

Fluids in granulites

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ABSTRACT

Since the discovery of CO₂ fluid inclusions in granulites, the role of fluids in the formation of these rocks has been widely studied. Owing to the complexity of the tectono-metamorphic history of granulite terrains, fluid inclusion data alone are not sufficient. They need to be integrated with geochemical and mineralogical studies done on the same rock samples. A clear understanding of the tectono-metamorphic history of granulite terranes is also indispensable. The widespread occurrence of CO₂ and the later discovered high-salinity aqueous fluid inclusions support the idea that the lower crust underwent fluid flow and that both carbonic and brine fluids played a role in its formation. Both low-H₂O-activity fluids play a similar role in destabilizing hydrous mineral phases. Furthermore, experimental studies have shown that brine fluids have a much larger geochemical effect on granulites than initially expected. These fluids are far more mobile in the lower crust compared with CO₂ and also have the capability for dissolving numerous minerals. As in the example of the Limpopo Complex, fluid inclusions and many metasomatic features observed in granulite terranes can thus be explained only by large-scale movement of high-salinity aqueous fluids and, to a lesser extent, CO₂, implying that lower-crustal granulites are not as dry as previously assumed. Similar brines and CO₂-rich fluids are also found in mantle material, most likely derived from deeply subducted supracrustal protoliths.

INTRODUCTION

The role of fluids in the formation of granulites has been a matter of discussion for many years. On the one hand, some investigators argue for a dry lower crust. This interpretation is largely based on experimental petrological work and the physical properties of the lower crust (e.g., Thompson, 1983; Clemens and Vielzeuf, 1987; Stevens and Clemens, 1993; Yardley and Valley, 1997). In this view, granulite metamorphism is

the result of vapor or fluid absent from the melting processes. Others, on the other hand, favor granulite metamorphism in which low-H₂O-activity fluids do play an essential role (e.g., Touret, 1981, 1986; Newton et al., 1998; Harlov and Wirth, 2000; Perchuk et al., 2000a). The purpose of this chapter is to give an overview of the constraints on this debate about the role of fluids in granulite metamorphism that can be offered by fluid inclusion research, with special reference to the Limpopo high-grade terrane.

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Fluid Inclusion Studies: Some General Considerations

Fluid inclusions, which occur in most rock-forming minerals as minute cavities containing liquid and/or vapor or solid phases, can provide valuable information on all steps of the rock's evolution. These inclusions were among the first objects discovered under a polarizing microscope (Sorby, 1858), but for a number of reasons, both instrumental and theoretical, they remained (and, to some extent, still remain) largely ignored in most petrological studies. The situation, however, changed markedly in the 1970s, when a generation of new instruments (heating-freezing microscopic stages, later completed by Raman and infrared micro-spectroscopy) was introduced. In addition, a better understanding of low-temperature fluid-phase behavior, in particular for carbonic fluids (e.g., Van den Kerkhof, 1990; Thiéry et al., 1994) and fluid-rock interaction for a wide range of pressure-temperature (P-T) conditions improved the interpretation of fluid inclusion data significantly. These developments allowed the integration of fluid inclusion data into a general scheme of petrological and geochemical studies.

Fluid inclusion studies are considered by many researchers as being highly specialized and needing to be done by experts. Fluid inclusion studies require adequate sampling and a time-consuming detailed study of individual samples. As a result, fluid inclusion studies are not always done, although they may add essential data. In many cases the fluid inclusion study is done independently by a specialist who is not involved with other aspects of the study, which may result in interpretation problems. This situation is obviously not satisfactory; inclusions are part of the rock, and, as such, they should be studied as systematically and in detail as in any other aspect. Moreover, as has been advocated in a number of publications (e.g., Touret, 2001, and references therein), fluid inclusion data can only be interpreted appropriately in combination with other geological data obtained from the same samples. In other words, the best chance of success requires that mineralogical, geochemical, and fluid inclusion studies are done by the same person or by a team of researchers working closely together.

Fluid inclusion studies have demonstrated the almost systematic occurrence of unexpected (i.e., not inferred from the mineral assemblage) fluids in the lower crustal or mantle rocks: CO₂ in granulites (Touret, 1971) and charnockites (Santosh, 1986), N₂ in eclogites (Andersen et al., 1989), brines in diamonds (Israeli et al., 2001, 2004), etc. These findings have raised a marked interest within the geological community as well as some doubts for numerous researchers on the issue of whether these inclusions are really representative remnants of fluids trapped at depth. These reservations include the fact that at deep crustal levels, open spaces will collapse, preventing the existence of a free fluid phase, or that they can only exist in small, chemically inert, isolated pockets (e.g., Yardley and Valley, 1997). Another objection against the reliability of fluid inclusions representing equilibrium fluids trapped at high pressure and temperature is that they cannot survive uplift to the

Earth's surface without any modification of their composition or density.

It is true that fluid inclusions in minerals are not simple, perfectly closed containers that give a direct indication of which fluids percolate through the rock system at the time of their formation. Factors complicating the interpretation of fluid inclusion data may include selective fluid trapping, selective water leakage (Bakker and Jansen, 1990), an increase of the fluid salinity from quartz recovery (Van den Kerkhof et al., 2004), fluid reactions with the mineral host or, above all, "transposition," i.e., the formation of successive fluid-inclusion generations at changing pressure and temperature conditions (e.g., Hollister and Crawford, 1981; Roedder, 1984; Shepherd et al., 1985; Andersen et al., 2001).

