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Carbonic fluid inclusions in ultrahigh-temperature granitoids from southern India

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Abstract

The granite plutons of Vattamalai (VT), Gangaikondan (GK) and Pathanapuram (PT) intruding granulite facies rocks in southern India were emplaced during the Late Neoproterozoic tectonothermal event. Feldspar thermometry of mesoperthites from the granites yield temperatures of 800–1000 °C indicating high- to ultrahigh-temperature conditions, comparable to similar estimates derived from some of the host granulite facies rocks in the region. This study reports results from a detailed investigation of fluid inclusions in the three granite plutons. Carbonic inclusions characterize the major fluid species in all the cases and their unique abundance in some of these plutons indicates up to 1 wt.% CO₂. In most of the cases, the inclusions show a near-pure CO₂ composition as deduced from melting temperatures which cluster close to -56.6 °C, and as confirmed by laser Raman spectroscopy. The VT granite preserves the highest density CO₂ fluids among all the three plutons with a density up to 0.912 g cm⁻³ (molar volume of 48.25 cm³ mol⁻¹). A combination of CO₂ isochores, feldspar thermometry data and dehydration melting curves, and liquidus for water-undersaturated granitic systems clearly bring out a genetic link between these granites and granulitic lower crust. The ultimate origin of the CO₂-rich fluids is linked to sub-lithospheric mantle sources through tectonic processes associated with the assembly of the Gondwana supercontinent. *To cite this article: M. Santosh et al., C. R. Geoscience 337 (2005).*

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Résumé

Les granites de Vattamalai (VT), Gangaikondan (GK) et Pathanapuram (PT), intrusifs dans les roches de faciès granulite du Sud de l'Inde, ont été mis en place lors d'un épisode tectonométamorphique Panafricain tardif. La thermométrie des feld-spaths sur mésoperthites indique des températures de 900–1000 °C, correspondant à des conditions de température élevée à ultra-élevée, comparable aux estimations faites sur certaines granulites de la région. Une étude détaillée des inclusions fluides contenues dans les trois plutons granitiques a été entreprise. Dans tous les cas, les inclusions les plus abondantes sont carboniques, soit inclusions primaires isolées ou en petits groupes, soit inclusions secondaires ou pseudosecondaires, disposées le

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long de microfissures recristallisées. Presque toujours, ces inclusions contiennent du CO₂ pur, identifié par une température de fusion proche du point triple ($-56,6^{\circ}$ C) et par microspectrométrie Raman. Dans un cas, des traces de N₂ (< 5 mol%) causent un faible abaissement de la température de fusion. Le granite VT a préservé les inclusions de plus haute densité (0,912 g cm⁻³, = volume molaire de 48,25 cm³ mol⁻¹). La combinaison des isochores du CO₂, la thermométrie sur feld-spath, les courbes réactionnelles de déshydratation et liquidus du système granitique sous-saturé font clairement ressortir un lien génétique entre ces granites et la croûte inférieure granulitique. L'origine ultime des fluides riches en CO₂ se trouve dans le manteau sub-lithosphérique, transférés dans la croûte inférieure par des processus tectoniques, lors de l'assemblage du supercontinent du Gondwana. *Pour citer cet article : M. Santosh et al., C. R. Geoscience 337 (2005).* © 2004 Académie des sciences. Published by Elsevier SAS. All rights reserved.

Keywords: Granite; Feldspar thermometry; Fluid inclusions; CO2; Southern India; East Gondwana

Mots-clés : Granite ; Faciès granulite ; Thermométrie sur feldspaths ; Inclusions fluides ; CO2 ; Sud de l'Inde ; Est Gondwana

1. Introduction

Fluid regimes attending granulite formation in the Earth's middle and lower crust provide important clues to lower crustal and crust-mantle interaction processes [12,23,24]. Granulite facies rocks that are characterized by dry mineral assemblages often contain CO₂-rich fluids trapped as fluid inclusions in various minerals [13,14,18,23,25]. Recently syn-metamorphic carbonic fluids were also recorded from ultrahightemperature granulites formed by extreme crustal metamorphism at temperatures exceeding 1100°C [26]. Precambrian high-grade terrains often associate late granite intrusions, and it is has been proposed that, in most cases, such granitoids emplaced into the upper continental crust were derived by partial melting of lower crustal granulites [3,4]. While the magma tectonics and geochemical features of these granitoids are well studied, information on their fluid characteristics is sparse. In this paper, we report results from a systematic fluid inclusion study of high to ultrahightemperature granite plutons that intrude Precambrian granulite facies rocks in southern India. These plutons belong to the Late Pan-African felsic magmatic suite recognized from several parts of the East Gondwana crustal fragments [11,16].

