

# Microthermometry of fluid inclusions in calcite from Fuerteventura carbonatites: composition and formation conditions

*Microtermometría de inclusiones fluidas en calcitas de las carbonatitas de Fuerteventura: composición y condiciones de formación*

Gabriele Carnevale<sup>1</sup>, Vittorio Zanon<sup>2</sup>, Ramón Casillas Ruiz<sup>3</sup> and Agustina Ahijado Quintillán<sup>3</sup>

<sup>1</sup> Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo, Via Archirafi, 22, 90123, Palermo. [gabriele.carnevale@unipa.it](mailto:gabriele.carnevale@unipa.it)

<sup>2</sup> Instituto de Investigação em Vulcanologia e Avaliação de Riscos (IVAR), Universidade dos Açores, Rua Mãe de Deus, 9501-801, Ponta Delgada, Portugal.

[Vittorio.VZ.Zanon@azores.gov.pt](mailto:Vittorio.VZ.Zanon@azores.gov.pt)

<sup>3</sup> Departamento de Biología Animal, Edafología y Geología. Facultad de Ciencias. C/ Astrofísico Sánchez s/n. Universidad de La Laguna. 38206. La Laguna. Santa Cruz de Tenerife.

[rcasilla@ull.edu.es](mailto:rcasilla@ull.edu.es); [aahijado@ull.edu.es](mailto:aahijado@ull.edu.es)

## ABSTRACT

The petrographic analysis in calcite minerals in carbonatitic dykes from Fuerteventura Basal Complex (Ajuy, Punta de la Nao) shows the presence of isolated primary fluid inclusions, corroborating their magmatic origin instead of a late-stage origin. Micro-thermometric studies in calcite show a restricted range of apparent eutectic temperature ( $T_{e^*} = -21.7 - -21.0$  °C) and final ice melting temperatures ( $T_{im} = -3.2 - -2.1$  °C). Homogenization temperatures and pressures are in the range of 140–210 °C and 4–16 bars respectively. Our results suggest the binary NaCl–H<sub>2</sub>O system as a characterizing chemical system in studied fluid inclusions, with the presence of low salinity fluids ( $\approx 5$  wt. % NaCl<sub>eq</sub>), probably related with fluid/rock interactions.

**Key-words:** carbonatites, microthermometry, fluid inclusions, Fuerteventura, Canary Islands.

## RESUMEN

El estudio petrográfico de los minerales de calcita en los diques carbonatíticos del Complejo Basal de Fuerteventura (Ajuy, Punta de la Nao) muestra la presencia de inclusiones fluidas primarias aisladas, corroborando su origen magmático más que un origen tardío. Los estudios microtermométricos en calcita muestran un intervalo de temperatura eutéctica aparente ( $T_{e^*} = -21.7 - -21.0$  °C) y de fusión final del hielo ( $T_{im} = -3.2 - -2.1$  °C) muy restringido. Las temperaturas y las presiones de homogenización están en un intervalo de 140–210 °C y 4–16 bares respectivamente. Nuestros resultados sugieren el sistema binario NaCl–H<sub>2</sub>O como sistema químico que caracteriza las inclusiones fluidas estudiadas, con la presencia de fluidos de baja salinidad ( $\approx 5$  % en peso NaCl<sub>eq</sub>), probablemente relacionados con interacciones fluido/roca.

**Palabras clave:** carbonatitas, microtermometría, inclusiones fluidas, Fuerteventura, Canarias.

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## Introduction

Many carbonatite-related Rare Earth Elements (REE) deposits show how a primary magmatic phase is often followed by a hydrothermal phase in which the infiltrating fluids play an important role in the transport and precipitation of REEs (e.g., Carnevale et al., 2020; Shu and Liu, 2019). The study of fluid inclusions (FIs) in carbonatite rocks is essential for understanding the processes involved in carbonatite-related hydrothermal mineralization, and micro-thermometric studies represent the most straightforward method to obtain information about fluid temperature, pressure and composition. Nevertheless, there are few studies on FIs composition in carbonatites, due also to the presence of complex chemical systems and diversities of FIs type in single

carbonatite occurrence (e.g., Walter et al., 2020). Here we present a micro-thermometric study of FIs in calcite from Fuerteventura carbonatites (Punta de la Nao), in order to characterize the composition and formation conditions of fluid inclusions.