Fluid inclusions can be, as a first approximation, considered constant volume and constant composition (i.e., constant molar volume or density) systems. This principle requires the following assumptions: (1) The volume of the cavity does not change after the fluid inclusion has been formed, (2) the fluid inclusion does not leak, and (3) the chemical composition of the fluid in the inclusion does not change. Constant density fluids show an approximately linear relationship between pressure and temperature: the isochore (Fig. 1). The isochore principle has some important implications for the interpretation of fluid inclusion data. First, fluid inclusions of a particular molar volume can be trapped at different pressure and temperature conditions along the corresponding isochore; i.e., high-density fluid inclusions do not necessarily indicate a high pressure and temperature of trapping (e.g., Morrison and Valley, 1988). Second, high-density fluid inclusions that are trapped at high pressure and temperature can be preserved during exhumation if the retrograde P-T path of the rock is approximately parallel to that of the isochore. Third, the distribution of fluid inclusion densities can be an important

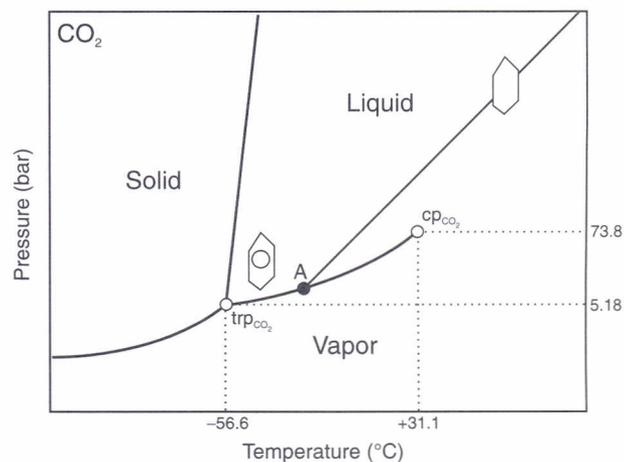


Figure 1. Low-temperature–pressure part of the CO₂ phase diagram. The isochore represents the univariant part of the homogeneous fluid inclusion; A—pressure and temperature of homogenization into the liquid phase; cp_{CO_2} —critical point of CO₂; trp_{CO_2} —triple point of CO₂.

tool in reconstructing the retrograde P-T path of a rock (Fig. 2) (e.g., Vityk and Bodnar, 1995).

FLUID INCLUSION STUDIES IN HIGH-GRADE METAMORPHIC ROCKS

Fluid inclusion studies in high-grade metamorphic rocks are more complicated than those in low-grade rocks. During high-grade metamorphism, rocks are typically subjected to prograde grain-size scale deformation and net-transfer reactions, making the preservation of fluid inclusions highly unlikely. During retrograde metamorphism, high-temperature grain-size-scale deformation may still occur, depending on the exhumation mechanism. Furthermore, retrograde hydration reactions may also occur, depending on the presence of aqueous fluids. In addition, the structural-metamorphic history of high-grade metamorphic rocks is generally complex. The rocks may have undergone more than one deformation event (possibly associated with infiltration of fluids) either in the deep crust under highly ductile conditions or during exhumation under brittle-ductile or brittle conditions. During exhumation, the rocks may also have been subjected to other geological processes such as, for example, contact metamorphic events related to magma emplacement and meteoric fluid infiltration (Huizenga et al., this volume). The identification of different fluid inclusion generations, and their association with specific tectono-metamorphic events, is, therefore, the most important and also the most difficult aspect of any fluid inclusion study in high-grade metamorphic rocks. We will use some examples from

the Limpopo high-grade metamorphic terrane to illustrate the above mentioned issues.

Fluids in the Limpopo High-Grade Terrane

The Limpopo high-grade terrane is subdivided into three subzones (Fig. 3, inset): the Southern Marginal Zone (SMZ), the Central Zone (CZ), and the Northern Marginal Zone (NMZ) (e.g., van Reenen et al., 1990). The Southern and Northern Marginal Zones are the high-grade metamorphic equivalents of the greenstone-gneiss terranes of the adjacent Kaapvaal and Zimbabwe Cratons, respectively, whereas the Central Zone comprises metasedimentary (e.g., marble, calc-silicate gneisses, garnet-biotite gneisses, banded iron formation) and meta-igneous rocks (e.g., van Reenen et al., 1990). Numerous fluid inclusion studies were carried out in the Southern and Central Zones, of which the results are summarized in Table 1.

Southern Marginal Zone

The Southern Marginal Zone (SMZ) (Fig. 3) is characterized by a northern high-grade granulite (800–900 °C) and a southern lower grade, hydrated granulite zone (~600 °C), and separated from each other by a retrograde orthoamphibole isograd (van Reenen, 1986). The SMZ is separated from the Kaapvaal Craton by the Hout River Shear Zone, which developed during the exhumation of the granulite terrane (Fig. 3). In the SMZ smaller thrust and strike-slip shear zones are present that are also associated with the exhumation of the granulites (Fig. 3) (Smit and van Reenen, 1997). The granulites of the SMZ (Fig. 3) are typically

