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P–T PATH AND FLUID EVOLUTION IN THE FRANQUEIRA GRANITIC PEGMATITE, CENTRAL GALICIA, NORTHWESTERN SPAIN

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ABSTRACT

In Galicia, in the northwestern part of the Iberian Peninsula, there are several occurrences of granitic pegmatites. One of them, known as Franqueira, is a metasomatic deposit of gem-quality chrysoberyl, emerald and phenakite. The pegmatite is associated with a two-mica peraluminous Hercynian granite, and intrude dunites of the Schistose domain in the Galician Tras-Os-Montes Zone. The composition of fluid inclusions in emerald and phenakite has been determined using a Raman microprobe to ascertain the paleofluid chemistry and the P–T conditions of fluid migration in the pegmatite. Three types of fluid inclusions have been identified in emerald and phenakite; three episodes of fluid circulation are distinguished. The first episode is represented by low-salinity aqueous-carbonic primary fluid inclusions in phenakite; these were trapped at 2.5 kbar and 400°C. An isothermal drop in pressure produced a second stage of fluid trapping under conditions of 400°C and 1 kbar. Fluid inclusions trapped in emerald indicate that during this second stage, it formed from phenakite and chrysoberyl in the presence of a CO_2- and CH_4-rich fluid. A third episode of fluid circulation suggests an independent stage of fluid circulation during late tectonic events, with temperatures ranging from 160° to 265°C and pressure below 0.5 kbar.

Keywords: granitic pegmatite, fluid inclusion, microthermometry, Raman microprobe, P–T path, fluid evolution, Franqueira, Galicia, Spain.

SOMMAIRE

En Galice, dans le secteur nord-ouest de la Péninsule Ibérique, on trouve plusieurs massifs de pegmatites granitiques. Un de ceux-ci, Franqueira, est le site d'un gisement métasomatique de chrysobéryl, émeraude et phénakite gemmes. La pegmatite est associée à un massif hercynien de granite hyperalumineux à deux micas, mis en place dans des dunites du domaine de schistes de la zone Tras-Os-Montes. La composition des inclusions fluides dans l'émeraude et la phénakite a été établie au moyen d'une microsonde Raman afin de déterminer la composition du paléofluide et des conditions de pression et de température au cours de sa migration dans la pegmatite. Nous avons identifié trois types d'inclusions fluides dans l'émeraude et la phénakite, qui témoignent de trois épisodes de circulation d'une phase fluide. Le premier a donné des inclusions primaires aqueuses et primaires dans la phénakite, piégées à 2.5 kbar et 400°C. Une chute isotherme de la pression a produit un second stade de piégeage, à 400°C et 1 kbar. Les inclusions associées à ce deuxième épisode piégées dans l'émeraude indiquent un mode de sa formation par remplacement aux dépens de la phénakite et du chrysobéryl par une phase fluide riche en gaz carbonique et en méthane. Un troisième épisode de circulation serait indépendant des deux premiers, développé au cours d'une déformation tardive à une température allant de 160° à 265°C et une pression inférieure à 0.5 kbar.

(Traduit par la Rédaction)

Mots-clés: pegmatite granitique, inclusions fluides, microthermométrie, microsonde Raman, tracé de pression et de température, évolution de la phase fluide, Franqueira, Galice, Espagne.

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INTRODUCTION

There are several occurrences of rare-element-enriched granitic pegmatite in the central part of Galicia, in the northwestern region of the Iberian Peninsula. One of these, Franqueira, is a well-documented example of a deposit of gem-quality chrysoberyl, emerald and phenakite in western Europe (Martin-Izard *et al.* 1995). The geological conditions of formation of the Franqueira deposit have led Martin-Izard *et al.* (1995) to include it in the suture-zone group (Snee & Kazmi 1989) or in the type-I deposit, the Ural Mountains type, in the classification of Giuliani *et al.* (1997), on the basis of exometasomatic phenomena (Fersman 1929, Sinkankas 1989, Giuliani *et al.* 1997). The deposit showing the closest similarity to Franqueira in its mineralogical association, geological environment and age of formation (Paleozoic), is Tokovaja, in the Ural Mountains, Russia (Sinkankas 1989, Laznicka 1985, Giuliani *et al.* 1997).

The purpose of this paper is to present the results of a combined Raman microprobe and fluid-inclusion study carried out on emerald and phenakite from the Franqueira deposit, located in the central part of Galicia, in the northwestern Iberian Peninsula. Results of these studies allow us to determine the evolution of fluids and the P–T–V–*X* conditions of the multistage circulation of fluids in the metasomatic zone around the pegmatite and also to establish the conditions of formation of the beryllium-bearing gems.

The origins of the fluids involved and the possible interaction between the pegmatite-derived fluids and those derived from the host rock also are discussed. From these results, a fluid immiscibility in the system $H_2O–CH_4–CO_2–NaCl$ likely contributed to the evolution of the fluid in the case of Be-rich pegmatites that metasomatized adjacent ultramafic rocks.

THE FRANQUEIRA DEPOSIT

The Franqueira pegmatite is located in the northwestern part of the Iberian Peninsula, in the Galician Tras-Os-Montes Zone (Matte 1968, Farias *et al.* 1987, Martínez Catalán *et al.* 1996) (Fig. 1). The Tras-Os-Montes Zone consists of two domains: (1) schistose rocks, including mafic–ultramafic overthrusted complexes (Cambrian to Silurian in age), and (2) granitic rocks, including two-mica peraluminous synkinematic granitic rocks (330–310 Ma, Priem & Den Tex 1984, Serrano Pinto *et al.* 1987, Van Calsteren *et al.* 1979). The former is composed of metamorphic rocks and the Lalín–Forcarei Unit, the southern end of the large Ordenes Complex (Barrera *et al.* 1989, Monterrubio 1991). The Ordenes Complex, as well as the Lalín–Forcarei Unit, which overthrusts the other groups of the schist domain during D1 and D2 Hercynian deformation events (360–330 Ma, Dallmeyer *et al.* 1997), consists of gabbro, amphibolite, orthogneiss, dunite and other ultramafic rocks (Monterrubio 1991). The regional

