

# High-density early CO<sub>2</sub> fluids in the ultrahigh-temperature granulites of Ihouhaouene (In Ouzzal, Algeria)

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## Abstract

Fluid inclusion studies in rocks from the Lower Proterozoic granulites from western Hoggar (Algeria) provide new evidence for the hypothesis that a CO<sub>2</sub>-rich, H<sub>2</sub>O-poor fluid was present during the high-grade metamorphism. CO<sub>2</sub> inclusions represent the main fluid trapped in the Ihouhaouene ultrahigh-temperature (over 1000 °C) and high-pressure (10 to 14 kbar) granulites. The microthermometric and Raman microspectrometric measurements indicate that the carbonic fluid is mainly composed of CO<sub>2</sub> with minor amounts of CH<sub>4</sub> and N<sub>2</sub> detected in some inclusions (<4 mol% CH<sub>4</sub>). Carbonic fluid densities range from 1.18 to 0.57 g/cm<sup>3</sup>. The highest densities are recorded in superdense carbonic inclusions presenting evidence of the earliest trapping and they correspond to the fluid densities expected for the P–T conditions of the peak of metamorphism in the area previously determined from mineral geothermobarometers. Lower densities of carbonic fluids mainly result from the reequilibration of earlier trapped fluid inclusions during retrograde metamorphism and final uplift of the metamorphic terrane, but a new influx of carbonic fluids during the retrograde event remains possible. Carbonic fluids can be produced in situ from decarbonation reactions in interlayered impure marbles during the prograde event or derived from CO<sub>2</sub> flushing from underlying basic intrusions. The aqueous fluids present large variations of composition (0.5 to 30 wt.% NaCl equivalent) and densities (1.16 to 0.57 g/cm<sup>3</sup>). They clearly correspond to post-metamorphic fluids because they mainly occur along microfractures, they do not show any evidence of immiscibility with the carbonic fluids and mixed aquo-carbonic inclusions have not been observed. The percolation of aqueous fluids is related to the Pan-African tectonometamorphic event.

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## 1. Introduction

Granulite facies domains may undergo large mass transfer. Several mechanisms have been recognized: (i) breakdown of the hydrous minerals and especially of the micas producing metal- and F-rich aqueous fluids which may occur well below partial melting temperatures for high CO<sub>2</sub> activity in the fluid phase, (ii) dehydration–

melting reactions generating water undersaturated felsic silicate liquids enriched in incompatible elements, and leading to the desiccation of the lower crust (Fyfe, 1973), (iii) percolation of melts, brines and/or CO<sub>2</sub>-, F-rich fluids extracted directly or indirectly from the mantle (Touret, 1971; Collerson and Freyer, 1988). In relation with these mechanisms, a fundamental debate exists about the origin of the low water activity required for the stability of the peak metamorphic mineral assemblages in granulite facies domains. Metamorphism in the presence of an essentially carbonic fluid phase (Touret,

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1971; Coolen, 1982; Srikantappa et al., 1992; Rakoton-drazafy et al., 1996; Tsunogae et al., 2002; Mohan et al., 2003; Santosh and Tsunogae, 2003), reduction of  $a_{\text{H}_2\text{O}}$  by the presence of a hypersaline fluid, immiscible with  $\text{CO}_2$  (Schmulovitch and Graham, 1996; Aranovich and Newton, 1998; Newton et al., 1998), or fluid absent metamorphism (Lamb et al., 1987; Stevens and Clemens, 1993) are the main models proposed to explain the low water activity for different granulite facies domains. The two first hypotheses imply that fluid transfer either of carbonic fluids or hypersaline fluids is the major mechanism for mass transfer in the lower crust. For the second hypothesis, partial melting is the major mechanism of mass transfer, and when the carbonic fluids do occur they correspond either to residual fluids after anatexis, water being strongly partitioned into the silicate melts (Kadik and Lukanin, 1973), or to a post-metamorphic infiltration despite their high densities and early trapping characteristics (Lamb et al., 1987). Heterogeneous fluid conditions may also occur and both models may exist in the same granulite facies domain. The trace element geochemistry of the Ihouahouene granulites has been discussed by Peucat et al. (1996), Bernard-Griffiths et al. (1996), but the mechanism of element transfer has not been addressed. In this paper we present a detailed study of fluid inclusions in the granulites of Ihouahouene (Hoggar, Algeria) formed at exceptionally high temperature and pressure. The discovery of superdense early carbonic inclusions in the Ihouahouene granulites, trapped under the same P–T conditions those indicated by the metamorphic mineral paragenesis, represents a new contribution to this debate.

## 2. Geologic setting

The Ihouahouene granulites belong to the In Ouzzal complex located in the western Hoggar structural domain. The In Ouzzal complex represents a 450-km-long and 100-km-wide Archaean–Proterozoic nucleus preserved in the Pan-African Pharusian belt (Fig. 1; Caby et al., 1981). The eastern and western sides of the nucleus are limited by 1- to 3-km-thick N–S shear zones. The Ihouahouene granulites are made of acid and basic gneisses of magmatic origin (charnockitic gneisses, anorthosites, norites and lherzolite lenses...) and metapelites, banded iron formations, quartzites, as well as marbles of sedimentary origin (Peucat et al., 1996). Banded iron formations only appear as discontinuous lenses. The majority of the metasediments consist of Al–Mg-rich granulites interlayered with olivine–spinel to highly impure pargasite–spinel–diopside–anorthite-bearing dolomitic marbles (Ouzegane and Boumaza, 1996). A number

of geochronological studies have resulted in two age groups for the Ihouahouene granulites: (i) 3.5–2.7 Ga (Lancelot et al., 1976; Ben Othman et al., 1984; Peucat et al., 1996) and (ii) 2.1–1.8 Ga (Lancelot et al., 1976). The first age group has been recorded in the charnockitic basement and corresponds to magmatic emplacement ages, which are confirmed by U–Pb single grain zircon ages ranging from 3.0 to 3.14 Ga (Haddoum et al., 1994). The second age group corresponds to granulite metamorphism, the youngest ages are also in agreement with Ar/Ar measurements on biotite (Maluski et al., 1990).

An ultrahigh-temperature prograde phase reaching temperatures over 1000 °C and pressures of 12 to 14 kbar and a low pressure retrograde phase (down to 640–820 °C and 6 to 2 kbar) has been recorded by thorough studies of the mineral paragenesis of these granulite facies rocks (Bertrand et al., 1992; Audibert et al., 1993; Mouri et al., 1996; Ouzegane and Boumaza, 1996). The two phases have been attributed to a single tectonometamorphic event at ca. 2.0 Ga with a clockwise evolution of the P–T conditions (Bertrand et al., 1992).

Three main magmatic to metamorphic events posterior to granulite facies have been recognized: (i) formation of syenitic and carbonatitic bodies which occur very locally and very shortly after granulitization at ca. 2.0 Ga (Fourcade et al., 1996); (ii) the Pan-African tectonometamorphic event, not recorded by the isotopic chronometers in the granulites, but which corresponds to the development of huge shear zones to the West and East margins of the Ihouahouene block, and NE trans-tensional faults crosscutting the metamorphic foliation (Fig. 1); phengite from the Western part of the In Ouzzal shear zone gives Pan-African ages (Caby and Monié, 2003); (iii) the intrusion of dolerite and rhyolite dikes, alkaline aplitic granites and widespread late Pan-African alkaline granites (Fourcade et al., 1996). Thus, the Pan-African orogeny represents the main geologic event which may have had some influence on the post-granulite metamorphism fluid regime.