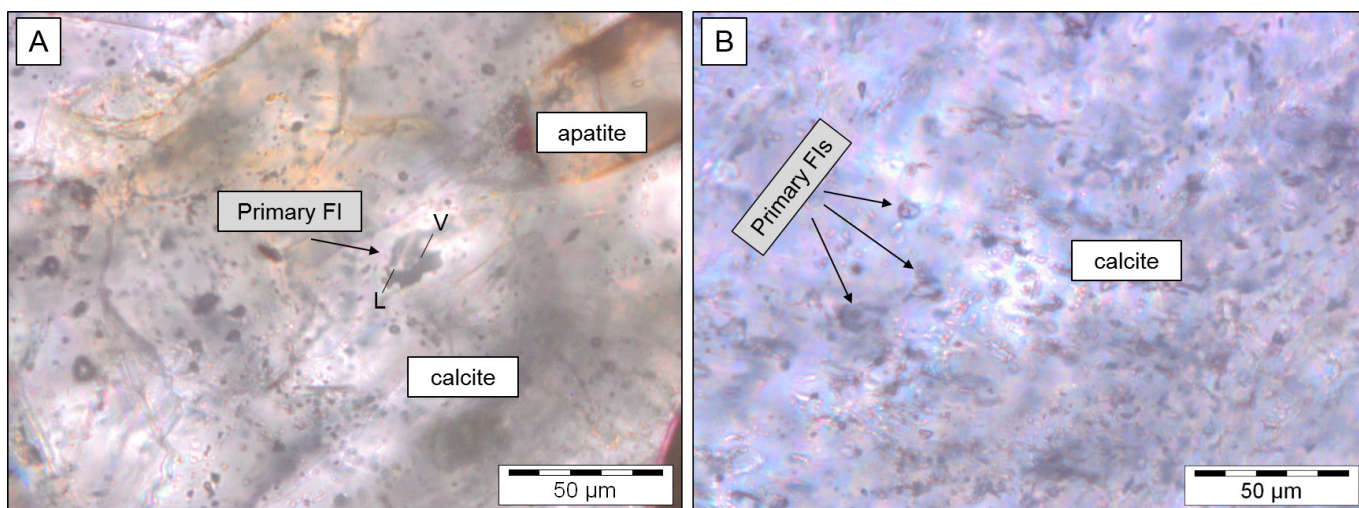
## Analytical methods

Fluid Inclusions were studied in doubly-polished 100–200  $\mu\text{m}$  thick wafers by a Linkam THMSG 600 microscopic heating/cooling stage, at the Instituto de Vulcanologia e Avaliação de Riscos (IVAR) (Ponta Delgada, Portugal). We followed the normal protocol of cooling the fluid inclusions to the lowest temperature that the stage can achieve and subsequently observing the phase changes during heating.

The stage was cooled with liquid nitrogen and calibrated using a single standard crystal of quartz with pure H<sub>2</sub>O and CO<sub>2</sub> inclusions. In order to minimize the effect of metastable transformations during cooling, very common in fluid inclusions, melting and homogenization temperatures were determined during heating at the minimum rate (1 °C/min). Salinities were calculated according to Bodnar (1993), while isochore curves were calculated using the software "Fluids" (Bakker, 2003).

## Fluid inclusions petrography

Fluid inclusions which are formed during the formation of the host mineral phase are considered primary in origin and they are generally trapped along the growth zone or tend to occur isolated.



**Fig. 1.- Photomicrographs of fluid inclusions from Fuerteventura carbonatites. A) Primary fluid inclusions in calcite (L=liquid phase; V=vapour phase). B) Different primary fluid inclusions in calcite.**