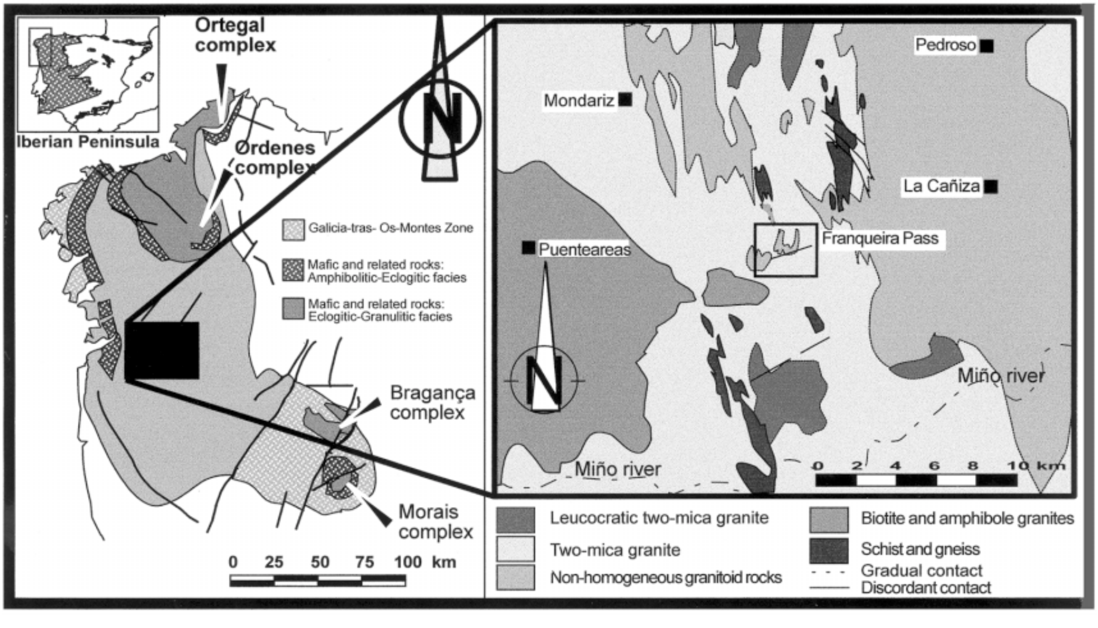

FIG. 1. Setting and schematic geological map of the Franqueira deposit, adapted from Barrera *et al.* (1989).

geological setting of the Franqueira pegmatite was outlined by Martin-Izard *et al.* (1995, 1996).

The Franqueira deposit occurs between ophiolite complexes of Galicia (Ordenes Complex) and Portugal (Bragança and Morais complexes). These complexes represent fragments of oceanic crust that were thrust over the schist of the schistose domain during the first and second phase of the Hercynian Orogeny. Heterogeneous two-mica granite (Barrera *et al.* 1989) were emplaced during the third tectonic phase (315 ± 10 Ma: Capdevila & Vialette 1970). At Franqueira, the pegmatite bodies, related to the heterogeneous two-mica granites, cross-cut an ultramafic rock of dunitic character and associated gabbroic rocks.

Martin-Izard *et al.* (1995) suggested that the dunite and hornblende gabbro considered here belong to a remnant of peridotitic and gabbroic rocks from the overthrusted complexes. This suggestion is supported by the fact that the geochemical and mineralogical characteristics of Franqueira dunite and gabbro are similar to those of the the Ordenes, Bragança and Morais complexes.

Later, during the intrusion of the Hercynian granites, the dunite and hornblende gabbro could have remained in the roof zone of the peraluminous heterogeneous two-mica granites, which normally have a suite of associated pegmatite bodies. The Franqueira pegmatite, which is enriched in Be, B and P, caused metasomatic alteration of the adjacent dunite, with formation of phlogopitite near the pegmatite, and tremolitite bodies and an anthophyllite rim close to the dunite. The Mg and Cr of these rocks were provided by the dunite. The addition of boron and phosphorus resulted in the formation of tourmaline and abundant apatite in the metasomatic facies, along with phlogopite. In the zones closest to the pegmatite, the Be spread out in the system and first developed chrysoberyl ("alexandrite") and phenakite porphyroblasts, isolated or intergrown in the phlogopitite.

The bodies of granitic pegmatites form a network of narrow, anastomosing subvertical dikes that trend approximately east–west. The dike system (Fig. 2) is exposed for 15–20 meters. Dike thickness ranges from 3 to 40 cm. Relics of dunite totally transformed to phlogopite are commonly found within the pegmatite.

The pegmatite bodies show a simple zonation with an aplitic border. Essential minerals are quartz, albite, muscovite and scarce K-feldspar, with apatite, tourmaline and zircon as accessory minerals. In the main zone of the pegmatite, albite is the most abundant mineral, with quartz in lesser proportion and some muscovite. Within the pegmatitic bodies of greater thickness, a banding can be observed in the central zone, in which a coarse-grained rock alternates with another of saccharoidal appearance. In the coarse-grained facies, there are crystals of coarse bladed albite with subhedral albite, interstitial euhedral quartz, and muscovite plates. In the saccharoidal facies, garnet and tourmaline abound.

The host rocks have a clearly defined contact with the pegmatites and are of a micaceous nature. The mica is phlogopite, and is the most abundant mineral (over 75%, up to 90%) in this facies (Fig. 2). The visible thickness of this rock is up to three meters, and it crops out for at least five meters. The accessory minerals are chrysoberyl ("alexandrite"), phenakite, beryl ("emerald"), tourmaline, garnet (mainly almandine), apatite (fluorapatite, 3.5 wt.% F) and zircon.

Chrysoberyl [Fig. 3A(C)] appears as subhedral porphyroblasts isolated in the phlogopite or as skeletal intergrowths within emerald, phenakite and apatite. Phenakite [Figs. 3A(P), 3B] appears as subhedral and colorless prismatic crystals up to 3 cm in size. Phenakite commonly has associated apatite crystals [Fig. 3A(A)]. Beryl appears as euhedral prismatic crystals with sizes

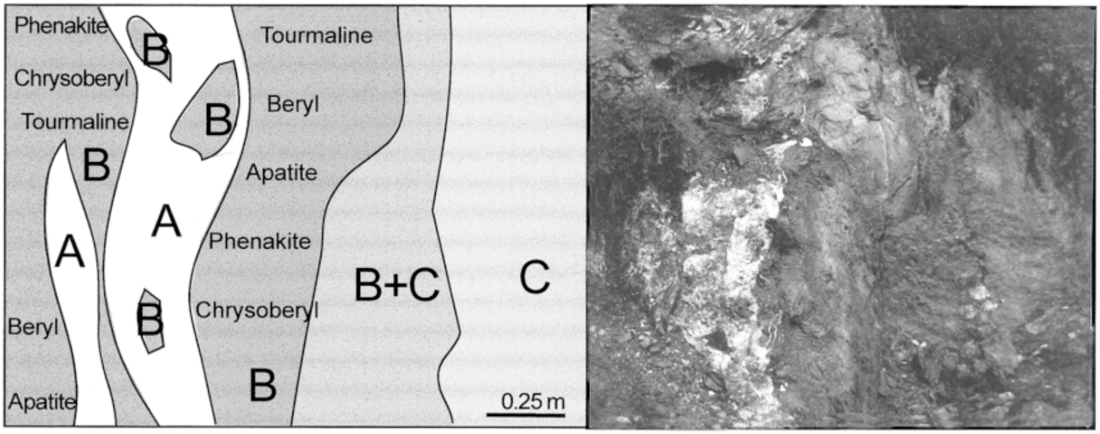

FIG. 2. View of the pegmatite dikes, which are lenticular (A). The pegmatite is hosted by phlogopitite (B) and tremolitite (C).