## 3. Methods

Fluid inclusions have been studied in 0.15-mm-thick doubly polished thin sections. Melting and homogenization temperatures were obtained with a Chaix Meca heating and freezing stage using an Olympus LWD-MS Plan  $\times 80$  objective with a long focal distance allowing the study of inclusions down to 5  $\mu\text{m}$  in diameter. The stage has been calibrated with synthetic and natural inclusions. The reproducibility of the  $\text{CO}_2$  melting ( $T_{\text{mCO}_2}$ ) point is estimated at  $\pm 0.1$  °C from repeated measurements on pure  $\text{CO}_2$  synthetic inclusions.  $\text{CO}_2$  homogenization

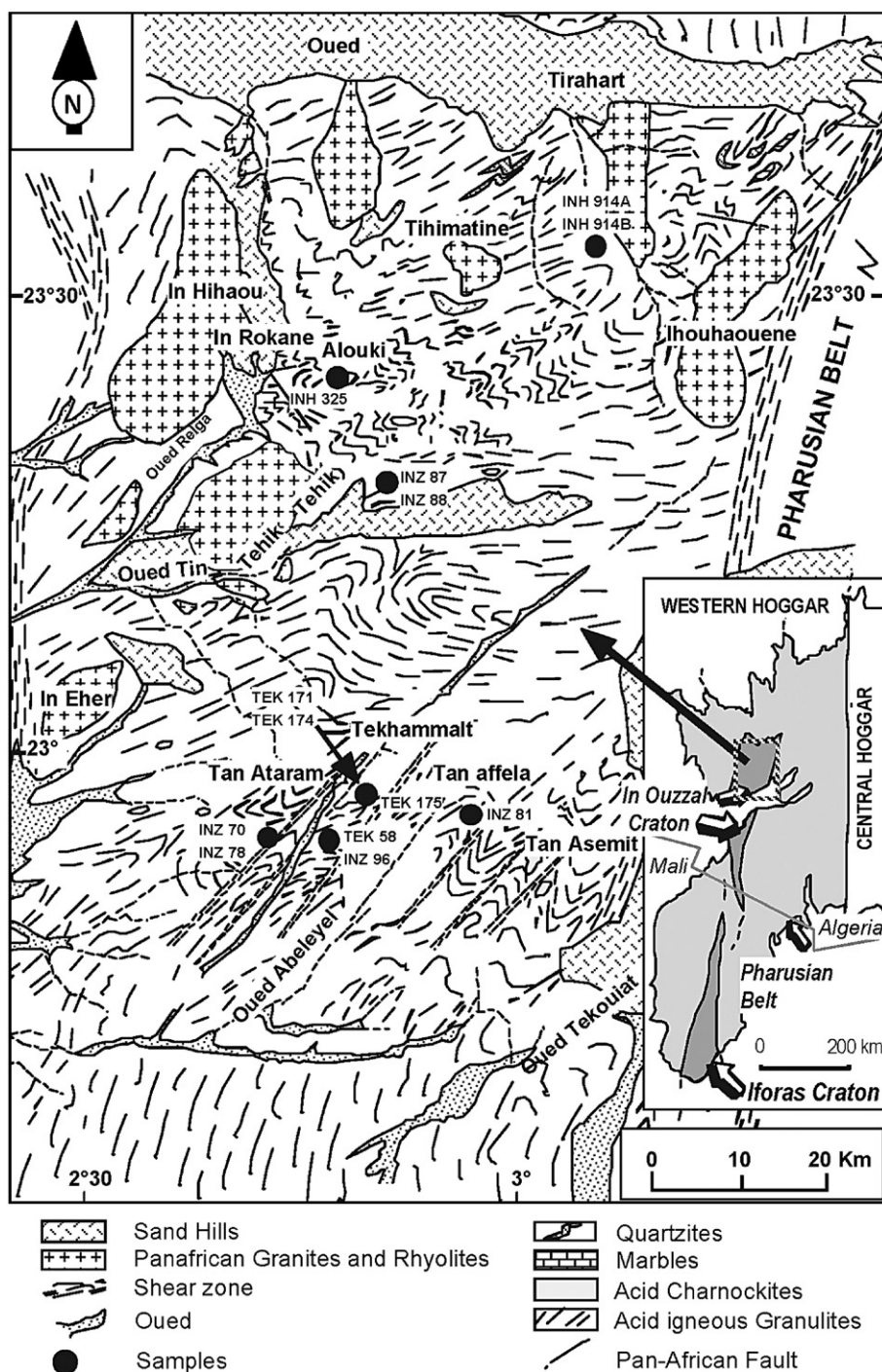


Fig. 1. Simplified geological map from the Ihouhaouene area (In Ouzal, western Hoggar, Algeria) (Caby et al., 1981). The location of the studied samples is indicated.

temperatures ( $Th_{CO_2}$ ) are reproducible within  $\pm 0.5$  °C, whereas total homogenization temperatures ( $Th$ ) are reproducible within  $\pm 2$  °C. To get statistically significant results, we have limited the number of data from each fluid cluster during the microthermometric investigations.

No more than about ten inclusions representative of the  $Th$  or  $Tm$  range of each isolated cluster of fluid inclusion or planar array have been measured.

The molar fractions of the main molecular species have been determined in selected fluid inclusions using a

Dilor X–Y multichannel laser Raman microprobe at CREGU (Dubessy et al., 1989). The bulk composition and density of the fluid inclusions were computed from the V–X properties of individual fluid inclusions in the C–H–O system (Thiery et al., 1994). The P–T properties of the inclusions were modelled using the equation of state of Kerrick and Jacobs (1981) and Jacobs and Kerrick (1981) for the H<sub>2</sub>O–CH<sub>4</sub>–CO<sub>2</sub> system and from Zhang and Frantz (1987) for the H<sub>2</sub>O–NaCl system.

#### 4. Petrography

Thirteen samples have been selected in the main lithologies derived either from sedimentary or igneous protoliths: five charnockitic gneisses, six metasedimentary granulite facies gneisses and two magnetite quartzites. These samples have been selected from the collection which has been used for the determination of the P–T conditions by Bertrand et al. (1992), Mouri et al. (1996), Ouzegane and Boumaza (1996). The selection has been based on the presence of fluid inclusions large enough to be studied by microthermometry.

The charnockitic gneisses belong to three bodies (Fig. 1): Tin Tchih Tchih (samples INZ 87 and 88), Tan Ataram (INZ 70 and 78) and Tan Afella (INZ 81), and belong to various granite types (Peucat et al., 1996). The Tin Tchik Tchik charnockite (INZ 87) has been dated at 2.7 Ga (Peucat et al., 1996). All samples present a weak foliation and do not show any evidence of rehydration minerals, except the two samples from Tan Ataram in which epidote occurs, probably in relation with the Pan-African event (Kienast, personal communication). Biotite is likely to be a primary mineral. Biotite occurs either as nearly idiomorphic crystals included in garnet, sapphirine and orthopyroxene or as larger flakes distributed homogeneously with the other matrix minerals. Its stability up to ca. 1000 °C results from its exceptionally high Mg, Ti and F (up to 4.6% F+Cl) content (Mouri et al., 1996). The mineral paragenesis of the samples is given in Table 1.

