Thus, the sulfide destabilization by weathering releases  $\text{Sn}^{2+}$  which, upon oxidation to  $\text{Sn}^{4+}$ , causes its fixation in the clayey materials. This explains why the main Sn anomalies have been found in the clays from the mineralized quartz vein.

According to the chemical composition of the accessory minerals and mineraloids associated with the clay minerals, Zn and, fundamentally, Cu are present in almost all these minerals. Thus, Cu is present in primary minerals inherited from the granite, like apatite, in minerals associated with the pitchblende mineralization, like barite, and in secondary  $\text{UO}_2^{++}$  minerals, like torbernite. Nickel seems to be controlled by Fe oxyhydroxides.

Though Sn has not been detected in any of the minerals and mineraloids of the clay, this element can be associated with Al oxyhydroxides as  $\text{Sn}(\text{OH})_4$  and/or free fine-grained cassiterite, inherited from the granite.

c) *V.* Vanadium has been detected in the fresh and altered granite with contents varying between 5 and 6 ppm, mainly concentrated in chloritized biotite and muscovite (Pérez del Villar *et al.*, 1990). Consequently, after the degradation of those phyllosilicates, V is concentrated in the beidellite and illite lattices, substituting octahedral Al. Although V has not been detected in the Fe oxyhydroxides, these and Mn oxyhydroxides are usually accompanied by V.

d) *Ba.* Given that the «El Berrocal» granite is highly evolved, its Ba content is low, though a remarkable increase is observed in the hydrothermally altered granite (Pérez del Villar *et al.*, 1990). The high Ba concentration detected in the  $< 2 \mu\text{m}$  fraction must, therefore, come from the alteration of the granite and, more specifically, from the destabilization of the K-feldspar. This element has been transported as  $\text{BaCl}_2$  and retained in the clays, either as cryptocrystalline barite or as an exchange cation. It should be noted that the U mineralization in the quartz vein is rich in barite, which explains the extremely high Ba contents of the samples from this zone. Barite has been detected in sample DAR-2 as an accessory mineral and coating the clay particles.

The possibility that some Ba could be found as an exchange cation in beidellite cannot be disregarded, given the high affinity between this mineral and Ba. The fact that this element has not been found in the CEC can be due to the use of  $\text{NH}_4\text{NO}_3$  as exchange agent and to the stronger adsorption of Ba by beidellite than by  $\text{NH}_4^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ . The exchange  $\text{NH}_4^+$  for  $\text{Ba}^{++}$  could not, therefore, have taken place.

e) *As.* The As concentration in the fresh and altered granite is  $< 25$  ppm (Pérez del Villar *et al.*, 1990). In the  $< 60 \mu\text{m}$  fraction and, particularly, in the  $< 2 \mu\text{m}$  fraction, the As contents are very high, specially in those samples from the mineralized quartz vein and the adjacent fractures to the North of the vein. The possible explanation for the As anomalies is that it also comes from the destabilization of the sulfides from the principal quartz vein, and is retained as  $\text{AsO}_4^{-3}$  by the Fe oxyhydroxides and other active surfaces, like the clay minerals (Sillen and Martel, 1964). This element has not been detected, however, in any of the minerals and mineraloids of the  $< 2 \mu\text{m}$  fraction.

It should be noted that, among the As anomalous samples, those from the sulfide mineralized vein (DAR-1, 2, 3 and 4) are the least anomalous. The

clue to this fact can be found in the  $\text{pH} \approx 3$  of the present percolating water. Thus, at these low pH values, As can form  $\text{H}_2\text{AsO}_4^-$ , which is more soluble in water and, therefore, could have been leached (Hem, 1970).

f) *Ca, Sr, Ce, Y, P and mineral C.* Calcium and mineral C are the only elements that show a remarkable enrichment in all the  $< 2 \mu\text{m}$  fractions compared with the  $< 60 \mu\text{m}$  fractions. This fact is explained as follows: i) Ca is the main exchangeable cation of the  $< 2 \mu\text{m}$  fractions and ii) the presence of cryptocrystalline calcite in the same fraction. On the other hand, some of the Ca-enriched samples are also enriched in  $\text{P}_2\text{O}_5$ . Consequently, a large part of the Ca is accounted for by the constant presence of apatite, sometimes in several percentages.