of up to 30 cm [Figs. 3A(B), 3B]; an intense green color and Cr content (up to 0.2 wt.%) give it its emerald-like character. It is the latest Be mineral and replaces the chrysoberyl and phenakite (Fig. 3A). Tourmaline (dravite) is developed at the contact between phlogopitite and the pegmatite.

Beryl porphyroblasts developed and partially replaced the other two Be minerals owing to the increasing activity of H_4SiO_4 (at constant temperature) in accordance with the reaction:

$$\text{chrysoberyl} + \text{phenakite} + 5H_4SiO_4 = \text{beryl} + 10H_2O \qquad (1)$$

proposed by Barton (1986). Invariably, where chrysoberyl and phenakite are together, they are replaced by beryl (emerald) and appear as a skeletal intergrown within the emerald.

The phlogopitite grades into a tremolitite in which pockets of phlogopite are ubiquitous (Fig. 2). The visible thickness of this rock is up to six meters. In the tremolitite, the rock is essentially composed of tremolite, but some phlogopite is always present and locally, along dunite contacts, the tremolitite is rimmed by anthophyllite and titanite. Accessory minerals include zircon, apatite and ilmenite. Over a short distance (5 cm), the tremolitite grades into an anthophyllite zone and then into dunite.

The dunite outcrops only as relics of about one meter thick inside the tremolite rock. It is dark in color, granoblastic and of very compact texture, and the olivine is partially altered to tremolite and phlogopite. Olivine ($Fo_{86.6}$) forms a hypidiomorphic, partially serpentinized and chloritized aggregate. Chromian spinel is found as an accessory mineral, usually disseminated, although occasionally forming small aggregates.

ANALYTICAL TECHNIQUES

Microthermometric studies of fluid inclusions were performed on sections 100 to 300 μm thick using a microscope equipped with a UMK50 Leitz objective and a Chaixmeca cooling and heating stage (Poty *et al.* 1976) in the Laboratory of Geology of the University of

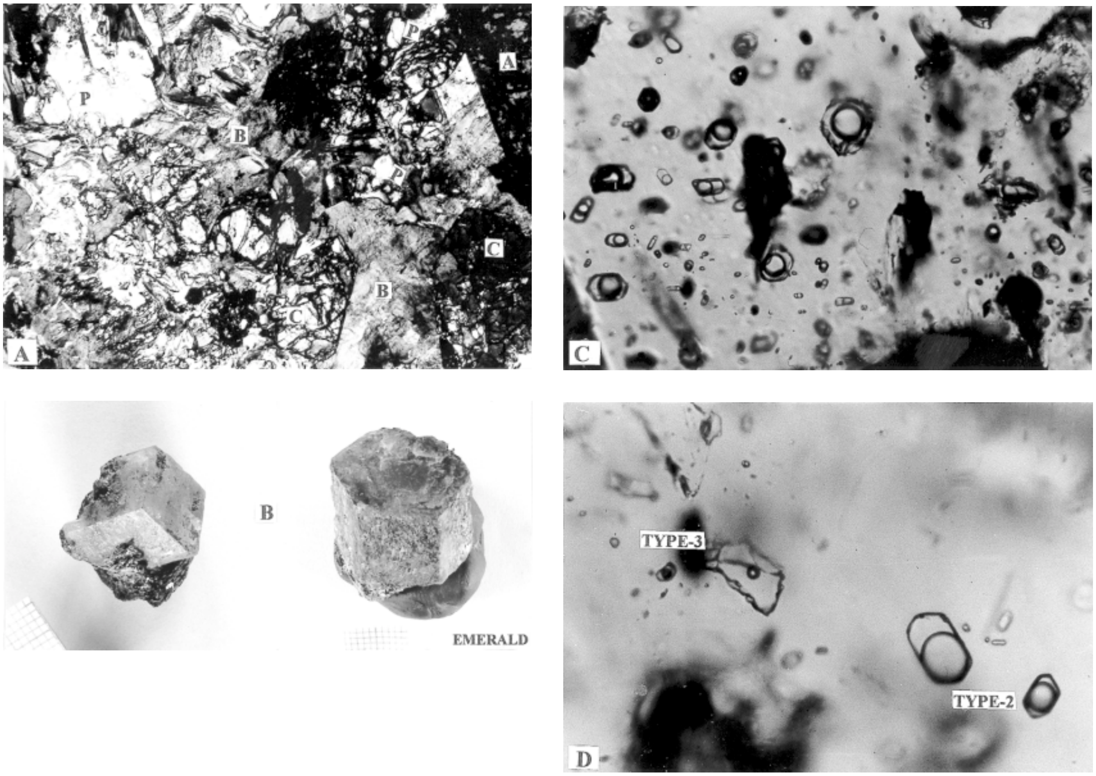

FIG. 3. A. Microscopic view of chrysoberyl (C), phenakite (P), beryl (B), and apatite (A). Phenakite and skeletal corroded crystals of chrysoberyl are included in emerald. XPL, 10×. B. Emerald and phenakite crystals used for the study of fluid inclusions. C. Primary complex CH_4 aqueous inclusions (type-1) in emerald crystals. XPL, 45×. D: Primary complex CO_2 aqueous inclusions (type-2) and secondary saline aqueous inclusions (type-3) in emerald crystals. XPL, 45×.

Las Palmas (Spain). The stage was calibrated according to the procedures outlined by Poty *et al.* (1976). The detailed analytical techniques of the microthermometric study are described in Martin-Izard *et al.* (1995).

The composition of the non-aqueous portion of individual inclusions was measured using a Dilor X–Y multichannel modular Raman spectrometer (at CREGU). Bulk composition and density were computed from the P–V–T–*X* properties of individual inclusions in the C–O–H–(N–S) system (Dubessy 1984, Dubessy *et al.* 1989, 1992, Thiery *et al.* 1994, Bakker 1995). All data were calculated from the microthermometric measurements and the Raman analyses of the gas, using a clathrate stability model in the system H_2O–CH_4–N_2–NaCl–KCl–$CaCl_2$, between 253 and 293 K and between 0 and 200 MPa (Bakker 1995, Bakker *et al.* 1996) and the computer program of Bakker (1997).