The metasedimentary granulite facies gneisses have been taken mainly in the Tekhamalt area (Fig. 1) (TEK 58, 171, 174, 175 and INZ 96). Only sample INH 325 has been taken in the northern part of the area near Alouki (Fig. 1). All the samples, except TEK 175, are Al–Mg gneisses derived from a mixing between sediments and hydrothermal alteration minerals of ultrabasic rocks (Bernard-Griffiths et al., 1996) which have mainly provided the mineral assemblages used for the P–T determinations in Mouri et al. (1996). Sample TEK 175 corresponds to an anatectic pod in the Al–Mg gneisses, an extremely unusual feature in this area. The remark-

Table 1

Metamorphic mineral parageneses of the charnockitic gneisses of Ihouhaouene

|        | Qtz | Perth | Pl | Cpx | Opx | Bt | Mgt | Ilm | Amp |
|--------|-----|-------|----|-----|-----|----|-----|-----|-----|
| INZ 70 | +   | +     | +  | +   |     |    | +   | +   |     |
| INZ 78 | +   | +     |    | +   |     |    | +   | +   |     |
| INZ 81 | +   | +     | +  |     | +   |    | +   | +   |     |
| INZ 87 | +   | +     | +  | +   | +   | +  | +   | +   | +   |
| INZ 88 | +   | +     | +  |     |     |    | +   | +   |     |

Qtz: quartz, Perth: perthite, Pl: plagioclase, Cpx: clinopyroxene, Opx: orthopyroxene, Bt: biotite, Mgt: magnetite, Ilm: ilmenite, Amp: amphibole.

able mineralogy of these rocks has allowed a tight reconstruction of the metamorphic history of the Ihouhaouene granulites. Two successive paragenesis have been observed (Table 2):

- Coarse-grained quartz, feldspar, garnet, orthopyroxene, sillimanite and rutile. F-rich biotite is also present in some of the samples.
- Cordierite, sapphirine and spinel are clearly secondary. They occur as coronitic symplectitic associations frequently associated with quartz around the minerals of the first paragenesis. Biotite crystals also present symplectitic alterations composed of orthopyroxene and K-feldspar.

The orthopyroxene+sillimanite+quartz or sapphirine+quartz and spinel+quartz parageneses correspond to the peak of metamorphism. They are only stable over 900 °C (Bertrand et al., 1992; Ouzegane and Boumaza, 1996; Mouri et al., 1996) for corresponding pressures of 10 to 14 kbar. The secondary paragenesis, in which cordierite is the characteristic mineral, corresponds to a clockwise retrograde evolution down to 6–2 kbar. Cordierite is associated with secondary orthopyroxene, sapphirine or spinel. The estimated P–T conditions are constant all over the investigated area, the variations in the P–T determinations mainly result from the differences obtained between the different geothermobarometers used for the estimations.

The magnetite quartzites (INH 914a and b), sampled in the northern part of the area (Fig. 1), present the same paragenesis as the Al–Mg gneisses but with different proportions of quartz, sillimanite, garnet, magnetite and hercynite. Early corundum can be observed to be included in magnetite and sometimes in contact with quartz. Such an association implies high temperatures and pressures similar to those determined based on mineral paragenesis of the Al–Mg metasedimentary gneisses.

Feldspar which occurs in most studied rocks, is perthitic with a composition varying between Or<sub>50</sub>–Ab<sub>48</sub> and

Table 2

Metamorphic mineral paragenesis of the metasedimentary granulites samples of Ihouhaouene

|         | Paragenesis I |       |    |     |     |     |    |    | Paragenesis II |     |     |
|---------|---------------|-------|----|-----|-----|-----|----|----|----------------|-----|-----|
|         | Qtz           | Perth | Pl | Grt | Opx | Sil | Bt | Rt | Crld           | Spr | Spl |
| TEK 175 | +             | +     | +  |     |     |     | +  | +  |                |     |     |
| TEK 174 | +             |       |    | +   |     | +   |    | +  | +              |     |     |
| TEK 171 | +             |       |    |     | +   | +   | +  | +  | +              |     |     |
| INH 325 | +             |       |    |     | +   | +   |    | +  | +              |     |     |
| TEK 58  | +             | +     | +  | +   | +   | +   | +  | +  | +              | +   | +   |
| INZ 96  | +             | +     | +  | +   | +   | +   | +  | +  | +              | +   | +   |

Qtz: quartz, Perth: perthite, Pl: plagioclase, Grt: garnet, Opx: orthopyroxene, Sil: sillimanite, Bt: biotite, Rt: rutile, Crd: cordierite, Spr: sapphirine, Spl: spinel.

Paragenesis I corresponds to the prograde metamorphic phase and paragenesis II corresponds to the retrograde phase.

Or<sub>86</sub>-Ab<sub>13</sub> according to the rock type (Mouri et al., 1996). Our observations confirm the conclusions of Ouzegane and Boumaza (1996), on the same samples, which have shown that K-feldspar derives either from the reaction of biotite with quartz to give orthopyroxene + K-feldspar,

or in the absence of quartz, from the breakdown of the biotite + sillimanite assemblage giving cordierite + spinel + K-feldspar. No secondary K-feldspar veining, in intergranular location or rimming the peak metamorphism minerals similar to those described by Ravindra Kumar (2004) has been observed. The only ambiguous evidence of secondary K-feldspar crystallization may correspond to the local occurrence of some irregular antiperthitic textures, which may be interpreted either as high temperature exsolutions or as secondary replacement.

## 5. Fluid inclusion data

More than nine hundreds inclusions have been studied by microthermometry in the different gneiss types (Table 3).

### 5.1. Fluid inclusion distribution and typology

Fluid inclusions have been mainly studied in quartz grains, but some have also been studied in garnet and

Table 3

Summary of microthermometric data for fluid inclusions from the Ihouhaouene granulites