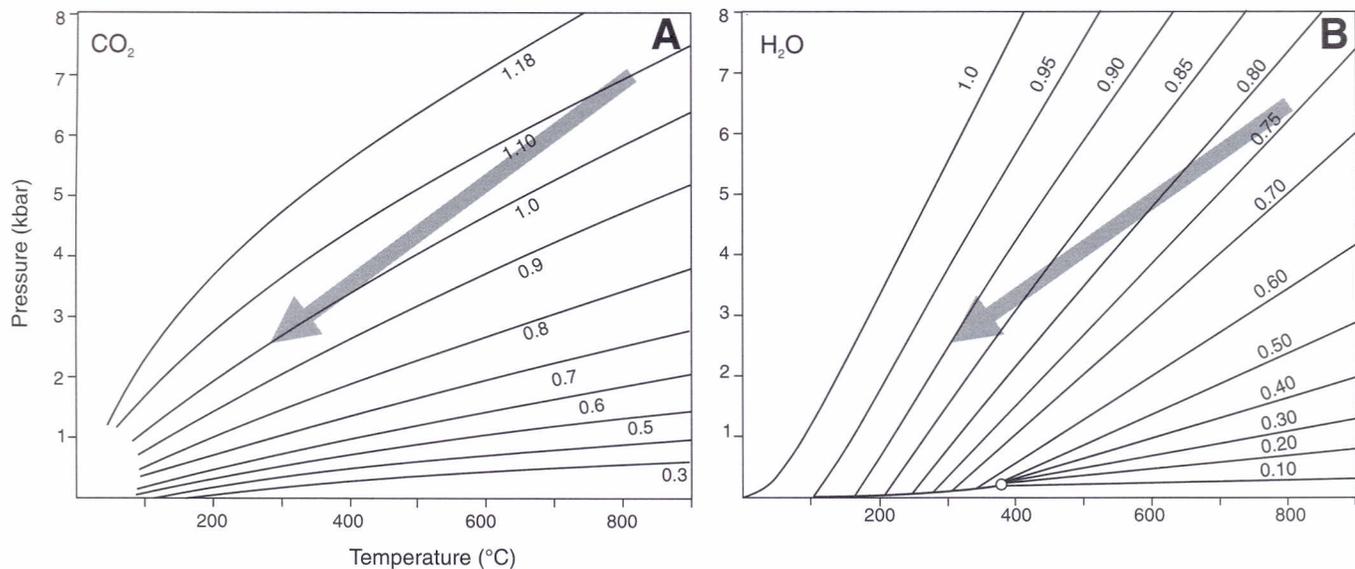


Figure 2. Cooling-decompression retrograde pressure-temperature (P-T) path superimposed on CO₂ (A) and H₂O isochores (B). During cooling and decompression, the CO₂ fluid trapped in the inclusion will become overpressured, whereas H₂O will become underpressured, which may lead to a volume change in the inclusion and thus a readjustment of the fluid inclusion density. Note that for the same decompression-cooling path (gray arrow), the density change for the H₂O (20% increase) is larger and opposite from that for CO₂ (9% decrease). In extreme cases, over- and underpressure may result in explosion and implosion of the inclusion, respectively.

characterized by high-grade granite-greenstone lithologies. Peak metamorphic conditions were followed by, depending on the structural setting, either decompressional cooling or a combination of early decompressional cooling, followed by near-isobaric cooling (Perchuk et al., 2000b).

Cooling and decompression took place during uplift and thrusting of the granulites along shear zones onto the relatively cold Kaapvaal Craton. This resulted in simultaneous cooling and heating of the hanging wall (granulites) and footwall (granite-greenstone terrane of the Kaapvaal Craton), respectively. The SMZ was affected by only one event of high-grade metamorphism, which makes it different from the Central Zone (CZ) of the Limpopo high-grade terrane that has been affected by (at least) two high-grade tectono-metamorphic events.

Evidence for peak-metamorphic fluids in the Southern Marginal Zone. Fluid inclusions and reaction textures. Fluid inclusion studies have provided evidence for the presence of

brines and carbonic CO₂-rich fluids, existing under conditions of immiscibility at the peak of granulite facies metamorphism (Table 1). Figure 4A shows pseudo-secondary fluid inclusions in orthopyroxene that constitute numerous unidentified solid phases, together with a pure low-dense CO₂ fluid phase. Similar fluid inclusions were also found in matrix quartz (Fig. 4B). These inclusions clearly indicate the coexistence of a highly saline fluid with almost pure CO₂ (<5 mol% CH₄) at the peak of metamorphism. There is no petrographic evidence for fluid-fluid immiscibility, but considering the high salinity of the brines, this is almost unavoidable (Johnson, 1991).

Other evidence of the presence of high-salinity aqueous fluids is the common observation of high-temperature reaction textures in granulites in the SMZ (Fig. 5). Both perthitic and antiperthitic feldspars occur at the contact of the matrix quartz with garnet and as rims around quartz inclusions within garnet porphyroblasts. Similar K-feldspar reaction textures have been