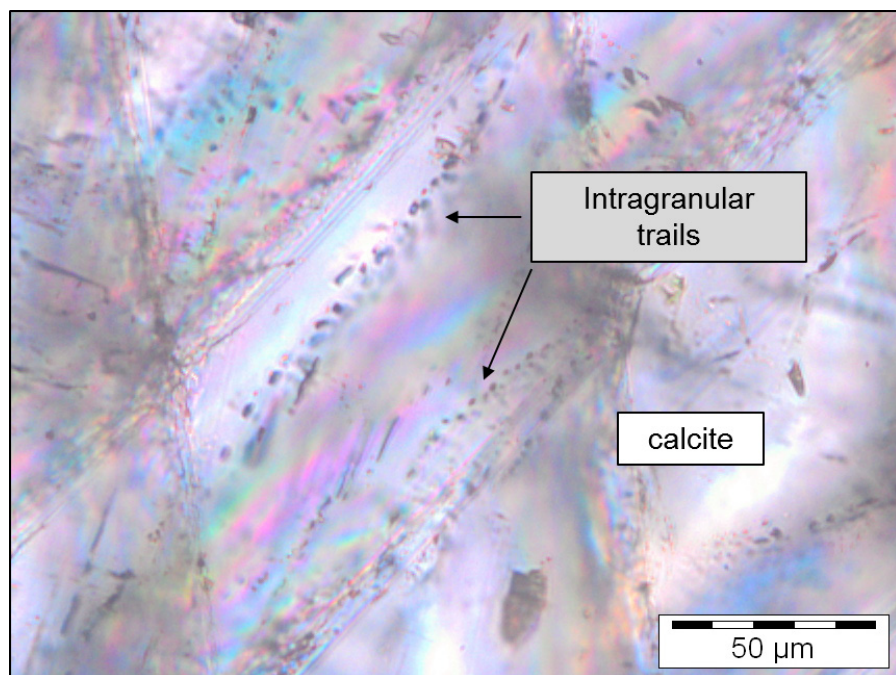
*Fig. 1.- Microfotografías de las inclusiones fluidas de las carbonatitas de Fuerteventura. A) Inclusiones fluidas primarias en calcita (L=fase líquida; V=fase vapor). B) Diferentes inclusiones fluidas primarias en calcita.*

Our petrographic study shows the presence of isolated FIs in host calcite minerals from Fuerteventura carbonatites (Figs. 1A and B), suggesting a primary origin, although additional criteria related to crystal growth would be useful to confirm their primary nature (see Carnevale et al., 2021 for detailed microscopic aspects of Fuerteventura carbonatites). The size of the inclusions is < 10 µm, and they mostly are in the range of 1-5 µm. Their shape is generally irregular, with negative-crystal forms and square shapes, according

to the host calcite mineral. Few rounded isolated FIs in apatite are also present (Fig. 1A). Some FIs show textural characteristics of partial decrepitation, such as haloes of tiny fluid inclusions (diameter < 0.1 µm) surrounding the inclusion cavity, revealing that some events of partial density re-equilibration have occurred. Some secondary inclusions (intragranular trails according with trail terminology described in Randive et al., 2014) confined within calcite grain-boundary and crystal interior are also found (Fig. 2).

### Fluid inclusions composition

In order to interpret micro-thermometric data and formation conditions of FIs in calcite from Fuerteventura carbonatites, it is necessary to know the composition of the inclusions for the appropriate chemical system. This is possible observing the temperatures of phase changes during heating/cooling analy-



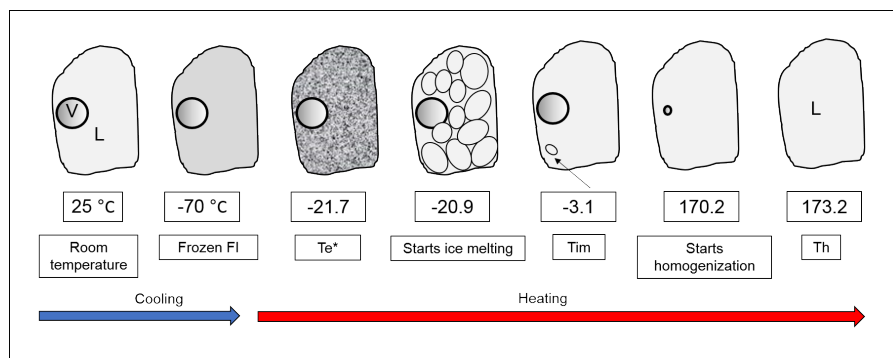
**Fig. 2.- Photomicrograph of intragranular fluid inclusions in calcite from Fuerteventura carbonatites.**

*Fig. 2.- Microfotografía de las inclusiones fluidas intragranulares en calcita de las carbonatitas de Fuerteventura.*