| Sample                                     | Fluid inclusions  |      |                        |          | Microthermometry       |       |             |          |         |      |
|--------------------------------------------|-------------------|------|------------------------|----------|------------------------|-------|-------------|----------|---------|------|
|                                            | Habitus           | Type | TmCO <sub>2</sub> (°C) | <i>n</i> | ThCO <sub>2</sub> (°C) | Mode  | Tm ice (°C) | <i>n</i> | Th (°C) | Mode |
| <i>Metasedimentary granulitic gneisses</i> |                   |      |                        |          |                        |       |             |          |         |      |
| TEK 58                                     | Primary           | H3   | −57.9/−56.8            | 22       | −4.1/30.4              | L (V) |             |          |         |      |
|                                            | Secondary         | w    |                        |          |                        |       | −0.9/−0.1   | 18       | 187/374 | L    |
| TEK 175                                    | Primary/Secondary | H3   | −60/−56.6              | 62       | −17.2/20.1             | L     |             |          |         |      |
|                                            | Secondary         | w    |                        |          |                        |       | −22.3/−21.6 | 12       | 221/356 | L    |
| TEK 174                                    | Primary           | H3   | −59.8/−56.6            | 80       | −57.2/12.4             | L     |             |          |         |      |
|                                            | Secondary         | w    |                        |          |                        |       | −38.3/−19.1 | 10       | 253/259 | L    |
| TEK 171                                    | Primary/Secondary | H3   | −57.7/−56.6            | 91       | −7.7/30.2              | L     |             |          |         |      |
|                                            | Secondary         | w    |                        |          |                        |       | −48.4/−21.7 | 9        | 250/317 | L    |
| INZ 96                                     | Primary           | H3   | −57.5/−56.6            | 67       | −6.6/25.1              | L     |             |          |         |      |
| INH 325                                    | Primary           | H3   | −59/−56.6              | 75       | −35.8/1.7              | L     |             |          |         |      |
|                                            | Primary           | S1   | −56.7 <sup>a</sup>     | 2        |                        |       |             |          |         |      |
| <i>Magnetite quartzite</i>                 |                   |      |                        |          |                        |       |             |          |         |      |
| INH 914A                                   | Secondary         | H3   | −58.6/−57.6            | 68       | −13.8/15               | L     |             |          |         |      |
|                                            | Secondary         | S1   | −58/−57.6 <sup>a</sup> | 4        |                        |       |             |          |         |      |
| INH 914B                                   | Primary/Secondary | H3   | −58.6/−57              | 67       | −14.6/26.3             | L     |             |          |         |      |
|                                            | Secondary         | S1   | −57.3 <sup>a</sup>     | 3        |                        |       |             |          |         |      |
| <i>Charnockitic gneisses</i>               |                   |      |                        |          |                        |       |             |          |         |      |
| INZ 70                                     | Primary           | H3   | −57.1                  | 1        | 20.4                   | L     |             |          |         |      |
|                                            | Secondary         | w    |                        |          |                        |       | −46.1/−15.5 | 24       | 117/221 | L    |
| INZ 78                                     | Secondary         | w    |                        |          |                        |       | −41.3/−14.5 | 40       | 61/299  | L    |
| INZ 81                                     | Secondary         | H3   | −57.9/−56.6            | 64       | 4.3/27                 | L     |             |          |         |      |
|                                            | Secondary         | w    |                        |          |                        |       | −13/−11.7   | 3        |         |      |
| INZ 87                                     | Primary/Secondary | H3   | −58.7/−56.8            | 65       | −30.1/25.6             | L     |             |          |         |      |
|                                            | Secondary         | w    |                        |          |                        |       | −21.5/−8.2  | 18       | 124/318 | L    |
| INZ 88                                     | Secondary         | H3   | −59.1/−56.9            | 67       | −33.6/22.8             | L     |             |          |         |      |

Fluid inclusions types : H3 and S1 = carbonic (see Van den Kerkhof, 1988; Dubessy, 1984); w = aqueous.

<sup>a</sup> Temperature of sublimation.

apatite. Two main types of fluid inclusions have been observed: carbonic inclusions, largely predominant in most rock samples, and aqueous inclusions. Despite detailed microscopic examination, no mixed aquo-carbonic inclusions have been detected. However, in most fluid inclusions having a diameter of a few microns to a few tens of microns, a significant amount of water can be present in apparently entirely carbonic fluid inclusions. As water preferentially wets the cavity walls of a mixed aquo-carbonic fluid inclusion up to 10 vol.% of water can be present in the inclusion but as such a thin film that it will be undetectable by examination with an optical microscope. No water film lining the cavity walls has been observed even in the largest irregularly shaped carbonic inclusions (with a diameter up to 25  $\mu\text{m}$ ). Thus, we have considered that approximately 10 vol.% water was present in the carbonic inclusions in some of our density and pressure calculations for bracketing the range of possible isochores.

#### 5.1.1. Carbonic fluids

Carbonic fluid inclusions have been observed in twelve of the thirteen studied samples. Small nahcolite ( $\text{NaHCO}_3$ ) crystals have been observed in some of these inclusions. Two types of inclusion distribution have been distinguished:

- Scattered fluid inclusions in quartz or garnet with nearly isometric shapes forming isolated clusters of inclusions distributed in three dimensions but without any well-defined orientation (Fig. 2A). They have been considered as corresponding to the earliest generations.
- Fluid inclusions distributed along well-defined planar arrays crosscutting one or several mineral grains (Fig. 2B and C). They clearly represent secondary inclusions.

Their shape is highly variable and the inclusions with the lowest densities generally present the most complex

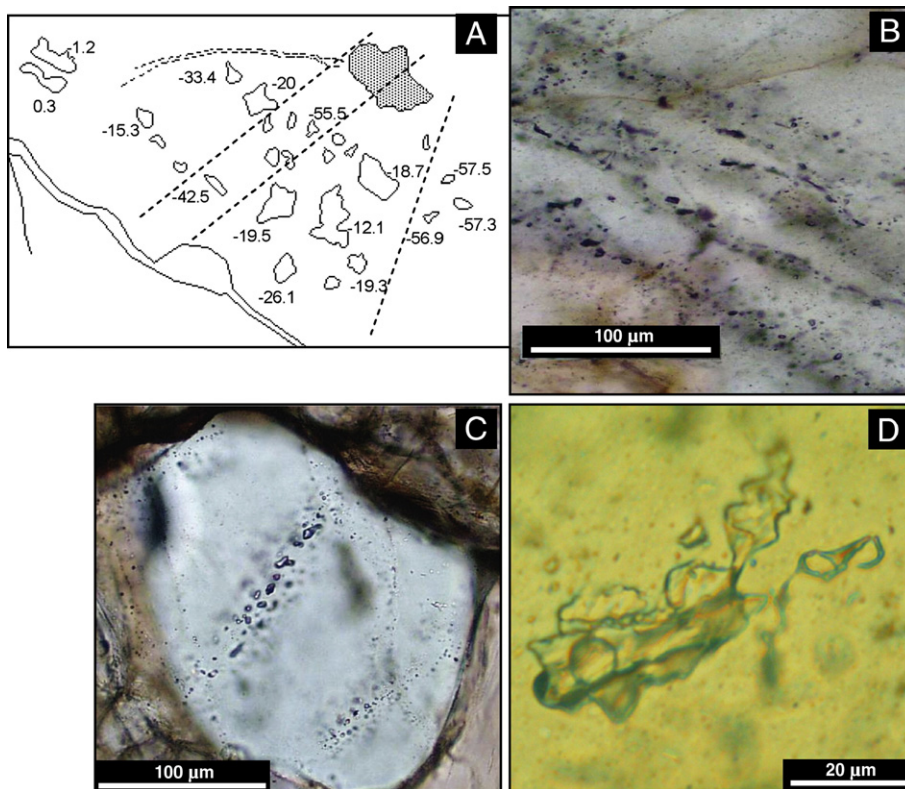


Fig. 2. Photomicrographs of  $\text{CO}_2$ -rich fluid inclusions: (A) an isolated cluster of inclusions with nearly isometric shapes presenting the highest densities with indication of the densities, and delimitation of the best preserved domains in quartz enclosing the inclusions with the highest densities (sample TEK 174); (B) well-defined planar arrays of carbonic inclusions with intermediate densities (sample INZ 81); (C) a more detailed view of a planar array of carbonic fluid inclusions with more variable shapes and a solid phase (nahcolite) present in one of the inclusions ( $\text{ThCO}_2$  varies from +2.8 to +12  $^\circ\text{C}$  but  $\text{TmCO}_2$  only from  $-56.9$  to  $-57.0$   $^\circ\text{C}$ ) (sample INZ 88); (D) a low-density two phase carbonic inclusion (L + V) with a very complex shape ( $\text{Th} = +25.2$   $^\circ\text{C}$  and  $\text{Tm} = -56.8$   $^\circ\text{C}$ ) (TEK 58).

shapes (Fig. 2D). They generally homogenize in the liquid phase. Homogenization in the vapor phase has been observed only in one sample (TEK 58).