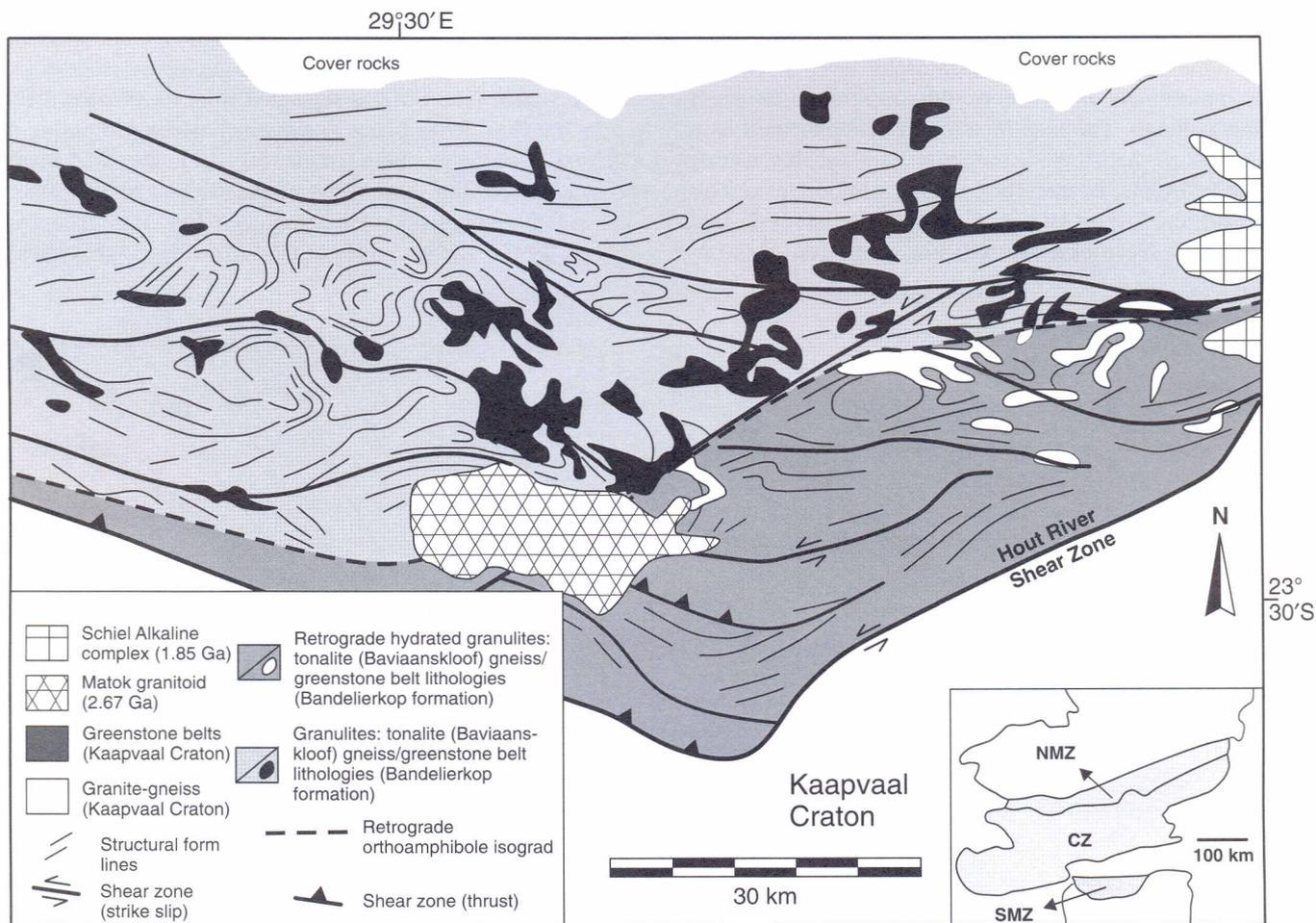


Figure 3. Geological map of the Southern Marginal Zone (SMZ) of the Limpopo Complex (modified from Smit and van Reenen, 1997), showing the granulite and retrograde hydrated granulite terranes, separated from each other by the retrograde orthoamphibole isograd. CZ—Central Zone; NMZ—Northern Marginal Zone.

TABLE 1. SUMMARY OF FLUID INCLUSIONS IN THE LIMPOPO HIGH-GRADE TERRANE

Rock type	Host mineral	Event with which fluid is associated	Fluid composition	Reference
<u>Southern Marginal Zone</u>				
Metapelites	Matrix quartz in unhydrated and hydrated granulites	Fluids are related to peak metamorphic conditions, high-temperature hydration of granulites, and retrograde metamorphism	Fluid inclusions found in unhydrated and hydrated granulites are the same and comprise a medium-density CO ₂ -rich fluid and aqueous fluids with variable salinities	van Reenen and Hollister (1988)
Quartz veins associated with high-temperature shear-zone hosted gold mineralization	Vein quartz	Fluids are related to high-temperature gold mineralization and retrograde metamorphism	Fluid inclusions include a medium CO ₂ -rich fluid, an aqueous fluid with variable salinities, and a low-density CH ₄ fluid	van Reenen et al. (1994)
Metapelites	Matrix quartz and garnet	Fluids are related to peak and retrograde metamorphism	Peak metamorphic fluids include brines and CO ₂ . Retrograde fluids comprise medium- and low-density CO ₂ and low-salinity aqueous fluids	Van den Berg and Huizenga (2001)
<u>Central Zone</u>				
Metapelites	Quartz associated with retrograde gedrite formation	Retrograde gedrite formation	Low-salinity aqueous fluid	Hisada et al. (1994)
Aluminous rocks	Matrix quartz	Retrograde metamorphism related to the 2.0 Ga event	Low-salinity aqueous fluid	Hisada and Miyano (1996)
Metapelite, granite, and migmatite	Matrix quartz, garnet, and andalusite	Fluids are related to retrograde metamorphism	Fluid inclusions contain a medium-density CO ₂ -rich fluid, an aqueous fluid with variable salinities, and a low-density CO ₂ fluid	Hisada et al. (2005)
Metapelites	Garnet, matrix quartz, and matrix plagioclase	Fluids are related to peak and retrograde metamorphism	Fluid inclusions contain medium- and low-density CO ₂ -rich fluids.	Tsunogae and van Reenen (2007)
Metapelites	Quartz in garnet and matrix quartz	Most fluids are related to peak and retrograde metamorphism of the 2.6 Ga event	Peak metamorphic fluids include brines and medium-density CO ₂ . Retrograde fluids include low-density CH ₄ and low-salinity aqueous fluids	Huizenga et al. (this volume)

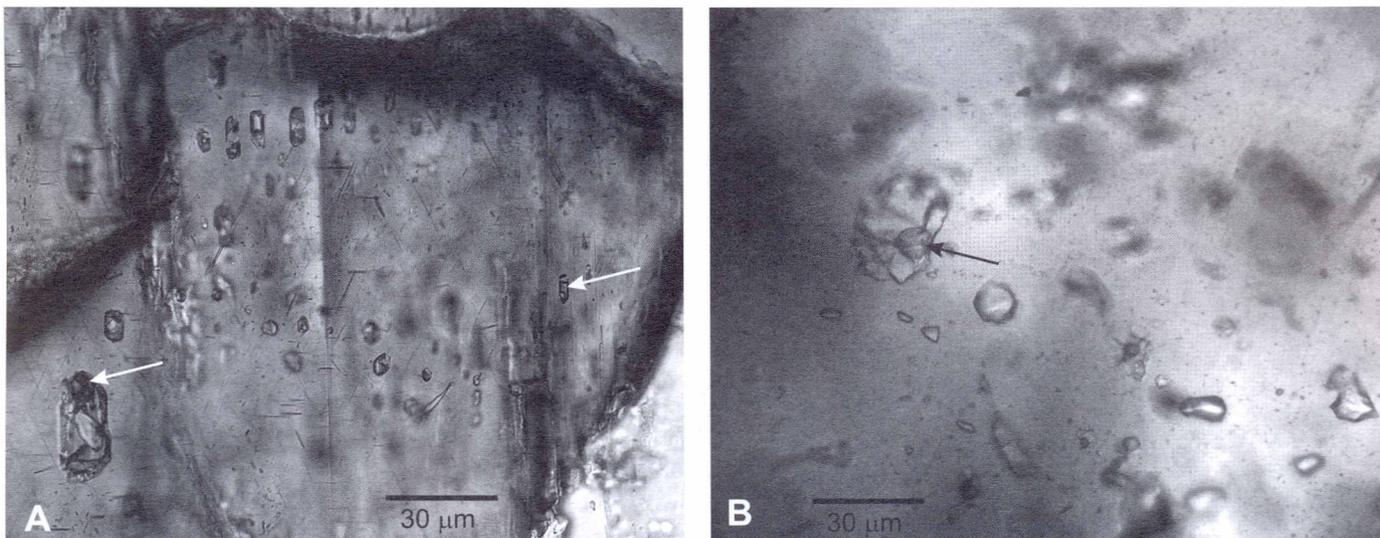


Figure 4. (A) Pseudo-secondary fluid inclusion in orthopyroxene (Southern Marginal Zone, SMZ, of the Limpopo Complex). The inclusions are characterized by a large number of unidentified isotropic and non-isotropic solid phases. In between the solid phases a CO₂ fluid phase is present (white arrow). Most likely the aqueous fluid phase has disappeared from the inclusion through reactions with the host mineral or, alternatively, the aqueous fluid phase approached the composition of a molten salt. (B) Isolated inclusion in quartz in a non-recrystallized section of a granulite sample from the SMZ. Relatively large CO₂ inclusions occur in a small area. The inclusion indicated by the arrow contains numerous unidentified isotropic and non-isotropic solid phases with a CO₂ fluid phase.