The P–V–T–*X* properties of aqueous carbonic inclusions were modeled in terms of the system H_2O–CO_2–CH_4 using the state equations of Kerrick & Jacobs (1981) and Jacobs & Kerrick (1981) and the computer code of Dubessy (1984). Only in one case (type-1 inclusions in phenakite) did we use the equation of state of Bowers & Helgeson (1983). For aqueous inclusions, the isochores have been drawn in the H_2O–NaCl system using the data from Zhang & Frantz (1987) and the computer program Macflincor 0.92 (Brown & Hagemann 1995).

SELECTING SAMPLES, INCLUSION TYPES AND MICROTHERMOMETRIC RESULTS

In the Franqueira deposit, samples of emerald and phenakite (Fig. 3B) have been taken from the metasomatic phlogopite-rich zone (Martin-Izard *et al.* 1995). Both minerals have the potential to provide information on the conditions of metasomatism around the pegmatite. Fluids inclusions in chrysoberyl are scarce and are too small (less than 1 μm) for study.

Observations show that emerald and phenakite have a significant number of inclusions, isolated or in groups; these are interpreted as primary (Figs. 3C, D). Other inclusions related to fractures are classified as pseudosecondary or secondary on the basis of the criteria of Roedder (1984) (Fig. 3D). Inclusion morphology is equally variable, being roundish, elongate, tubular, subhedral negative crystal or irregular. The size of the inclusions studied ranges from 5 to 60 μm in size (Figs. 3C, D).

One hundred and twenty-five fluid inclusions were selected and studied by microthermometry in the two minerals. In all emerald and phenakite crystals studied (more than 10), fluid inclusions have the same morphological characteristics and volumetric ratios.

The fluid-inclusion studies of the Franqueira deposit reported by Martin-Izard *et al.* (1995) indicate the presence of three types of inclusions. Type 1 consists of complex CH_4-bearing aqueous inclusions (Fig. 3C). These show two phases at room temperature. The vapor phase occupies between 20 and 50% of the total volume of the inclusions. We consider these inclusions to be primary or pseudosecondary, and they are the most representative of emerald and phenakite.

After cooling and subsequent heating, the CH_4 liquid and vapor phases homogenized to either the vapor (V) or liquid (L) state or critical (C) stage. This occurs at temperatures ranging from –83 to –106°C into V and from –82 to –90°C into L phases in the emerald, and from –86 to –106°C into V, –88.5 to –110.5°C into L, and –86.5 and –89°C into C phases in the phenakite.

The temperature of initial ice melting, where measurable, was found to be mostly around the stable eutectic for the NaCl–H_2O system, –20.8°C (Potter & Brown 1977). Although the use of wt.% equivalent NaCl in such inclusions seems inappropriate, the overestimated salinity based on the final temperature of ice melting, with reference to the H_2O–NaCl system (Potter *et al.* 1978), ranges between 5 and 8 wt.% equivalent NaCl.

Total homogenization temperatures range between 318° and 369°C in the liquid state and between 354° and 373°C in the vapor state. Some of the measured inclusions decrepitated before total homogenization was achieved.

Type-2 inclusions are complex CO_2-bearing aqueous inclusions (Fig. 3D). These inclusions contain two phases at room temperature and show volumetric proportions Vg/Vt (vapor volume/total volume) below 50%. The inclusions appear only in the core of emerald crystals and have the same distribution as the type-1 inclusions, but are less abundant. Martin-Izard *et al.* (1995) considered these inclusions as primary or pseudosecondary and contemporaneous with type-1 inclusions. During cooling, the two-phase inclusions in some cases transform into three-phase inclusions (H_2O L + CO_2 V + CO_2 L). The melting of solid CO_2 has been measured at between –60.8° and –62.1°C. Salinities were overestimated approximately from the final melting of ice values and the formulae proposed by Potter *et al.* (1978) for the system H_2O–NaCl, and ranged from 5 to 10.5 wt.% equivalent NaCl.

Most of the total homogenization in the liquid state occurs between 320° and 378°C; only two inclusions homogenized into the gas and critical state at 381°C. This degree of variability in pattern of homogenization can be explained by small differences in the bulk composition of the fluid.

Type-3 inclusions are mixed-salt aqueous inclusions. These show two phases at room temperature in which the vapor bubble occupies less than 10% (Fig. 3D). These inclusions occur in both emerald and phenakite and are relatively scarce. The inclusions are secondary in character. Temperatures of first melting of ice vary between –45° and –55°C; these temperatures are lower than the eutectic temperature of the H_2O–NaCl system (Potter & Brown 1977). The temperature of final melting of ice ranges between –2.1 and –23°C. Taking into account these temperatures and the experimental data of Potter *et al.* (1978) for the system H_2O–NaCl, the salinity ranges between 3.5 and 24.7 wt.% equivalent NaCl. Homogenization temperatures range between 160° and 265°C in the liquid state.

The microthermometric measurements of Martin-Izard *et al.* (1995) are summarized in Table 1.

Clearly, from the above microthermometric data, no great differences exist between the fluid inclusion populations of emerald and phenakite; two discontinuous hydrothermal stages can be distinguished. The first hydrothermal stage was characterized by the circulation and trapping of aqueous fluid with some volatiles of type-1 and -2 inclusions (complex CH_4–CO_2 aqueous inclusions), with salinities below 10 wt.% equivalent NaCl, and a low density of bubbles. This fluid circulated at minimum temperatures of between 318° and 381°C, and the lithostatic or hydrostatic pressure was high enough to prevent boiling.

The characteristics of type-3 inclusions, showing a secondary character, lower temperatures of homogenization, lacking CH_4, CO_2 and other volatiles, having a variable salinity, and with solutions containing several cations, suggest an independent episode of hydrothermal fluid circulation during the later tectonic events. Thus, the second hydrothermal stage corresponds to the circulation and trapping of aqueous solutions of salinity below 24.7 wt.% equivalent NaCl, containing cations such as Ca, Mg, K and Na, among others, with densities ranging 0.9 to 1.15 g/cm^3, at minimum trapping temperatures ranging 160 and 265°C.