A few inclusions present an unusual phase transition, corresponding to sublimation between  $-58$  and  $-57$  °C of small amounts of solid  $\text{CO}_2$  formed during cooling. They also present a very irregular shape compared to other inclusions, suggesting very late trapping or reequilibration. They have been observed in three samples only (INH 325, INH 914a and b), all located in the northern part of the study area (Fig 1).

### 5.1.2. Aqueous fluids

Aqueous inclusions have not been observed in samples located in the northern part of the study area (samples INH 325 and INZ 96 (metasediments), INH 914a and b (magnetite quartzite), and INZ 88 (charnockitic gneiss)). In all samples located in the southern part of the study area (except INZ 96), aqueous fluid inclusions trails are common, but are generally much less abundant (<10%) than the carbonic inclusions. However, in acid meta-igneous rocks (INZ 70, 78 and 81) aqueous fluid inclusions may exceed 50% of the inclusions. Aqueous inclusions are the only inclusion type observed in sample INZ 78. They generally occur along well-defined planar arrays which crosscut and disrupt the continuity of the carbonic inclusions trails indicating a secondary origin. Thus, the aqueous inclusions appear clearly younger than the carbonic inclusions.

One hundred thirty-eight aqueous fluid inclusions have been studied, from which three types of aqueous inclusions can be distinguished:

- (1) Three phase inclusions ( $\text{H}_2\text{O}$  liquid,  $\text{H}_2\text{O}$  vapor, NaCl solid) with rounded isometric shapes, which always homogenize into the liquid phase. The salt cube never exceeds 10 to 15 vol.% of the fluid inclusion. Extreme salinities as described by Touret (1995) have not been observed. Three phase inclusions may occur as isolated clusters, but they are more generally distributed along well-defined planar arrays. Some of the three phase inclusions probably represent the earliest generations of aqueous fluids, but they have never been observed in close association with carbonic fluid inclusions. No implosion structure, with salt representing the main component of the inclusions, has been observed. Thus, there is no direct evidence of fluid immiscibility between an hypersaline aqueous fluid and a carbonic fluid in the studied samples.

- (2) Two phase inclusions ( $\text{H}_2\text{O}$  liquid– $\text{H}_2\text{O}$  vapor), with rounded to elongated shapes, which always homogenize in the liquid phase.
- (3) One phase metastable inclusions: no vapor phase is observed at room temperature. The vapor phase nucleates only during cooling but may persist up to 60–100 °C. Their very irregular shape and size (4 to 45  $\mu\text{m}$ ) suggest very late trapping. No detailed microthermometric investigations have been performed on these inclusions.

## 5.2. Microthermometric data

### 5.2.1. Carbonic fluids

Melting temperatures of carbonic fluids ( $T_{\text{mCO}_2}$ ) range from  $-59.8$  to  $-56.6$  °C (Fig. 3). However, more than 90% of the carbonic inclusions present  $T_{\text{mCO}_2}$  between  $-58.6$  and  $-56.6$  °C. The inclusions with the highest densities present  $T_{\text{mCO}_2}$  very close to pure  $\text{CO}_2$  at about  $-57.5$  °C, as confirmed by Raman microprobe analysis (Table 4).

Homogenization temperatures ( $T_{\text{hCO}_2}$ ) spread from  $-57.5$  to  $+30.4$  °C with a well-defined mode at 0 °C and a nearly perfect Gaussian distribution (Fig. 4). Only four inclusions homogenize into the vapor phase. More than 98% of the inclusions homogenize between  $-25$  to  $+30$  °C. The lowest  $T_{\text{hCO}_2}$  have been observed in very small sized fluid inclusions (3 to 7  $\mu\text{m}$ ) occurring as an isolated cluster in the core of a quartz crystal in the metasedimentary granulite TEK 174. The  $\text{L} + \text{V} \rightarrow \text{V}$  transition occurs just at  $T_{\text{mCO}_2}$  and corresponds to a fluid density of 1.18  $\text{g}/\text{cm}^3$ . Such a density corresponds to the limit of the so-called “superdense” carbonic fluids as defined by Van den Kerkhof and Olsen (1990). Isolated clusters of fluid inclusions and most planar

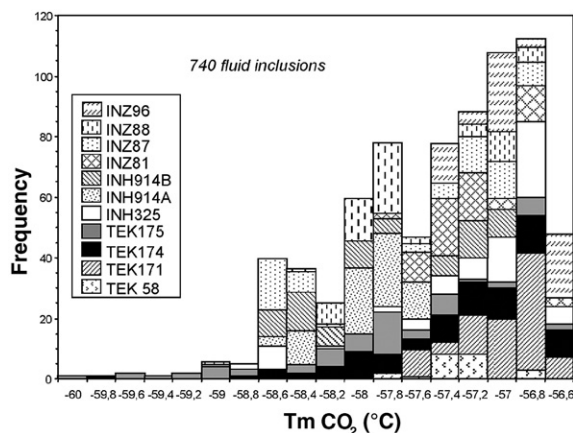


Fig. 3. Histogram of  $\text{CO}_2$  melting temperatures for the carbonic fluid inclusions.

Table 4

Microthermometric data and Raman microprobe analyses of the gas phase for selected carbonic inclusions

| Sample  | Incl. Nb | Microthermometry (°C) |                   |      | Raman (mol%)    |                 |                |         | Bulk composition (mol%) |                 |                 |                |
|---------|----------|-----------------------|-------------------|------|-----------------|-----------------|----------------|---------|-------------------------|-----------------|-----------------|----------------|
|         |          | TmCO <sub>2</sub>     | ThCO <sub>2</sub> | Mode | CO <sub>2</sub> | CH <sub>4</sub> | N <sub>2</sub> | Density | H <sub>2</sub> O        | CO <sub>2</sub> | CH <sub>4</sub> | N <sub>2</sub> |
| TEK 175 | 1(2)     | −56.9                 | −8.2              | L    | 97.4            | 0.3             | 2.3            | 0.95    | 22.2                    | 75.5            | 0.2             | 1.8            |
|         | 1(16)    | −58                   | −17.2             | L    | 96.1            | 3.9             | nd             | 0.98    | 21                      | 76              | 3               | 0              |
|         | 1(20)    | −57.4                 | −8.6              | L    | 98.2            | 1.8             | nd             | 0.95    | 21.8                    | 76.8            | 1.4             | 0              |
|         | 2(4)     | −58.2                 | 3.8               | L    | 99              | 1               | nd             | 0.91    | 22.6                    | 76.6            | 0.8             | 0              |
|         | 2 (8)    | −58.3                 | 8.4               | L    | 98.6            | 1.4             | nd             | 0.84    | 24                      | 75              | 1               | 0              |
|         | 2(9)     | −58.2                 | 9                 | L    | 98              | 1.8             | nd             | 0.82    | 24.4                    | 74.3            | 1.3             | 0              |
|         | 3(10)    | −59.6                 | −8.5              | L    | 97.5            | 2.5             | nd             | 0.92    | 22.2                    | 75.9            | 1.9             | 0              |
|         | 4 (10)   | −57.9                 | −6.2              | L    | 97.8            | 2.2             | nd             | 0.92    | 22.2                    | 76              | 1.8             | 0              |
| TEK 174 | 3(2)     | −57.5                 | −57.3             | L    | 99.7            | 0.3             | nd             | 1.16    | 17.8                    | 82              | 0.2             | 0              |
| TEK 58  | 7 (3)    | −57.4                 | 24.7              | V    | 99.6            | 0.4             | nd             | 0.24    | 47.9                    | 51.9            | 0.2             | 0              |
| INZ 88  | 1 (1)    | −57.9                 | −0.5              | L    | 99.8            | 0.2             | nd             | 0.91    | 22.7                    | 77.1            | 0.2             | 0              |
| INH 325 | 5(16)    | Sublimation at −56.7  |                   |      | 2.3             | nd              | 97.7           |         |                         |                 |                 |                |