FIs ID	Te* (°C)	Fim (°C)	Salinity (wt. % NaCl <sub>eq</sub> )
1	not visible	-3.1	5.1
2	not visible	-3.2	5.3
3	-21.7	-3.1	5.1
4	not visible	-2.1	3.6
5	-21.0	-2.5	4.2
6	not visible	-2.3	3.9
7	not visible	-2.3	3.9
8	not visible	-2.3	3.9
9	not visible	-3.0	5.0
10	-21.5	-3.0	5.0
11	not visible	-2.3	3.9
12	not visible	-2.2	3.7
13	not visible	-2.7	4.5
14	not visible	-2.2	3.7
15	not visible	-2.7	4.5

**Table 1.- Apparent eutectic temperatures (Te\*), final ice melting temperatures (Fim) and salinity values of FIs in calcite from Fuerteventura carbonatites (salinity values from Bodnar, 1993)**

*Tabla 1.- Temperatura eutéctica aparente (Te\*), temperaturas de fusión final del hielo (Fim) y valores de salinidad en las inclusiones fluidas en calcita de las carbonatitas de Fuerteventura. (valores de salinidad de Bodnar, 1993).*



**Fig. 3.- Sketch showing the phase behaviour of an H<sub>2</sub>O-NaCl fluid inclusion during a complete procedure of a micro-thermometric analysis. The fluid inclusion is first cooled and then heated in order to observe the phase changes. The sketch shows the example of a studied fluid inclusion (sample ID 3).**

*Fig. 3.- Esquema que muestra el comportamiento de fase de una inclusión fluida de H<sub>2</sub>O-NaCl durante un procedimiento completo de análisis microtermométrico. La inclusión fluida se enfría y posteriormente se calienta para observar los cambios de fase. El esquema muestra el ejemplo de una inclusión fluida estudiada (muestra ID 3).*

ses. Since each chemical system has its own eutectic temperature (Te), investigating the Te it is possible to recognize the chemical composition of the investigated fluid inclusions system. However, some authors suggest to use the term "first melting temperature" (T<sub>fm</sub>) or "apparent eutectic temperature" (Te\*) instead of eutectic temperature as this

term is more observational rather than theoretical (Chi et al., 2021). Indeed, results of apparent eutectic temperatures should be considered as approximate rather than exact.

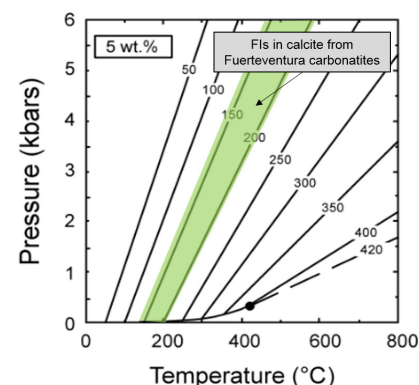
Our results show apparent eutectic temperatures ranging from -21.7 to -21.0 °C (Table I), although the small dimension of FIs did not allow the correct determination of Te\* for almost all inclusions. Thus, the eutectic behavior and the narrow range of measured Te\* suggest the well know binary NaCl-H<sub>2</sub>O system (Te = -21.2 °C) as a characterizing chemical system in studied FIs. No CO<sub>2</sub> was detected (the eutectic temperature of pure CO<sub>2</sub> is -56.6 °C).

At room temperature the studied fluid inclusions were essentially two phases, liquid and vapour (L + V), with a variable % ratio of liquid and vapor, or rarely multiphase with the presence of daughter phases (probably hydrohalite, NaCl · 2H<sub>2</sub>O). With the Te\* range and the chemical system, we also measured the final ice melting temperatures (Tim) during heating, in order to calculate the salinity (expressed as wt. % NaCl<sub>eq</sub>) using the NaCl-H<sub>2</sub>O phase diagram of the empirical expression given by Bodnar (1993) (Table I). The final ice melting temperatures range between -3.2 and -2.1 °C, corresponding to salinities of 5.3 and 3.6 wt. % NaCl<sub>eq</sub>, respectively. Therefore, our results show the presence of low salinity fluids, slightly higher than values measured by Mangas et al. (1997) (< 1.6 wt. % NaCl<sub>eq</sub>), in a simple biphasic NaCl-H<sub>2</sub>O chemical system.