described in other granulite facies terranes (e.g., Perchuk and Gerya, 1993; Franz and Harlov, 1998; Harlov et al., 1998; Harlov and Wirth, 2000; Harlov and Förster, 2002). The following reaction is suggested for the formation of the feldspar micro-veins (e.g., Huizenga et al., this volume): $\text{garnet} + \text{quartz} + (\text{K}, \text{Na})_{\text{fluid}} = \text{K-feldspar} + \text{albite} + \text{biotite}$. In addition to the above, potassium alteration in sheared tonalitic granulites, exemplified by the

replacement of oligoclase with perthite and mesoperthite, has also been described (Smit and van Reenen, 1997), which occurred at peak metamorphic temperatures of 800–850 °C (Hoernes et al., 1995). Unfortunately, fluid inclusions and metasomatic reaction textures alone cannot be used to determine the fluid/rock ratio in the lower crust of the Limpopo terrane. However, what can be concluded is that CO₂ and high-salinity fluids were definitely present during peak metamorphism.

Considering the fact that a significant part of the granulites of the SMZ represent high-grade equivalents of greenstone belt lithologies, it is likely that a major part of both the CO₂-rich fluids and the brines were internally derived. Prograde devolatilization reactions of typical greenstone belt lithologies produce an H₂O-CO₂ fluid phase (Powell et al., 1991). Such a fluid becomes CO₂ rich as a result of (1) increasing temperature at typical crustal oxygen fugacities with values near the fayalite-magnetite-quartz (FMQ) buffer system (e.g., Ohmoto and Kerrick, 1977), and (2) partitioning of H₂O into the melt phase during partial melting (e.g., Fyfe, 1973).

Fluids during exhumation of the Southern Marginal Zone. Samples from the SMZ show a consistent picture of secondary fluid inclusions in matrix quartz (see Table 1). These include aqueous inclusions with variable salinities (up to ~40 wt% NaCl equivalent), and CO₂-rich (<10 mol% CH₄) fluid inclusions. It is difficult, however, if not impossible, to establish petrographically a relative chronology between these fluid inclusion generations. The only way to explain the fluid inclusion observations is to use the tectono-metamorphic history of the area to predict which fluids can be expected.

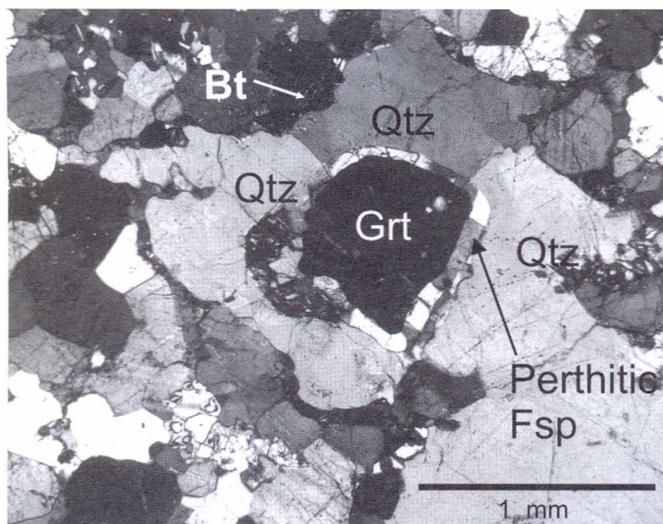


Figure 5. Perthitic K-feldspar micro-veins between quartz and garnet formed as a result of the metasomatic reaction. Bt—biotite; Fsp—feldspar; Grt—garnet; Qtz—quartz.

The mineral assemblages found in the hydrated part of the SMZ were used to calculate H_2O activities in both mafic rocks and metapelites (e.g., Van den Berg and Huizenga, 2001). These calculations show that the retrograde hydration event is related to two compositionally different fluids present at the same time, one with an H_2O activity of 0.1–0.2, and one with an H_2O activity of 0.8–0.9, suggesting that at least two different fluid sources were available during retrograde metamorphism. The low H_2O activity fluid corresponds to the CO_2 -rich fluids and the highly saline fluids. The high H_2O activity fluid, on the other hand, corresponds to the low-salinity aqueous fluids.

The most likely crustal fluid sources include devolatilization reactions in the footwall of the Hout River Shear Zone (i.e., the greenstones of the Kaapvaal Craton), crystallizing granitic melts in the middle crust releasing water-rich fluids (Stevens, 1997), and meteoric water infiltration along shear zones (e.g., Yardley et al., 2000). The emplacement of hot granulites onto the Kaapvaal Craton during exhumation (van Reenen and Hollister, 1988) initiates devolatilization reactions in the underlying greenstone belt lithologies, producing H_2O - CO_2 fluids. These fluids migrate upward along active shear zones into the granulites that are uplifted, and may become progressively enriched in CO_2 as water is removed by retrograde hydration reactions. In addition to this process, water-rich fluids may be introduced into the middle crust either from the surface through shear zones (Yardley et al., 2000) or from crystallizing granitic melts in the middle crust (Stevens, 1997). These fluids may either remain water rich or become more enriched in carbonic fluid species as a result of water-graphite interaction (Stevens, 1997; Huizenga et al., this volume). The exact fluid composition will then depend on the availability of graphite and the prevailing oxygen fugacity. Irrespective of whether a water-rich fluid or an aqueous-carbonic fluid is formed, both fluids will additionally be affected by retrograde hydration reactions. The water-rich fluid will then evolve into a high-salinity aqueous fluid (e.g., Bennett and Barker, 1992; Markl and Bucher, 1998; Markl et al., 1998), whereas the aqueous-carbonic fluid becomes more carbonic. From the above it is clear that different fluid sources and fluid-rock interaction have resulted in compositionally different fluid inclusions. Furthermore, fluid infiltration through shear zones is variable on a small scale (e.g., Pili et al., 1997), which will contribute even further to the complexity of the interpretation of the fluid inclusion results.