nd=Not detected. The bulk composition (mol%) has been calculated assuming 10 vol.% H<sub>2</sub>O in the inclusion. The large variation in the calculated molecular composition reflects the large variation of the density of the different inclusions.

arrays show always a large variation of ThCO<sub>2</sub> (Fig. 5). In sample TEK 174, the isolated cluster with the superdense inclusions presents one of the most extreme ThCO<sub>2</sub> variations, from −57.5 to 0 °C (Fig. 5). Only rare fluid inclusion planar arrays, such as sample TEK 171, show homogeneous ThCO<sub>2</sub> distribution (Fig. 5).

Homogenization temperatures of CO<sub>2</sub> for the carbonic inclusions are not correlated with TmCO<sub>2</sub>. Therefore, the strong variations of fluid densities do not depend on their compositions. No relationship has been detected between the density of the carbonic inclusions and the mineralogy of the host mineral or the geographic distribution of the samples. However, a relationship seems to exist between the lithology of the fluid inclusion-bearing rocks and the fluid densities. Metasedimentary gneisses have preserved the

fluid inclusions with the highest densities. All ThCO<sub>2</sub> modes are lower than 0 °C for the carbonic inclusions in the metasediments. In contrast, carbonic fluid inclusions from the magnetite-bearing quartzites present the lowest densities: 95% of the ThCO<sub>2</sub> values are between 0 and +30 °C. This may reflect their higher ductility during deformation because they are mostly composed of quartz (Kirby and Kronenberg, 1987), and consequently their easier reequilibration during exhumation. The carbonic fluid inclusions from the gneisses of igneous origin have intermediate to high densities but 95% of the inclusions have densities lower than 1 g/cm<sup>3</sup>.

### 5.2.2. Aqueous fluids

Melting temperatures of H<sub>2</sub>O (Tm<sub>ice</sub>) vary from −48.4 to −0.1 °C with two main modes at −20 and 0 °C (Fig. 6). Most of the inclusions are very saline, the main mode is at −20 °C. Their salt content vary from 0.5 to 29.9 wt.% NaCl equivalent. However, eutectic temperature is recorded around −60 °C, and Tm<sub>ice</sub> values below −21.1 °C indicates the occurrence of divalent cations and other cations in many inclusions.

Homogenization temperatures are between 40 and 373.8 °C (Fig. 7) with four modes at 160, 220, 260, and 300 °C. Their densities vary from 0.57 to 1.16 g/cm<sup>3</sup>. Three main inclusion groups can be differentiated in a Th<sub>H<sub>2</sub>O</sub>/Tm<sub>ice</sub> diagram:

- (1) for −40 < Tm<sub>ice</sub> < −20 °C and 150 < Th<sub>H<sub>2</sub>O</sub> < 375 °C, there is a positive correlation between Tm<sub>ice</sub> and Th<sub>H<sub>2</sub>O</sub>.
- (2) for −20 < Tm<sub>ice</sub> < −7 °C and 150 < Th<sub>H<sub>2</sub>O</sub> < 350 °C, most of the inclusions have microthermometric

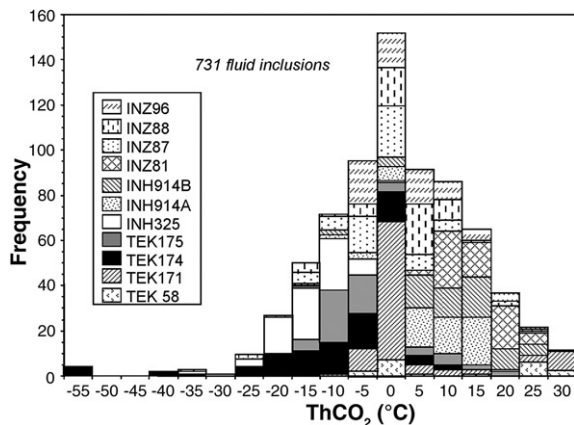


Fig. 4. Histogram of CO<sub>2</sub> homogenization temperatures for the carbonic fluid inclusions.

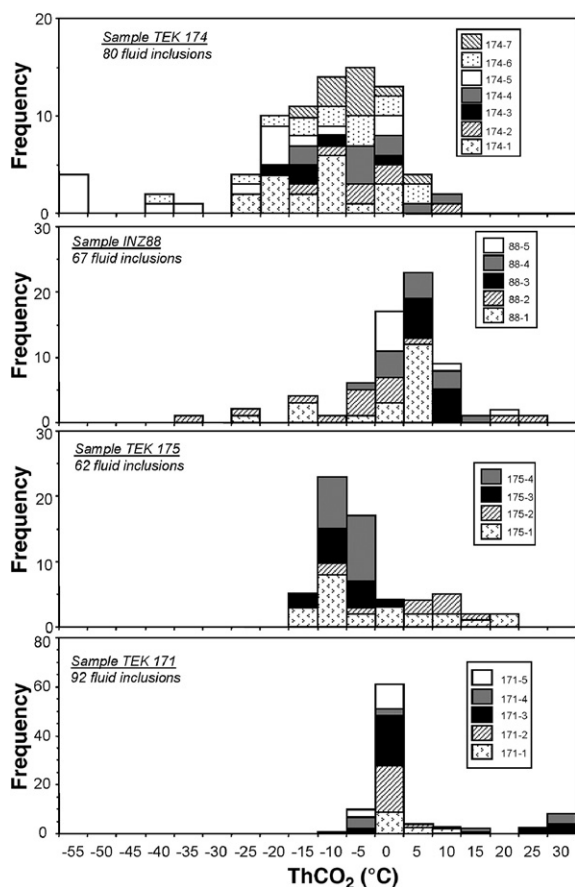


Fig. 5. Histogram of CO<sub>2</sub> homogenization temperatures for the carbonic fluid inclusions from 4 samples distinguishing the data for each inclusion cluster or planar array.

characteristics compatible with the H<sub>2</sub>O–NaCl system.

- (3)  $T_{m_{ice}} \approx 0^\circ\text{C}$  and  $175 < Th_{H_2O} < 400^\circ\text{C}$  is characteristic of sample TEK 54.