RAMAN DATA

Raman microprobe analyses were carried out on type-1 (in phenakite and in emerald) and type-2 inclusions from Franqueira. From Raman analyses and microthermometric data, the density and composition of the volatile-rich phase together with the bulk density and composition were calculated. In order to obtain these data, the above-mentioned clathrate stability model was applied, but in the case of type-1 phenakite inclusion, results could not be obtained because the clathrate melting temperature (>20°C) is above the limits of stability of the model (between 253 and 293 K) and, moreover, there is a large difference between ice and clathrate melting temperatures. Nevertheless, it was possible to obtain a solution if we assumed that there was no salt in the system. This hypothesis is probably a reasonable estimate because the measured final ice melting temperature in these inclusions is low (–4°C), thus salinity is close to 6 wt.% equivalent NaCl. This value is low and, in any case, overestimated owing to the fact that the clathrate is present when the ice melts. On the basis of these facts, we assumed that there is no salt in the fluid trapped by phenakite.

All data are shown in Table 2. Raman microprobe analyses show that type-1 inclusions in emerald have a different density and composition of the volatile-rich phase than type-1 inclusions in phenakite.

H_2O is the main component of the fluid phase in type-1 inclusions trapped in emerald and phenakite. The volatile-rich phase of inclusions in both minerals is dominated by CH_4. In the case of type-1 inclusions trapped in phenakite, N_2 is present in higher quantities than in type-1 inclusions trapped in emerald; moreover, the type-1 fluid in emerald also contains CO_2. The composition of the volatile phase of type-1 inclusions in phenakite is 80.5 to 85.2 mole % CH_4 and 14.8 to 19.5 mole % N_2. The composition of the volatile phase in type-1 inclusions in emerald is 78.9 to 80 mole % CH_4, 2.5 to 15.7 mole % CO_2 and 5.4 to 7.5 mole % N_2.

Type-2 inclusions have also an aqueous composition and their volatile-rich phase is dominated by CO_2 and minor quantities of CH_4 and N_2. The volatile phase composition of type-2 inclusions is 52 to 68 mole % CO_2, 19.5 to 41.2 mole % CH_4 and 6.7 to 12.5 mole % N_2.

TABLE 1. SUMMARY OF THE MICROTHERMOMETRIC DATA FOR THE DIFFERENT TYPES OF FLUID INCLUSIONS IN THE FRANQUEIRA DEPOSIT

Types	host-mineral	N°	$TmCO_2$	$ThCO_2$	$ThCH_4$	Tm_{cl}	Tm_{ice}	Th
Type-1	emerald	39	-	-	-82 to -90 L -83 to -106 G	11.5 to 19	-3.5 to -5.2	318 to 369 L 354 G 320 to 378 L
Type-2	emerald	31	-60.8 to -62.1	-11.2 to 10 G	-	11.9 to 22	-3 to -7	381 G 381 C
Type-3	emerald	7	-	-	-	-	-1.3 to -23	160 to 245 L
Type-1	phenakite	40	-	-	-88.6 to -109 L -86 to -106 G -86.7 to -89 C	14.8 to 18.3	-3.5 to -5.2	322 to 350 L 363 to 373 G
Type-3	phenakite	8	-	-	-	-	-2.1 to -11	193 to 265 L

$TmCO_2$: melting temperatures of CO_2; $ThCO_2$: homogenization temperature of CO_2, gaseous state (G), liquid state (L) and critical state (C); Tm_{cl}: melting temperature of clathrate; Tm_{ice}: melting temperature of ice; Th: total homogenization temperature, gaseous state (G), liquid state (L) and critical state (C). All temperatures are given in °C. N°: number of measurements. The data are summarized from Martin-Izard *et al.* (1995).

TABLE 2. RAMAN DATA AND BULK COMPOSITION OF THE FLUID INCLUSIONS SELECTED FROM THE FRANQUEIRA DEPOSIT, AND CORRESPONDING MICROTHERMOMETRIC DATA

			MICROTHERMOMETRY							RAMAN DATA				BULK COMPOSITION				
TYPES	host mineral	N°	Vg/ Vt	Tm_{CO2}	Th_{CO2}	Th_{CH4}	Tm_{cl}	Tm_{ice}	Th	CO_2	CH_4	N_2	δv	X_{H2O}	X_{CO2}	X_{CH4}	X_{N2}	X_{NaCl}
Type-1	phenakite	Fe-1	60	-	-	110.4 G	24	-4	371 G	-	80.5	19.5	0.28	70.2	-	24	5.8	-
		Fe-2	60	-	-	99.5 G	21.7	-4	370 G	-	85.2	14.8	0.23	73.8	-	22.4	3.8	-
Type-1	emerald	Esb-2	50	-	-	-91 L	14	-5	369 L	15.7	78.9	5.4	0.13	88.5	2.3	8	0.5	0.7
		Esb-1	50	-	-	-91 G	14	-	354 G	2.5	90	7.5	0.12	88.3	0.4	9.5	0.8	1
Type-2	emerald	Es3-3	50	-59.4	10.2 G	-	13.4	-6.5	381 G	68	19.5	12.5	0.18	87	7.5	1.6	1	2.9
		Es3-1	50	-62	8 G	-	13.4	-7	371 G	52.1	41.2	6.7	0.21	84.5	7.5	2.9	0.7	3

Raman data from the Franqueira deposit. Composition are given in mole %. Vg/Vt: volumetric ratio; Tm_{CO2}: melting temperatures of CO_2; Th_{CO2}: homogenization temperature of CO_2, gaseous state (G), liquid state (L) and critical state (C); Tm_{cl}: melting temperature of clathrate; Tm_{ice}: melting temperature of ice; Th: total homogenization temperature, gaseous state (G), liquid state (L) and critical state (C). All temperatures are given in °C. δv: density of the volatile-rich phase.

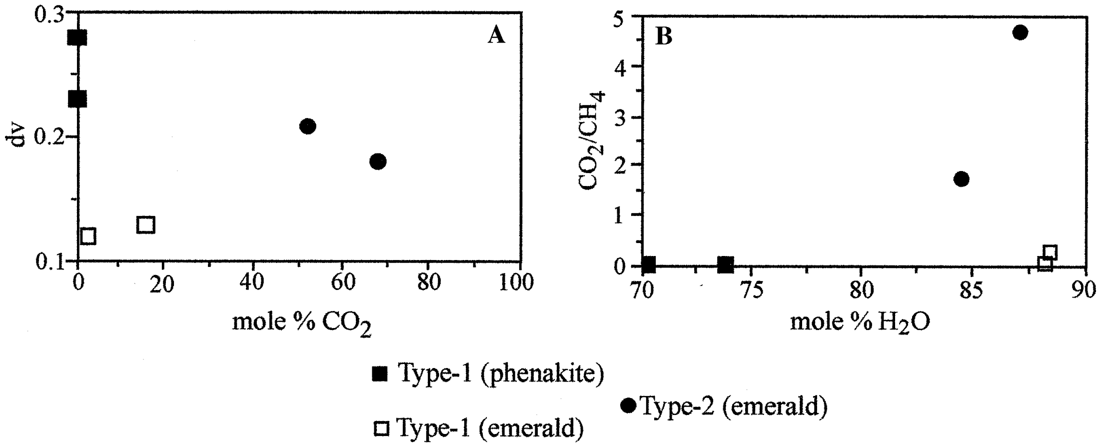

FIG. 4. A. Volatile density (δv) *versus* CO_2 mole %. B. CO_2:CH_4 ratio *versus* H_2O mole %. Determined from Raman analysis of individual fluid inclusions from the Franqueira deposit.