**Table II.- Homogenization temperatures (Th), densities (ρ) and homogenization pressure (Ph) values of FIs in calcite from Fuerteventura carbonatites**

*Tabla II.- Temperaturas de homogenización (Th), densidades (ρ) y valores de presión de homogenización (Ph) de las inclusiones fluidas en calcita de las carbonatitas de Fuerteventura.*

FIs ID	Th (°C) <sub>uncorrected</sub>	ρ (g/cm <sup>3</sup> )	Ph (bar)
1	190.5	0.91	10.2
2	195.7	0.91	11.4
3	173.2	0.93	7.0
4	182.1	0.91	8.5
5	182.1	0.91	8.5
6	208.7	0.88	15.3
7	208.7	0.88	15.3
8	208.7	0.88	15.3
9	184.5	0.89	8.9
10	150.8	0.95	4.9
11	150.9	0.95	4.9
12	196.8	0.90	11.7
13	142.7	0.95	4.6
14	196.7	0.90	11.7
15	143.1	0.95	4.6



**Fig. 4.- Iso-Th curves for NaCl-H<sub>2</sub>O inclusions having salinity of 5 wt.% NaCl. Th range of studied fluid inclusions depicted in green.**

*Fig. 4.- Curvas Iso-Th para las inclusiones NaCl-H<sub>2</sub>O con salinidad del 5 % en peso de NaCl. El intervalo de Th de las inclusiones estudiadas está representado en verde.*

### Formation conditions of trapped fluids

The first step to determine the formation conditions of trapped fluid inclusions (temperature and pressure formation) is to measure the homogenization temperature (Th) of the inclusions, that represents the temperature at which a fluid inclusion gets transformed from a heterogenous (biphase or multiphase) to a homogenous (monophase) state. All studied fluid inclusions homogenize to liquid phase (Th<sub>L</sub>; L + V → L), with homogenization temperature ranging from 142.7 to 208.7 °C (corresponding to densities of 0.95 and 0.88 g/cm<sup>3</sup>, respectively) and homogenization pressures ranging from 4.6 to 15.3 bars (Table II). A sketch showing the complete procedure of cooling and heating analyses of studied fluid inclusions in order to measure apparent eutectic temperature (Te\*), final ice melting temperature (Tim) and homogenization temperature (Th), is presented (Fig. 3).

Normally, the homogenization temperature is less than the real trapping temperature, although if there is no evidence that fluid inclusions have re-equilibrated and they were trapped in an immiscible fluid system, then the homogenization temperature is equal to the real trapping temperature (Bodnar, 2003). In this case a pressure correction (the difference between homogenization temperature and estimated trapping temperature of the fluid inclusions) must be added to the

measured homogenization temperatures to obtain the trapping temperatures. Indeed, our study shows no evidences of immiscible fluid system with the presence of some fluid inclusions with partial decrepitation.

In order to estimate a pressure correction, it is necessary to determine the slope of the isochores along which the fluid inclusions were trapped. We reported in Figure 4 the results of the equation described in the fluid inclusion technique of Bodnar and Vityk (1994), with the relationship between trapping temperature and pressure, salinity (about 5 wt % NaCl<sub>eq</sub> in our case) and homogenization temperatures. Figure 4 shows the slope of the iso-Th lines ( $\cong$  isochores) for NaCl-H<sub>2</sub>O solutions with salinity of 5 wt. % and homogenization temperatures ranging from 50 to 700 °C, with an upper limit of 6 kbars.

## Discussion and conclusion

Although calcite, normally, presents different fracturing and recrystallization processes, and it is complicated to interpret its trapped fluid inclusions, the presence of primary fluid inclusions in calcite minerals from Fuerteventura carbonatites (Punta de la Nao), reflects the magmatic origin of non-recrystallized carbonatite.

Micro-thermometric studies show

apparent eutectic temperatures related to the binary NaCl-H<sub>2</sub>O system (Te\* ranging from -21.7 to -21.0 °C) as a characterizing chemical system in studied Fls. Furthermore, measured final ice melting temperatures, show the presence of low salinity fluids (from 3.6 to 5.3 wt. % NaCl<sub>eq</sub>), probably related with fluid/rock interactions. Homogenization temperatures and pressures are in the ranges of 140-210 °C and 4-16 bars.

Future research should be focused on obtaining fluid inclusions data in a larger set of samples and in different host minerals, such as apatites (a common accessory mineral and commonly present as the liquidus phase), in order to detect possible liquid immiscibility processes with the presence of CO<sub>2</sub> fluid inclusions.

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