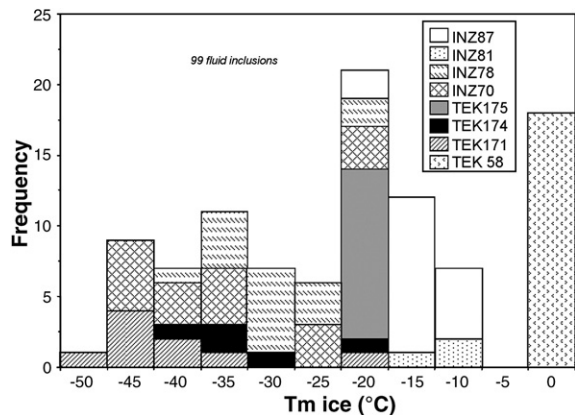


Fig. 6. Histogram of ice melting temperatures for the aqueous fluid inclusions.

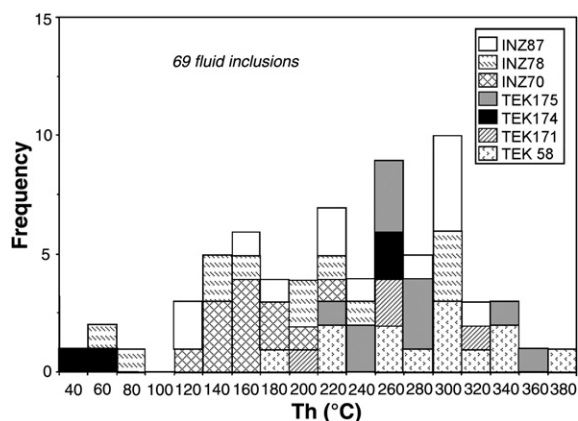


Fig. 7. Histogram of homogenization temperatures for the aqueous fluid inclusions.

### 5.3. Raman microprobe data

Selected fluid inclusions belonging to the main types have been analyzed by Raman microprobe for CO<sub>2</sub>, CO, N<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, and hydrocarbons with higher carbon numbers (Table 4). Only CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> have been detected in some inclusions. The CH<sub>4</sub> content does not exceed 3.9 mol%. One of the inclusions belonging to the cluster with the lowest homogenization temperatures (TEK 174 3-2,  $Th_{CO_2} = -57.3^\circ\text{C}$ ) contains only 0.3 mol% CH<sub>4</sub>. N<sub>2</sub> has been only detected in one inclusion (2.3 mol%). The highest molar volume has been obtained for inclusion TEK 58 7-3.

Taking into account the occurrence of 10 mol% H<sub>2</sub>O and a few mol% CH<sub>4</sub> in the carbonic inclusions for the calculation of the isochores leads to an increase of only 250 bars for pressures of the order of 10 kbar. Thus, the uncertainty about fluid composition for the calculation of the isochores is very limited at such high pressures. The pressure increase related to the occurrence of water in the carbonic inclusions becomes more important at high temperatures for lower CO<sub>2</sub> densities.

Calculated oxygen fugacities for a composition corresponding to the inclusions with the highest densities are slightly lower than the QFM buffer at 1000 °C, which is expected for metasedimentary granulites.

## 6. Discussion and conclusions

### 6.1. Immiscible aqueous fluid or late aqueous fluid percolation?

The frequency of aqueous inclusions in the different samples does not depend on the host rock lithology, but corresponds to a specific geographic distribution. All the

samples located in the northern part, except INZ 87, are devoid of aqueous fluid inclusions. In all the samples located in the southern part of the study area, except INZ 96, aqueous fluid inclusion trails are common. In the acid meta-igneous rocks (INZ 70, 78 and 81), aqueous fluid inclusions are very abundant or the only ones which are observed as in sample INZ 78. Such a geographic distribution can be related to the presence of well-developed ductile shear zones (N30–40°E) related to the Pan-African tectonometamorphic event, which have been recorded in the samples from the southern area (Fig. 1). The occurrence of retrogression epidote in the vicinity of two of the studied acid meta-igneous rock samples with abundant aqueous fluid inclusions strongly supports a relation between the influx of aqueous fluid and the Pan-African event. Furthermore, the lack of composite aqueous carbonic fluids and the absence of evidence for fluid immiscibility between carbonic and saline aqueous fluid inclusions further support a late introduction of the aqueous fluids.

## 6.2. Fluid present or fluid absent in granulite facies metamorphism?

The earliest fluid observed in the Ihouhouene granulites corresponds to a carbonic fluid with less than 1 mol% CH<sub>4</sub> and densities reaching 1.18 g/cm<sup>3</sup>. These inclusions occur as isolated clusters in a quartz grain core which have not been affected by later recrystallization. The superdense carbonic inclusions from Ihouhouene have the highest densities recorded for pure carbonic fluids in granulite facies domains, close to those obtained in the granulites of the Furua complex in Tanzania (1.21–1.22 g/cm<sup>3</sup>, Coolen, 1982). For a temperature of 970 ± 60 °C, a pressure of 12.2 ± 0.5 kbar is obtained from the 1.18 g/cm<sup>3</sup> isochore (Fig. 8). The 1.18 g/cm<sup>3</sup> isochore intersects the middle part of the P–T field defined from the metamorphic mineral paragenesis according to the most recent estimations (Mouri et al., 1996) (970 ± 60 °C and 10 to 14 kbar). The trajectory of the isochore corresponding to the superdense carbonic inclusions also excludes the trapping of such a fluid during the retrograde evolution of the Ihouhouene metamorphic domain (see Fig. 8). Synmetamorphic superdense CO<sub>2</sub> inclusions have been reported in numerous other granulite facies domains, e.g., Doda-beta, southern India (Touret and Hansteen, 1988; Srikantappa et al., 1992); Tonagh Island, Enderbyland, East Antarctica (Tsunogae et al., 2002); Nuliyam, Kerala Belt (Fonarev et al., 2001); Eastern Ghats, India (Mohan et al., 2003); Shevaroy Hills massif, India (Santosh and Tsunogae, 2003), Nagercoil, India (Santosh et al., 2003).

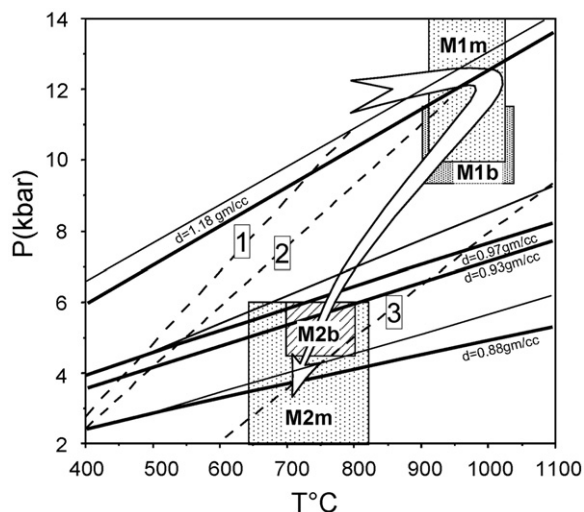


Fig. 8. Fluid inclusion isochores of the main types of fluids and P–T fields of the two metamorphic events (M1b and M2b from Bertrand et al., 1992; M1m and M2m from Mouri et al., 1996) estimated from the mineral parageneses of the Ihouhouene granulites. The large arrow represents the clockwise retrograde metamorphic path. The thick solid lines correspond to the isochores for selected pure CO<sub>2</sub> inclusions, whereas the thin solid lines correspond to the isochores for the same CO<sub>2</sub> inclusions but with 10 vol.% H<sub>2</sub>O. The dotted lines correspond to the isochores for aqueous fluid inclusions representative of the main types: (1) Th=350 °C, Tm=−1 °C and  $d=0.59 \text{ g/cm}^3$ , (2) Th=250 °C, Tm=−15 °C and  $d=0.96 \text{ g/cm}^3$ , (3) Th=250 °C, Tm=−20 °C and  $d=0.98 \text{ g/cm}^3$ .