Figure 4A shows density *versus* CO_2 content of the volatile-rich phase for each inclusion type. It can be observed that type-1 inclusions may be divided into two groups, depending on whether they appear in phenakite or emerald. In the first case, the volatile-rich phase has a higher density, and no CO_2 is detected. But in the second case, there is CO_2, and the volatile-rich phase has a lower density. The type-2 inclusions, which only appear in the core of the emerald, reveal an increase in density and CO_2 content of the volatile-rich phase in relation to type-1 inclusions of the same mineral.

Taking into account the bulk composition of both types of inclusion, the CO_2/CH_4 ratio *versus* H_2O content (Fig. 4B) also shows two different groups in type-1 inclusions, depending on whether they appear in emerald or phenakite. Thus from type-1 fluid trapped in phenakite to type-1 fluid trapped in emerald, there is an increase in H_2O at a similar CO_2:CH_4 ratio. The fluid trapped in the emerald core (type 2) has a H_2O content similar to type-1 fluid in emerald but a higher CO_2:CH_4 ratio.

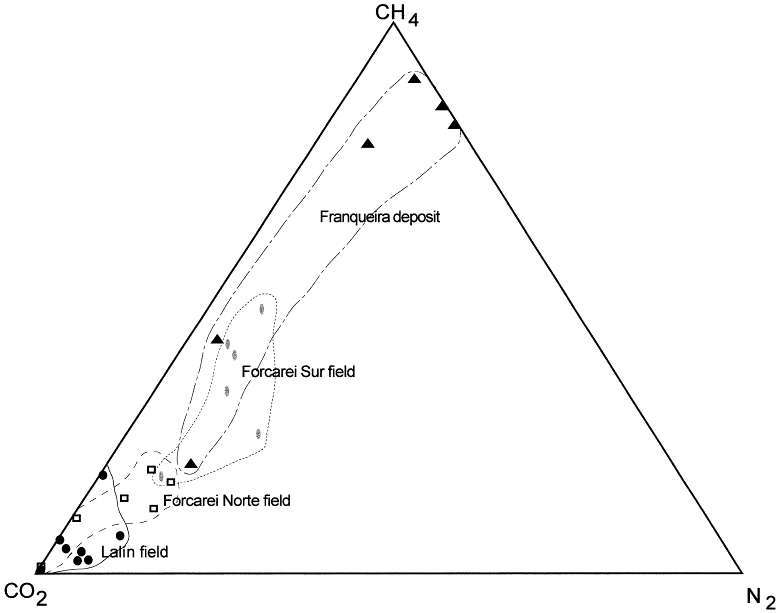

FIG. 5. CO_2–CH_4–N_2 ternary plot of the volatile-rich phase in the inclusions studied from the Franqueira deposit and each pegmatitic field from AEGC (Fuertes-Fuente *et al.* 2000). The plot shows selected results of Raman analyses of the aqueous–carbonic fluid of the Franqueira deposit and the three pegmatite fields from the AEGC.

The aqueous–carbonic fluids found in Franqueira can be compared with fluids from other granitic pegmatites of central Galicia (Fuertes-Fuente & Martin-Izard 1998, Fuertes-Fuente *et al.* 2000). These are known as AEGC pegmatites; they outcrop in three different pegmatite fields: Forcarei Sur (Fuertes-Fuente *et al.* 1995, Fuertes-Fuente & Martin-Izard 1998), Forcarei Norte and Lalín (Fuertes-Fuente 1996). The metasomatic fluids found (Fuertes-Fuente *et al.* 2000) have a composition, mainly that of their volatile phase, different for each AEGC pegmatite field, as demonstrated in the CO_2–CH_4–N_2 ternary plot (Fig. 5). Franqueira is the richest in CH_4 and, in the AEGC pegmatites, the CH_4 content of the aqueous–carbonic fluids increases from Lalín to Forcarei Sur, with an intermediate value in Forcarei Norte. The Franqueira samples were extracted from metasomatic wallrock, and this fact may explain why they are richer in CH_4 than the Forcarei Sur minerals in the pegmatite samples, which were extracted from minerals close to the pegmatite border (Fuertes-Fuente & Martin-Izard 1998). The minerals of the pegmatites from Forcarei Norte and Lalín were not extracted from the border of these bodies. This fact suggests a minor CH_4 content. The fact that Forcarei Norte is enriched in CH_4 compared to Lalín may be due to the fact that the metasediments in which Forcarei Norte pegmatites are enclosed have graphite horizons; these are absent in the metasedimentary units in which the Lalín pegmatites were emplaced (Fuertes-Fuente *et al.* 1995, 2000).

P–T RECONSTRUCTION

The calculated isochores of inclusions in emerald and phenakite from the Franqueira deposit are shown in Figure 6. The P–T evolution of the metasomatic fluids at Franqueira are discussed with reference to this figure. From these isochores, two stages of fluid circulation have been established during the metasomatic event.

The first stage is represented by trapping of type-1 fluid in phenakite at relatively high P–T conditions. The minimum conditions of trapping are those given by the Th–Ph pair, which is 370–371°C and 2–2.5 kbar. Martin-Izard *et al.* (1995) proposed temperatures between 380 and 420°C; we consider an average temperature of 400°C as the temperature closest to conditions of formation (Fig. 6). In this way, the fluid inclusions and Raman data in phenakite allow us to calculate a pressure for the first stage between 2.2 and 2.7 kbar, in agreement with the maximum of 4 kbar and, the most probable value, 2 kbar, proposed by Martin-Izard *et al.* (1995) on the basis of the thermodynamic equilibrium model in the system BeO–Al_2O_3–SiO_2–H_2O developed by Barton (1986) (Fig. 7).