2. Geological framework

The three granite plutons investigated in this study are the Vattamali (VT) within the Palghat–Cauvery Shear Zone system in the north, the Gangaikondan (GK) at the southern part of the Madurai Block, and the Pathanapuram (PT) within the central part of the Achankovil Shear Zone (Fig. 1) from the Proterozoic granulite facies terrain of southern India. The GPS coordinates for the samples locations of VT, GK and PT plutons are 10°56.47'N–77°32.67'E, 8°51.95'N–77°46.67'E and 9°9.32'N–76°51.56'E, respectively.

The study area around VT granite falls within the central part of the Palghat-Cauvery Shear Zone system (PCSZ) (Fig. 1), a zone that marks the Archean-Proterozoic terrane boundary in southern India [6, 20]. The dominant lithological units in the region are charnockites, ultrahigh-temperature granulites, hornblende gneisses, quartzofeldspathic gneisses, and intrusive granites. The granite shows coarse, massive texture without any visible foliation. Pink feldspar is the dominant constituent with subordinate plagioclase and quartz and accessory biotite. The pluton shows broad ovoidal shape and concordance of the contacts with the regional fabric of the host orthogneisses. The GK granite pluton occurs at the southern margin of the Madurai Block (cf. Fig. 1) and intrudes granulite facies gneisses. The highlands in this block are occupied dominantly by massive enderbitic granulites and charnockites, while the lowlands are intercalated with metasedimentary and meta-igneous rocks. The granite is medium grained and dominantly comprises pink K-feldspar, subordinate plagioclase and quartz with biotite as the major accessory. Few thin pegmatites and quartz veins several centimeters thick traverse the granite body. Development of a weak foliation and stretching of quartz in the granite indicate post-emplacement deformation. The PT granite occurs in the central domain of the Achankovil Shear Zone



Fig. 1. Geological framework of southern India (inset) showing major granulite blocks and shear zones. (**a**) Geology surrounding Vattamalai granite. (**b**) Geological map of the southern part of South India showing the locations of Gangaikondan and Pathanapuram granites (geological maps modified after [5]).

Fig. 1. Cadre géologique du Sud de l'Inde (insert) indiquant les principaux blocs granulitiques et zones de cisaillement. (a) Géologie autour du granite de Vattamalai. (b) Carte géologique de l'extrémité méridionale du Sud de l'Inde, indiquant l'emplacement des granites de Gangaikondan et Pathanapuram (carte géologique modifiée d'après [5]).

(ACSZ) (cf. Fig. 1) and is elongated parallel to the trend of the shear zone as well as the foliation of the host charnockites that carry cordierite and orthopyroxene. The granite is massive and shows no shearing or deformational features indicating that its emplacement post-dated shear deformation along the ACZ. The rock is medium to coarse grained with pink alkali feldspar and subordinate plagioclase and quartz. The major mafic mineral is hornblende. Biotite occurs as accessory. Minor quartz veins and pegmatites traverse the rock.

U–Pb electron microprobe dating of monazite grains from the VT granite yielded ages of 500–520 Ma [21]. Monazites from the PT granite have 520–580 Ma cores mantled by rims as well as bright overgrowths ranging in age between 500–540 Ma. Zircons from the GK granite belong to two distinct populations defining ages of 680 ± 30 Ma and 570 ± 10 Ma

[20]. The younger age is also identical to the 574-Ma ages from the cores of monazites in the PT granite. The ages of the granite plutons closely compare with the U–Pb monazite ages obtained from for the host granulite facies rocks [20]. Thus, a close spatial and temporal link can be inferred between the granulite facies host rocks and the granite plutons, correlating with the Late Pan-African tectonothermal event.

3. Analytical techniques

Petrographic studies were carried out on polished thin sections and modal analyses of the granites were performed using a point counter. Electron microprobe analyses of the mesoperthites were done using a JEOL JXA-8600M instrument housed at the Kochi University. An acceleration voltage of 15 kV, probe current of

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 1.5×10^{-8} A and beam diameter of 1 µm were used. The data reduction was performed using Oxide-ZAF model corrections. Fluid inclusion studies were done on doubly polished granite wafers following standard techniques [27]. A total of 15 wafers (five samples each from three plutons) were examined. Microthermometric studies were done on representative inclusions using a LINKAM TH 600 heating-freezing stage at the Kochi University, calibrated with a precision of ± 0.1 °C for freezing runs using natural and synthetic standards of CO₂.