Central Zone

The Central Zone (CZ) is situated between the Northern and Southern Marginal Zones of the Limpopo Complex terrane (Fig. 3). The CZ has three distinct structural domains (Smit et al., this volume). The first domain comprises large-scale isoclinal folds and sheath folds, whereas the second domain comprises the major SW-NE-trending Tshipise Straightening Zone (TsSZ), which bounds the first domain in the south. These structures developed before ca. 2.6 Ga (van Reenen et al., 2008). Superimposed onto these early structural features is a system of discrete

high-grade shear zones that reflect evidence for a superimposed tectono-metamorphic event dated at ca. 2.0 Ga (van Reenen et al., 2008). High-grade gneisses associated with ca. 2.6 Ga structures show relatively high pressure during decompression cooling, whereas sheared gneisses that developed within ca. 2.0 Ga shear zones indicate a relatively low pressure during decompression cooling (Boshoff et al., 2006; van Reenen et al., 2008).

The high-pressure P-T path is linked to the low-pressure P-T path by an isobaric (5.5 kbar) heating path that occurred at ca. 2.0 Ga, resulting in the widespread formation of polymetamorphic granulites in the CZ (Boshoff et al., 2006; van Reenen et al., 2008). In addition, certain areas have also been subjected to mid-crustal local contact metamorphism such as the area around the ca. 2.61 Ga Bulai intrusive (e.g., Huizenga et al., this volume). The above shows that the structural-metamorphic complexity of the CZ makes the interpretation of fluid inclusion data far more complicated compared with those of the SMZ.

Fluids in the Central Zone rocks. Numerous fluid inclusion studies have been done on rocks from the CZ (Table 1). Only two of those studies (Hisada et al., 2005; Huizenga et al., this volume) were done on rocks for which their timing in the structural-metamorphic history is known. The other studies were done on rocks that cannot be placed in the structural-metamorphic context, and their results are therefore difficult, if not impossible, to interpret.

The ca. 2.6 Ga metapelitic rocks that were studied by Huizenga et al. (this volume) show similar results compared with those of the SMZ. Peak metamorphic fluids that were found in high-temperature Mg-rich garnet include CO_2 . Brine inclusions in quartz blebs in garnet, and the presence of metasomatic K-feldspar veining around quartz (Fig. 5), which is identical to the ones that occur in the SMZ, indicate the coexistence of this fluid with CO_2 . The studied metapelites were subjected to contact metamorphism during the emplacement of the Bulai granitoid intrusive. This has resulted in a second generation of garnet that has lower Mg concentrations compared with the first garnet generation. This garnet is unfortunately fluid-inclusion free, so one cannot determine in which fluid regime the Bulai emplacement took place.

The retrograde fluid evolution cannot be established with certainty. Although the studied samples do not show any evidence for a ca. 2.0 Ga deformation or metamorphism, it cannot be excluded that existing fluid inclusions were affected by this event or that a fluid phase infiltrated these rocks during the ca. 2.0 Ga event. Therefore, the interpretation of fluid inclusions in matrix quartz becomes almost impossible.

Hisada et al. (2005) studied ca. 2.0 Ga migmatites and metapelites, which are reworked 2.6 Ga granulites. Most of the fluid inclusions in these rocks were observed in quartz, which makes it impossible to put them in a metamorphic context. Metamorphic zoning textures in the rocks, however, are proof that a water-rich fluid was present during migmatization and retrograde metamorphism. CO_2 was also present, but the exact relationship between CO_2 and H_2O could not be established.

THE ROLE OF FLUIDS IN GRANULITES

Regional granulite terranes comprise mainly high-grade metamorphosed supracrustal rocks (such as those in the Limpopo Complex), whereas lower crustal xenoliths in volcanic material include mafic igneous rocks derived from the crust-mantle boundary (Bohlen and Mezger, 1989). This suggests that the continental lower crust is granulitic and interacts with the underlying continental upper mantle. These findings imply a division of the lower continental crust in two entities, an upper (U) lower crust, and a lower (L) lower crust, respectively (Fig. 6A). The possible existence of remnants of a free fluid phase in granulites thus relates to a larger scale issue: the role of fluids in the deepest part of the continental crust. The conventional view, best illustrated by the classical model of Etheridge et al. (1983), is that a free fluid phase, mainly aqueous, occurs only at peak conditions in the upper part of the continental crust (Fig. 6B). In this model,

however, a free H₂O-rich fluid phase does not exist in mid-crustal migmatites, the source of most granite. H₂O can occur in mica and amphibole or, when these minerals are broken down, by partial melting reactions immediately dissolved in the granitic melts. This marks the onset of the “vapor (or fluid)-absent” regime, supposed to extend into the lower crust and underlying mantle (H₂O barrier in Fig. 6A).

Fluid-inclusion studies, combined with petrologic observations, however, require substantial modifications to this model. These fluids must have a low-water activity in order for them to coexist with granitic melts and anhydrous mineral phases: Any H₂O-rich fluid will immediately induce partial melting of the surrounding rock, generating a granitic melt that will dissolve the interstitial fluid (e.g., Stevens and Clemens, 1993).