Fluid-inclusion data give us temperatures of formation much lower than those corresponding to the chrysoberyl + quartz stability field (Fig. 6), close to the

euclase = beryl + phenakite + chrysoberyl (2)

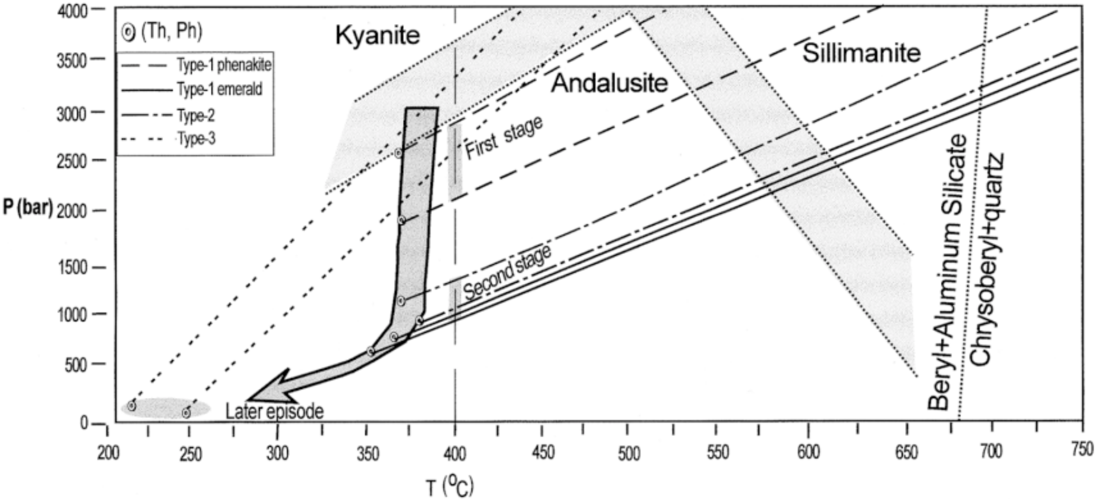

FIG. 6. P–T reconstruction, with the isochores representative of the different types of fluid inclusion in the Franqueira deposit. The dark zones are the minimum P–T conditions for the different stages of trapping of type-1 fluid inclusions in phenakite and emerald, type-2 and type-3 inclusions. The open circles on isochores represent the homogenization temperature and pressure. The vertical dashed line represents an average temperature (400°C) from the temperature range proposed by Martin-Izard *et al.* (1995) taking into account that the mineralization is formed by a contact metamorphic–metasomatic process.

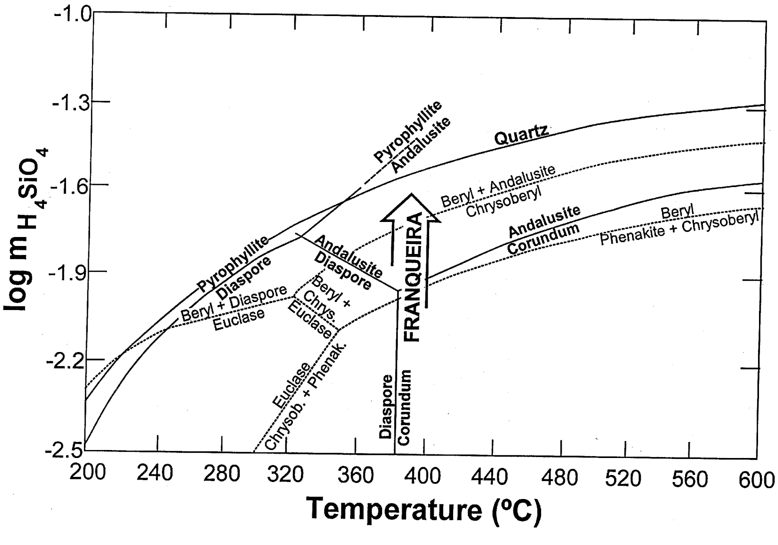

FIG. 7. Log mH_4SiO_4 – temperature projection at P = 1 kbar and activity of beryl = 0.1, showing a path consistent with the evolution of Be-assemblages at Franqueira (from Martin-Izard *et al.* 1995).

join. The absence of euclase indicates a minimum range of temperatures and pressures, *i.e.*, a P of 4 kbar and a T ranging from 350°C (for P = 1 bar) to about 450°C (for P = 4 kbar), in the stability field of andalusite.

The type-1 and type-2 fluids trapped in emerald display a lower density than type-1 fluid trapped in phenakite, yielding lower minimum pressures (Ph), in the 0.75–1 kbar range and a minimum temperatures (Th) in the 354–381°C range. Taking into account the evolution of Be-bearing assemblages at Franqueira (Martin-Izard *et al.* 1995), we consider that the temperature did not change with respect to the first stage, around 400°C (Fig. 6). If so, the pressure of this second stage is around 1 kbar. These data are also in agreement with the proposal by Martin-Izard *et al.* (1995).

During the first hydrothermal stage, the most probable pressure of trapping of type-1 fluid in phenakite is around 2 kbar and a temperature around 400°C. This pressure probably represents a lithostatic pressure indicative of a relatively deep structural level (7–8 km). The type-1 and type-2 inclusions in emerald display lower densities, thus these inclusions were trapped in the range of 1 kbar. Such variation could be explained by a pressure drop from lithostatic to partially hydrostatic conditions during decompression.

The characteristics and isochores of type-3 fluid inclusions (Martin-Izard *et al.* 1995) suggest a later unrelated episode of hydrothermal fluid circulation at minimum trapping temperatures ranging from 160°C to 265°C and pressures below 0.5 kbar.

DISCUSSION

The evolution of the fluid associated with the metasomatic process is as follows. Under pressures between 2 and 2.5 kbar and a temperature close to 400°C, a first stage is developed in which an aqueous–carbonic fluid, dominated by H_2O and of very low salinity, is trapped. The fluid is composed of a volatile phase made up of methane and minor quantities of nitrogen, with an average composition of 72 mole % H_2O, 23.2 mole % CH_4 and 4.8 mole % N_2. A pressure drop produced a second stage of fluid trapping at 400°C and 1 kbar. During this latter stage, emerald formed from phenakite and chrysoberyl (reaction 1 and Fig. 6), thus indicating an increase in silica activity (Barton 1986). At that moment, two different fluids were simultaneously trapped by emerald: (1) an aqueous low-salinity fluid with a CH_4-rich volatile phase (type-1 inclusions), and (2) a CO_2-rich fluid with higher salinity (type-2 inclusions).