4. Petrography and feldspar thermometry

The modal analyses data from point counting when recalculated and plotted in Q-A-P diagram classify all the three plutons as granite. The K-feldspar in all the three plutons shows mesoperthitic texture with coarse exsolution lamellae of Na-feldspar within host K-feldspar. We analysed representative mesoperthites from the VT and PT plutons using an electron microprobe. The re-integrated chemical composition of the mesoperthites was obtained using the modal ratio of host lamella and their respective chemical compositions following the techniques developed in recent studies [7,28]. The integrated compositions of the mesoperthites in the VT granite lie around 800-900 °C solvus for 5 kbar in An-Ab-Or diagram. Those of the PT granite cluster along the 900-1000 °C ternary feldspar solvus curves. These high temperature estimates compare with identical values of 900-1000 °C from mesoperthites in the host granulite facies rocks in the region [19] indicating the ultrahigh-temperature history for the Late Pan-African thermal event in southern India. The data also compare with temperature estimates from sapphirine and spinel bearing ultrahigh-temperature metamorphic rocks in this region [10].

5. Fluid inclusion studies

Fluid inclusions are commonly present in quartz and subordinately in feldspar in all the three plutons. They are ubiquitous in quartz grains within the granite matrix (Fig. 2) and range in size from less than 5 μ m up to 30 μ m. Majority of the fluid inclusions in all the three plutons occur scattered and azonal, or as isolated groups within various domains in the quartz grain, termed here as group 1. A second (group 2) occurs as arrays that pinch out within the grains. Subsequent late-generation inclusions (group 3) that transect grain boundaries and aligned along healed cracks are present in VT granite.

The most common phase category among all the three groups is represented by monophase inclusions that show a single fluid phase at room temperature, and are notably abundant in the studied rocks, in contrast to normal granites which often lack CO₂ inclusions. Results of microthermometric measurements of all the categories of inclusions from the three granite plutons are summarized in Table 1, along with computations of molar volumes and density values in terms of CO2 densities. Histograms compiling homogenization temperatures are shown in Fig. 3. The melting temperature data indicate that majority of the monophase inclusions in all the three plutons contains pure CO₂ fluid. Only those from the PT pluton show slight depression in melting temperatures. Laser Raman microscope (LRM) analyses of representative inclusions from the granite plutons showed distinct Raman shift at 1283 and 1388 cm⁻¹ peak positions corresponding to CO2. No peaks for CH4 or N₂ were detected in the primary carbonic inclusions. However, those inclusions with the highest melting point depression from the PT pluton showed a minor Raman shift at 2331 cm⁻¹, indicating traces of N₂. An approximate estimation of the concentration of additional volatile phase that causes melting point depression in carbonic inclusions can be made by combining the melting and homogenization data and employing the thermodynamic data for CO_2-N_2 mixtures [22]. From the minor peak for N2 in laser Raman data, we estimate a maximum of less than 5 mol% N₂ from the curve intersection method using combined melting and homogenization data for the corresponding inclusions showing maximum melting point depression. It is therefore evident that the dominant fluids in the granitic plutons of present study are pure CO_2 .

The lowest homogenization temperatures $(2.0 \,^{\circ}\text{C})$ were yielded by group-1 inclusions in the VT pluton. The highest homogenization temperature $(29.9 \,^{\circ}\text{C})$ is recorded by group-2 inclusions in PT granite. The peak homogenization temperatures for group-1 inclu-



Fig. 2. Photomicrographs of carbonic fluid inclusions in quartz from the Vattamalai (VT), Gangaikondan (GK) and Pathanapuram (P-T) granites. **A**, **C** and **E** show primary monophase CO₂ inclusions. **B**, **D** and **F** show the distribution pattern of pseudosecondary/secondary inclusions as trails.