The large variations in fluid inclusion densities are not correlated with variations in fluid composition, but are observed at the scale of most individual inclusion clusters and planar arrays. Consequently, most medium- to low-density inclusions may be interpreted as the result of physical reequilibration during the retrograde metamorphic phase, rather than from a continuous influx of carbonic fluid during decreasing P–T metamorphic conditions. However, the occurrence of some fluid inclusion planar arrays with similar homogenization temperatures and densities corresponding to the P–T conditions of the retrograde phase indicates that at least a second stage of carbonic fluid circulation occurred during this phase. The main mode in the cumulative homogenization temperature histogram (Fig. 4) is at 0 °C and corresponds to a fluid density of 0.93 g/cm<sup>3</sup>. For a temperature of 700–800 °C a pressure of 4.4 to 4.9 kbar is obtained from the 0.93 g/cm<sup>3</sup> isochore (Fig. 8). Therefore, the most common densities recorded for the carbonic fluid in the granulites fits well with the pressure estimations for the retrograde phase as defined by the metamorphic mineral paragenesis by Bertrand et al. (1992) and Mouri et al. (1996). According to this, a new influx of CO<sub>2</sub> during the retrograde event cannot be excluded.

The hypothesis that a fluid phase of essentially carbonic composition was present during the granulite facies metamorphism is strongly supported by the facts that: (i) the earliest carbonic fluid inclusions observed in the Ihouhaouene metasedimentary granulites have densities which are compatible with the peak metamorphic conditions determined independently by the mineral geothermobarometry; and (ii) they could not have been trapped during the retrograde event. The density of these early carbonic fluid inclusions was subsequently reequilibrated during the decrease of the P–T conditions as indicated by: (i) the variation in the fluid densities within most single inclusion planar arrays or clusters, and (ii) the agreement between the carbonic fluid density corresponding to the main mode of carbonic fluid inclusion homogenization temperature in the histogram and the P–T conditions of the retrograde metamorphic event estimated independently from the retrogression mineral paragenesis. The lowest densities ( $<0.9 \text{ g/cm}^3$ ) indicate that further reequilibration of some of the carbonic inclusions occurred during the final uplift of the metamorphic terranes.

Fluid inclusions with densities and compositions compatible with the peak metamorphic conditions are difficult to detect because they present the following characteristics: (i) they are generally very scarce, occurring in one sample among 10 or more studied samples, and representing only a few inclusions for 1000 studied inclusions. However, exceptions exist such as sample C179.1 of the Furua granulites (Coolen, 1982); (ii) they have a very small size (a few microns in diameter) and tend to present isometric shapes. Large and/or complexly shaped inclusions do not resist strong internal overpressurization; (iii) they occur as isolated clusters composed of a very limited number of inclusions; (iv) they are located in the core of such clusters which may display a progressive decrease of density towards the cluster margins (see for example Figs. 8–6 in Touret, 1981); and (v) in exceptional cases, they may occur along the growth zones of a mineral crystallized during peak metamorphic conditions, such as corundum (Rakotondrzafy et al., 1996). Several mechanisms may lead to the destruction of fluid inclusions corresponding to peak metamorphic conditions. When subjected to a later high T–low P event, fluid inclusions may decrepitate but typical textures of decrepitated inclusions have not been observed in the present study. More commonly, ductile deformation of quartz after peak metamorphism leads to its recrystallization and the destruction of formerly trapped fluid inclusions, or to a density reequilibration of these inclusions.

### 6.3. Origin of the carbonic fluids

Several hypotheses have been proposed for the origin of carbonic fluids in granulite facies domains (see Hansen et al., 1984 for a review of these hypotheses). Enrichment in  $\text{CO}_2$  of the metamorphic fluid may result from the partitioning of  $\text{H}_2\text{O}$  into an anatectic melt. However, the Ihouhaouene granulites do not display any textural evidence of partial melting except for very local anatectic pods. The Al–Mg-rich composition of the metasediments is attributed to the specific pre-metamorphic chemical characteristics of the protoliths (Mouri et al., 1996). Enrichment in  $\text{CO}_2$  may also result from the trapping of water in hydrous minerals during retrogradation. However, this hypothesis cannot be considered here because the only samples presenting evidence of a retrograde hydrous paragenesis (orthogneisses with epidote) are the richest in aqueous inclusions (see below).

Several authors have suggested that  $\text{CO}_2$  can be enriched at the inclusion scale by selective loss of other components such as  $\text{H}_2\text{O}$  and  $\text{CH}_4$  (Roedder, 1981; Sterner and Bodnar, 1986). A selective loss of  $\text{H}_2\text{O}$  or  $\text{CH}_4$  would have decreased the density of the fluid and consequently the estimated pressure (Hansen et al., 1984). In the Ihouhaouene inclusions, there is no evidence for such a mechanism. The extent of diffusive reequilibration of  $\text{H}_2\text{O}$  or  $\text{CH}_4$  should increase with the surface/volume ratio of each fluid inclusion. Therefore, the smallest inclusions in a given isolated cluster or planar array should show the lowest densities and a reverse correlation should be observed between density and water content of the inclusions. Such correlations have not been observed even within a single inclusion cluster. To the contrary, the superdense inclusions observed in the present study are among the smallest ones. Moreover, recent studies (Vityk and Bodnar, 1995) tend to show that synthetic inclusions in quartz may preserve their original density even when subjected to an overpressure of 2 kbar, if the confining pressure increment is progressive instead of instantaneous, which would be unrealistic for natural geological processes.

Although, the origin of the carbonic fluids cannot be tightly constrained from the present data, two major sources can be proposed for the Ihouhaouene area. The most evident source is carbon dioxide produced in situ by the decarbonation reactions occurring in the impure dolomitic marbles intimately interlayered with the metasedimentary formations. The marbles show extensive evidence of mineral reactions during granulite metamorphism.  $\text{CO}_2$  may alternatively have also been provided by the synmetamorphic basic igneous rocks (anorthosites, norites and lherzolites) occurring in the

area (see Peucat et al., 1996). If marbles are considered as the main source of CO<sub>2</sub>, dilution of the water produced by the breakdown reactions of hydrous minerals must have occurred during the early stage of the high temperature prograde metamorphic evolution when the main decarbonation reactions did occur, which would have prevented partial melting in the more favourable lithologies. Although outcropping basic rocks presently form lenses of very limited extension, they may correspond to much larger intrusions at depth as expected for such high P and T granulites which most likely correspond to the base of the continental crust. So, a direct influx of mantle derived CO<sub>2</sub> cannot be excluded.

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