Pure CO₂ and high-salinity brines meet these conditions, and although it has taken some time for this to be widely accepted, there is little doubt that both were present during

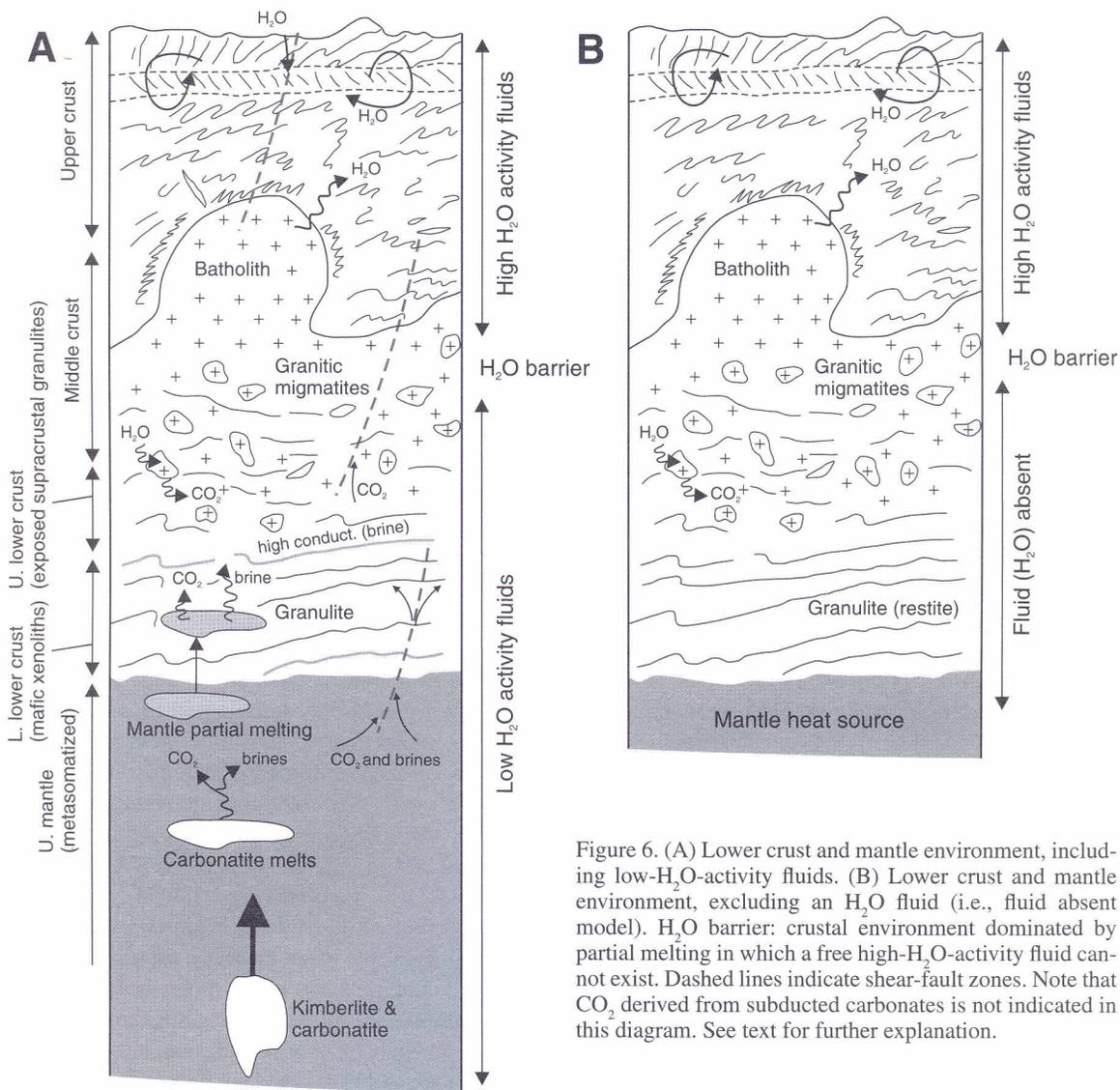


Figure 6. (A) Lower crust and mantle environment, including low-H₂O-activity fluids. (B) Lower crust and mantle environment, excluding an H₂O fluid (i.e., fluid absent model). H₂O barrier: crustal environment dominated by partial melting in which a free high-H₂O-activity fluid cannot exist. Dashed lines indicate shear-fault zones. Note that CO₂ derived from subducted carbonates is not indicated in this diagram. See text for further explanation.

most of the metamorphic evolution, notably at peak conditions. Virtually all regionally exposed granulite terranes that have been studied so far contain pure CO₂ inclusions of variable density, reaching extreme values (>1.1 g/cm³) in the case of the superdense inclusions (e.g., Tsunogae et al., 2002; Santosh and Tsunogae, 2003). It has been argued (Lamb et al., 1987) that these inclusions were late, trapped during the final stage of retrograde evolution. Although this may be true for secondary CO₂-rich fluid inclusions in quartz, this cannot be the case for primary CO₂-rich fluid inclusions in peak metamorphic minerals, of which the pressure-temperature data obtained from fluid inclusions show a perfect match with those obtained from mineral geothermobarometry (e.g., Touret and Hartel, 1990; Santosh et al., 2008). In these cases the existence of peak metamorphic CO₂ fluids at high and ultrahigh temperatures cannot be questioned.

Brine inclusions occur in much smaller quantities and are much smaller and therefore more difficult to detect. Some contain only a small amount of aqueous liquid at room temperature, in many cases without a vapor bubble. Very often the cavity is squeezed around a number of solid minerals, commonly carbonates and/or salts (Touret and Huizenga, 1999; Van den Berg and Huizenga, 2001). In some cases high-salinity fluid inclusions may be metastable. In these initially halite-free inclusions a halite crystal will only grow upon heating during microthermometric heating experiments (e.g., see figs. 2b and 2c in Huizenga et al., 2005).

There is, however, compelling evidence that, unlike CO₂, brine remnants found in inclusions represent a major fraction of the fluids, which existed at peak or close to peak conditions. As in Limpopo, the widespread occurrence of microtextures like myrmekites or K-feldspar veining indicates extensive metasomatic phenomena, which can only have been caused by a brinelike fluid having circulated at intergranular boundaries. Summarizing, we consider that the existence of both granulite fluids is proven. They are either directly observed as remnants still present in protected areas (e.g., CO₂ primary inclusions in the core of garnet) or, for the brines indirectly, by the traces that they have left in the rock mineral assemblage.