Fig. 2. Microphotographies d'inclusions fluides carboniques dans le quartz des granites de Vattamalai (VT), Gangaikondan (GK) et Pathanapuram (PT). A, C et E : inclusions à CO_2 primaire, monophasées. B, D et F : distribution des inclusions secondaires/pseudosecondaires le long de microfissures recristallisées.

sions in GK (16.0 °C) and PT (17 °C) are similar, but for those in the VT pluton, the temperatures are distinctly lower (2.5 °C). The homogenization temperature of group-1 inclusions in GK and PT are similar to the late inclusions (group 3) in VT (peak at 17 °C). Clearly, the VT pluton preserves the highest density CO₂ fluids among all the three locations with a density up to 0.912 g cm⁻³ and molar volume of 48.25 cm³ mol⁻¹. Also, the homogenization data show that there is systematic decrease in the density values from group-1 through group-2 inclusions in all the plutons. In VT, a late category of group-3 inclusions is also identified, showing the lowest density among the three groups of inclusions. Thus, although the absolute densities are different in the different plutons, in general, the primary inclusions in all cases preserve the highest density fluid.

Knowledge on the composition and density of a fluid constrain it to lie along an isochore in the P-T space. In the present study, the density data from CO₂ inclusions have been employed in constructing representative isochores. Representative isochores of fluid

	Inclusion	Host	Melting	r temperati	Ire	Homoge	enization	temperature	Molar Volume	Density	Type of inclusion
	group	mineral	Min.	Max.	Peak	Min.	Max.	Peak	$(\text{cm}^3 \text{ mol}^{-1})$	$(g cm^{-3})$	
	group 1	quartz	-57.2	-56.6	-56.9	2.0	5.0	2.5	48.25-50.22	0.912-0.876	primary
	group 2	quartz	-57.8	-56.6	-56.9	6.2	12.4	10.0	50.26-52.88	0.876 - 0.832	pseudosecondary
	group 3	quartz	-58.3	-56.6	-56.9	13.6	21.2	17.0	53.42 - 56.90	0.824 - 0.773	secondary
ıdan	group 1	quartz	-57.8	-56.8	-56.9	15.8	18.1	16.0	54.05-55.93	0.814 - 0.787	primary
	group 2	quartz	-57.0	-56.6	-56.6	18.6	23.6	19.5	56.15-60.24	0.784 - 0.731	pseudosecondary
ram	group 1	quartz	-58.7	-56.8	-57.2	12.2	17.9	17.0	52.13-55.37	0.844 - 0.795	primary
	group 2	quartz	-58.3	-56.9	-57.2	18.1	29.9	29.0	55.51-73.59	0.793 - 0.598	pseudosecondary

Fluid inclusion microthermometric data

Table 1



Fig. 3. Histograms showing homogenization temperatures of carbonic inclusions in VT, GK and P-T plutons. The arrows denote the ranges of values used to compute the isochores shown in Fig. 4. Fig. 3. Histogrammes des températures d'homogénéisation des inclusions carboniques dans les plutons VT, GK et PT. Les flèches indiquent les valeurs utilisées pour calculer les isochores indiqués sur la Fig. 4.

inclusions in the three plutons are shown in the P-Tspace in Fig. 4.

6. Discussion

The temperature estimates from feldspar thermometry in the granites (800-1000 °C) are similar to the recent estimations of high and ultrahigh-temperatures (900-1000 °C) for granulite facies metamorphism in the region (e.g., [8,10]). The isochores of fluid inclusions computed from density data can be used in conjunction with the feldspar thermometry data to derive broad position of the P-T box. We show the com-



Fig. 4. Combined P-T diagram showing CO₂ isochores for primary inclusions in the granite plutons and temperature data from feldspar thermometry in mesoperthites. Also shown are phlogopite dehydration melting curves (marked as **a** and **b**, after Johannes and Holtz, 1966, see [2]) and liquidus for water undersaturated granitic systems with 1, 2 and 3% H₂O (curves **c**, **d** and **e**, respectively, from Johannes and Holtz, 1966, see [2]). P-T box for granulitic lower crust is also shown. See text for discussion.

Fig. 4. Diagramme P-T synthétique, indiquant les isochores d'inclusions primaires dans les plutons granitiques et les températures déduites par thermométrie sur feldspaths dans les mésoperthites. On a aussi indiqué les courbes de fusion par déshydratation du phlogopite (**a** et **b**, d'après Johannes et Holtz, 1966, voir [2]), ainsi que les liquidus pour les systèmes granitiques sous-saturés en eau à 1, 2 et 3 % H₂O (courbes **c**, **d** et **e**, respectivement, d'après Johannes et Holtz, 1966, voir [2]). Les conditions P-T de la croûte inférieure granulitique sont également indiquées. Voir le texte pour la discussion.

bined plots in Fig. 4. Assuming that the granites were generated from granulitic lower crust (see below) at ca. 800–900 °C and 10 kbar, the possible model for dehydration melting in this domain is given by phlogopite dehydration curves of Johannes and Holz, 1996 (quoted in Barbie and Libourel [2]) and can be bracketed by the following reactions:

At low T:

$$Qtz + Phl + Ab \rightarrow Liq (melt) + Enst + Aksp$$
 (a)

At high *T*:

 $Qtz + Phl \rightarrow Liq + Enst + Ksp$ (b)

The granulite P-T box shown in Fig. 4 is clearly bound by the above two reactions. The second reaction (reaction (b) also passes through the P-T window for the VT granite. We also compare in Fig. 4, the position of the P-T boxes with respect to the liquidus for water-undersaturated granitic system from the work of Johannes and Holz (1966, quoted in Barbie and Libourel [2]). Curves c, d and e in Fig. 4 represent 1, 2 and 3% H₂O in the melt, respectively. Curve **c** penetrates the P-T box for GK and PT granites, while curve **e** passes through the P-T box for VT granite. These results are in good agreement with the P-T conditions of crystallization of the granite plutons. The consumption of the dissolved aqueous phase for the formation of biotite upon crystallization of the melt would explain the lack of common occurrence of aqueous inclusions. The relatively higher water content in the magma indicated for VT granite also accounts for the higher modal abundance of biotite in this granite. The host granulite facies rocks record a steep isothermal decompression event after the high to ultrahigh temperature metamorphism, correlated to a distentional tectonic regime (e.g., [8]). The emplacement of the felsic plutons are also perceived to have occurred during extensional collapse following suturing of the East and West Gondwana megacontinents [17], with a clockwise exhumation path (not shown in the figure). Thus, the P-T paths of the granitic plutons are characterized by decompression at high temperatures (adiabatic intrusion) during the magmatic stage, followed immediately by sub-isobaric cooling upon crystallization, and finally decompression during erosion and unroofing. The preservation of high density negative-crystal shaped inclusions indicates that the P-T path closely followed the slope of the isochore.

Carbonic fluid inclusions are known to occur in a wide variety of rock types formed under variable pressure-temperature conditions and under different tectonic settings. CO₂-rich fluid inclusions have also been reported from mantle xenoliths [1]. CO₂ forms the dominant fluid species in high-grade metamorphic rocks [24], including deep crustal and ultrahigh temperature granulites [18,26]. Touret [23] proposed a model of fluid stratification in the earth's crust with the upper regions dominated by H₂O and brine solutions incorporating variable amounts of CH_4 and/or N_2 . The deeper domains, on the other hand, are rich in CO_2 – H_2O fluids that merge into a dominantly CO_2 -rich lower crust. The observation of common occurrence of CO_2 -rich fluids in rocks derived from the deep crust and upper mantle, some of which show extremely high density [18] has validated this proposal.

The spectacular abundance of CO2-rich fluid inclusions in the three granite plutons of the present study closely correlate with the fluid inclusion characteristics of the host granulite facies rocks in the terrain [12– 14,25], but is distinct from normal mid-crustal granites which do not contain CO2 in abundance. Following the techniques outlined by Touret and Hansteen [25], we estimate up to 1 wt% CO₂ in our samples, which suggests that these magmas were substantially enriched in CO₂. Recent studies show that partial melting reactions which generate granite magmas under upper amphibolite to granulite facies conditions were water deficient [4]. Since the granulite facies protoliths were already water deficient, it is unlikely that the CO₂charged granites reported in this study were generated through vapor-absent processes. Preliminary carbon isotope data from fluid inclusions in the Pan-African felsic magmatic rocks from this region show a range of δ^{13} C values from -7.3 to -13.6% [15]. Identical carbon isotope composition (-7.5 to -12.3%) has been recorded for CO2 extracted from fluid inclusions in granulite facies rocks of the region [19]. From stable isotopic studies, Pili et al. [9] reported CO₂-rich fluids of mantle origin tapped by deep-rooted shear zones in Madagascar. The proximity of the granite plutons of present study to deep-seated shear zones and their link with CO₂-rich granulite facies rocks suggest that the carbonic fluids may have ultimately originated from sub-lithospheric mantle sources.

Available geochronological data indicate that the latest granulite facies metamorphism and felsic magmatism in this region are broadly coeval, related to the Late Pan-African tectonothermal event associated with the collision and subsequent extensional collapse accompanying the birth of the Gondwana supercontinent within which southern India was an integral part [20]. Southern India and Madagascar preserve crucial evidence for CO_2 infiltration from mantle sources during supercontinent assembly.

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