Two possible explanations are presented for discussion:

1) At the beginning of emerald crystallization, probably due to a drop in pressure during the second stage and an increase in SiO_2 activity, the initial metasomatic fluid trapped in phenakite evolved into two different aqueous fluids, CO_2-rich and CH_4-rich, in accordance with the reaction of CH_4 with H_2O to form CO_2 and H_2, the latest of which may diffuse away. Both fluids (CO_2-rich and CH_4-rich) have different densities, with the CO_2-rich fluid having the higher density (Fig. 4A). This fact could explain why the volatile phase with higher density and H_2O salinity was concentrated in the fluid trapped by the emerald core (type-2, CO_2-rich), whereas the volatile phase with the lower density and H_2O salinity (type-1, CH_4-rich) kept on getting trapped during the remainder of the emerald growth. In this way, two immiscible fluids are trapped in the emerald core. This agrees with a growth of emerald during a stage of heterogeneous trapping in the system H_2O–NaCl–CH_4–CO_2–N_2, as was proposed by Martin-Izard *et al.* (1995).

2) At the begining of emerald crystallization, a fluid (type-2) from the pegmatite body circulated through the host rock and mixed with type-1 fluid found in phenakite, from which phenakite and, probably, chrysoberyl were formed. Note that several authors have observed that fluids in pegmatitic systems are generally dominated by CO_2 and H_2O: London (1986), Thomas & Spooner (1988), Konnerup-Madsen & Rose-Hansen (1982), and Fuertes-Fuente *et al.* (2000) So, the methane becomes more diluted with CO_2, and there is an enrichment in H_2O, the result of this mixture being the type-1 fluid, found in emerald. The aqueous–carbonic fluids from metasomatic tourmaline of the Tanco (Manitoba) pegmatite host-rock (Thomas & Spooner 1988) have an average composition of 91 mole % H_2O, 6 mole % CH_4, 1 mole % CO_2, and 2 mole % NaCl, which is comparable with that of type-1 fluid in emerald from Franqueira. These authors suggested that the unusual chemistry of these fluids result from mixing of a wallrock-derived CH_4–H_2O fluid, possibly of metamorphic origin, with a fluid released from the pegmatite. At the Gravelotte mine (Nwe & Morteani 1993), phenakite and emerald, which replaces the former mineral, occur on the flanks of a highly metasomatized albitite pegmatite body and in the biotite schist at and near its contact. Nwe & Morteani (1993) described an earliest type-1 inclusion, found in phenakite and emerald, with low salinity (<6 wt% NaCl in phenakite and <7 wt% NaCl in emerald) and up to 18 mole % CH_4 and small amounts of CO_2, Th between 250 and 400°C (Th phenakite > Th emerald), a type-2 fluid inclusion found in emerald, which is variable in both CH_4–CO_2 contents and salinity (6 to 20 wt% NaCl), Th between 170 and 400°C, and later type-3 and type-4 inclusions with up to 38 wt% NaCl, CH_4–CO_2-free. They indicated that the earliest fluids in type-1 inclusions in the phenakite become slighty more saline in the early emerald, rimming the phenakite, with a reduction of the CH_4 content. With progressive crystallization of more emerald and formation of type-2 inclusions, salinities increase and become more variable within individual crystals. Moreover, CH_4 decreases, whereas CO_2 increases. These authors explained these facts as the result of a mixture between type-1 fluids with a dense, high-salinity NaCl brine during this stage, causing a continous trend from type-1 to type-3 inclusions.

The fluid inclusions found in Franqueira are rather similar to those at Gravelotte; nevertheless, there are some important differences, which indicate a somewhat different evolution of the fluid. We consider that type-1 fluid, found in phenakite at Gravelotte and Franqueira, are quite similar, but at Franqueira they have no CO_2. However, the emerald from Franqueira has two types of fluid inclusion, type-1 (emerald) and type-2 (only found in the emerald core). Neither type of fluid inclusion shows a variable range of salinity, and their homogenization temperatures lie within a narrow interval. In some cases, the type-2 Th is higher than type-1 Th and, in other cases, both Th ranges overlap each other (Table 1). Thus, at Franqueira, the main difference between the two types of fluid inclusion in emerald is the variable CO_2 and CH_4 contents. We thus consider that a mixture with a high-salinity NaCl brine, as at the Gravelotte deposit, is unlikely to have taken place at Franqueira. However, a mixture between a CH_4–H_2O fluid, which was perhaps derived from the wallrock, with a fluid released from the pegmatite, as at Tanco, seems to be more likely.

Nevertheless, the presence of the H_2O–CO_2 (± CH_4) inclusions in the emerald crystal core only and the H_2O–CH_4–(± CO_2) inclusions in the whole of the emerald crystal, along with the fact that both inclusion types homogenize to vapor, liquid and in some cases the critical state, indicate that the immiscibility process is the more likely. If a CO_2-rich fluid is added during emerald growth, CO_2-rich inclusions should be found within the whole of the emerald crystal and should only homogenize in one way (liquid or vapor). On the other hand, in the case of an immiscibility due to the reaction proposed above, the CO_2-rich inclusions should be formed when the oxidation process occurs, in other words, during the crystallization of the emerald core. Moreover, the salt content is very constant and low in all type-1 and type-2 inclusions, but it is a little high in type-2 inclusions. Mixing of fluids probably generates fluids with different salinity and CO_2:CH_4 ratios, as is the case at Gravelotte (Nwe & Morteani 1993). In Franqueira, the very constant salinity and CO_2:CH_4 ratios agree with an immiscibility model more than with a mixing of fluids.

Corncerning the origin of type-1 (phenakite) CH_4-rich fluid, Thomas & Spooner (1988) postulated that the wallrock-derived CH_4–H_2O fluid formed as a result of metamorphic reactions involving graphitic sediment. The CH_4 content of fluid inclusions from the AEGC pegmatite fields (Fig. 5) is clearly correlated with the abundance of graphitic horizons in the host rocks and the closeness of the pegmatite samples selected to the host rock, this attesting the role of the host rocks in the geochemical signature of the fluids (Fuertes-Fuente *et al.* 2000). The Franqueira samples were extracted from metasomatic wallrock, whereas the samples of AEGC pegmatites were extracted from zones within the pegmatite bodies. This fact may have an influence on the richness in CH_4 of the fluid inclusions at Franqueira (Fig. 5). However, graphite has not been reported from the pegmatite's host-rock at Franqueira nor at Gravelotte (Nwe & Morteani 1993). Moreover, we discard the possibility of a purely metamorphic origin for type-1 (phenakite) fluid; some components of this fluid must have been derived from the pegmatite, since Be, Al and Si are necessary for the formation of phenakite and chrysoberyl. These minerals could not have come from the host rock because beyond the metasomatic zone; it contains no phenakite. Thus we leave open the dicussion about the source of type-1 (phenakite) CH_4-rich fluid.

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