The fact that calcite and apatite occur as stable phases, despite the more or less acid pH of the percolating waters, suggests that those minerals must be protected by the clay minerals themselves.

The  $< 2 \mu\text{m}$  fractions enriched in  $\text{P}_2\text{O}_5$  are also generally enriched in Sr, Ce and Y, elements which usually replace Ca in the apatite, as is the case of this mineral in the fresh granite (Pérez del Villar *et al.*, 1990). At the same time, monazite and other undetermined Ca, Y, Ce, La and REE phosphates, similar to xenotime, have also been detected in the  $< 2 \mu\text{m}$  fractions.

The existence of Ca, Y, Ce, La and REE complex silicate gels, trapped by clay minerals, suggests that, during the illitic process, monazite was partially destabilized, leading to the mobilization of these elements, which precipitated as silicates, given the high  $[\text{H}_4\text{SiO}_4]$  in the environment. However, it must be noted that part of the Y and lanthanides could be leached from the mineralized quartz vein, since these elements are particularly mobile under acid conditions, under which kaolinite is, in turn, stable (Burkov and Podporina, 1967).

g) *Organic C.* The organic C enrichment observed in all the clay fractions is due to any or both of the following reasons: i) existence of present algal and/or bacterial activity in the clayey zones, and ii) the possible existence of clay-organic matter complexes. In this last case, the humic and/or fulvic acids, formed at the topographic surface are transported by percolating waters and retained by the clays.

### Concluding remarks

1. The clayey materials associated with N110°-100°E fractures in the «El Berrocal» mine were formed by the interaction between the granitic fault gouges and hydrothermal solutions originated during the fracturation phase. They should not, the-

refore, be considered as fracture fillings «sensu stricto».

2. The argillitization process of the granite was probably produced by two or three phases: the first, of illitic nature, was originated by the interaction between acid KCl-rich hydrothermal solutions and the granitic fault gouges, at a T ranging from 120-70° C. The second phase, of smectitic nature, probably took place during ancient and/or present weathering processes. In this last phase, the interaction between the pre-existing illitic material and more alkaline solutions took place, causing a partial transformation of illite to beidellite. During these weathering phases, the illite and/or beidellite were transformed to kaolinite in those fractures where a strong K<sup>+</sup> leaching was produced and enough sulfide content remained to acidify the percolating water, after the sulfide oxidation. Furthermore, in this phase, carbonates, pitchblende and apatite were totally or partially oxidized and dissolved. Consequently, Al gels, gibbsite, Fe oxyhydroxides, jarosite, Fe<sup>3+</sup> sulfates and UO<sub>2</sub><sup>++</sup> phosphates, autunite and torbernite, were formed. The presence of residual carbonates and apatite is possible due to their protection by the clay minerals themselves.

3. The accessory minerals and mineraloids, and in far less proportion the clay minerals, play a leading role in the retention of the heavy elements released during the alteration of the granite, sulfides and uraniferous mineralizations.

In relation to the natural radionuclides, U is either precipitated as UO<sub>2</sub><sup>++</sup> phosphates, mainly autunite and torbernite, adsorbed by Fe oxyhydroxides or retained by calcite and Th-U-REE unidentified mineraloids. Monazite and apatite, which are inherited from the granite, also contain U. Thorium is principally present in the minerals inherited from the granite, mainly monazite, and retained by Th-U-REE unidentified and secondary mineraloids.

Among the non-radioactive heavy elements, V would be fundamentally localized in the clay mineral lattices. Yttrium, Ce and La are present in the inherited minerals of the granite and forming Th-U-REE unidentified minerals and mineraloids. Strontium substitutes Ca in apatite, and Ba is found as cryptocrystalline barite and, probably, as an exchange cation in beidellite. Copper and Zn occur in almost all the secondary minerals and mineraloids, whereas Ni seems to be controlled by the Fe oxyhydroxides. Arsenic is possibly retained by Fe oxyhydroxides and clay minerals. Tin is associated with Al gels and/or as cassiterite inherited from the granite.

4. Concerning the light elements, organic C could be due to present biological activity in the clayey materials or to organic acids transported from the topo-

graphic surface. In this last case, it is probable that organic-clay complexes exist along the fractures.

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