It must be mentioned that there is a notable difference among the relative abundance of both (CO₂ and brine) inclusion types, depending on granulite P-T conditions. Well preserved large (30–50 μm in size) CO₂ inclusions dominate in high- to ultrahigh temperature granulites, typically emplaced at 900 to >1000 °C and at a depth <30 km (5–8 kbar). The P-T data obtained from these inclusions show a good match with mineral data. They occur in quartz and in other minerals, notably pyroxene, feldspar, and cordierite. They can be abundant, representing up to 5 vol% of the mineral host, provided that no recrystallization has occurred. In high-pressure granulites, on the other hand, brine remnants are more abundant and, moreover, they predate CO₂ inclusions, which occur only during the final stage of the P-T path, corresponding to a significant temperature increase, i.e., granulitized eclogites. Generally speaking, it

can be concluded that CO₂ inclusions occur mainly in domains that have undergone partial melting (e.g., Touret and Dietvorst, 1983; Olsen, 1987; Whitney, 1992), whereas brine inclusions are much more widespread and more transposed.

Fluid Quantity

Fluid inclusions alone are unable to give information about the absolute fluid amount present at the time of their formation. For CO₂, one can obtain a lower constraint on the amount of fluid that was present from the fluid preserved in the inclusions, which in a few cases is surprisingly high. In some high-temperature granulites (e.g., Indian charnockites and/or enderbites) the presence of primary inclusions in garnet cores amounts to a few weight percentages, high enough to suggest that the fluid amount at peak conditions was quite large. Evidence provided by isotope signatures of carbon (Hoefs and Touret, 1975) and helium (e.g., Dunai and Touret, 1993) shows that CO₂ has mainly a mantle origin, brought into the lower crust by magmatic melts, mainly gabbroic or intermediate in composition, which are also responsible for the high temperature of granulite metamorphism (e.g., Touret and Huizenga, 1999). Therefore, it is not surprising that large amounts of CO₂ fluid inclusions are always found in intrusive rocks, which escaped postmagmatic recrystallization. In the case of the Southern Marginal Zone of the Limpopo Complex there is certainly a clear indication that internally derived fluids were present as well.

The case of brines is far more complicated. For example, Bennett and Barker (1992), Markl and Bucher (1998), and Markl et al. (1998) showed that brines could be formed from a water-rich fluid, which becomes enriched in salts through progressive retrograde hydration reactions. Van den Kerkhof et al. (2004) also demonstrated that high-salinity fluids may be formed during quartz recovery in granulites. Furthermore, it is also true that many brine inclusions appear to be re-equilibrated during post-metamorphic evolution. However, in some cases, brine inclusions are directly linked to their protolith (e.g., former evaporites) so that they must be remnants of the pre-metamorphic sedimentary fluids (e.g., Touret and Dietvorst, 1983). Then, when they followed a metamorphic P-T path parallel to the fluid isochore, minute salinity differences could be preserved, even in rocks that went through extreme metamorphic conditions. The best example to illustrate the preservation of sedimentary fluids through the metamorphic cycle include high- to ultrahigh-pressure rocks of the Dabie Shan in China, where the stable isotope oxygen signature points to pre-metamorphic interaction with fresh (meteoric) waters and also seawater (Fu et al., 2002).

Overall, the fluids preserved in inclusions are quite small, and their interpretation is not straightforward. The extent of mineral reactions at intergranular boundaries suggests that the amount that was present cannot be neglected. The saline aqueous fluids circulate easily along grain boundaries (Watson and Brenan, 1987) and induce mineralogical changes, which remain

quite apparent when the deep rocks have been exhumed to the Earth's surface. Feldspar micro-veining is an example of these metasomatic mineralogical changes, which have been described in detail for many regions such as the Ivrea Zone (Harlov and Wirth, 2000), in Sri Lanka (Perchuk et al., 2000a), and the Limpopo Complex (Van den Berg and Huizenga, 2001), but it is our experience that they occur virtually in any granulite terrane. Moreover, a number of other features point to large-scale activity of saline aqueous fluids during peak and early retrograde granulite conditions. These include incipient charnockites (i.e., fluid-assisted dehydration zones) (e.g., Perchuk and Gerya, 1993), regional oxidation of granulite terranes (Harlov et al., 1997), and carbonated megashear zones (e.g., Newton, 1989; Newton and Manning, 2002). All these features, surprisingly underestimated in most recent metamorphic petrology textbooks, have been discussed in detail elsewhere in the literature (e.g., Newton et al., 1998).

Another important observation that suggests the possible existence of abundant lower crustal brines is obtained from seismic reflectivity and/or electrical conductivity. The presence of horizontal reflectors and large, regional-size conductive layers in tectonically active areas and extensional basins (Wannamaker et al., 1997, 2004) are interpreted to have been caused by the presence of large volumes of saline fluids.

Summarizing, besides CO₂, large amounts of saline fluids did exist at peak granulite conditions. Except for a few remnants preserved in inclusions, they were expelled from the rock system during post-metamorphic uplift, leaving only the traces that indicate that large fluid quantities must have percolated through these "dry" rocks. A large amount of fluid may have remained in the lower crust for a long period of time. This is supported by the abundance of CO₂ inclusions found in late shear zones and, above all, the existence of high-conductivity layers in Paleozoic granulite terranes after thermal re-equilibration (e.g., Touret and Marquis, 1994).

Now that we have showed the evidence for the systematic occurrence of two granulite fluid types, namely dense, pure CO₂ and high-salinity aqueous brines, it must be emphasized that their respective roles were very different owing to their contrasting possibilities for dissolving minerals or elements at high pressure and temperature. CO₂ has a low solubility for most mineral phases and elements and acts almost as an inert component, only reducing the H₂O activity to stabilize anhydrous mineral assemblages. Mineral (e.g., calcite, anhydrite, corundum, quartz) and element solubilities (including Al), on the other hand, are high in brines at granulite facies P-T conditions. This fluid is thus able to induce large-scale metasomatic effects, for which the ones described in the literature so far are probably only the tip of the iceberg. A notable amount of experimental data has been produced by Newton and Manning (2002, 2005, 2006, 2008), and Tropper and Manning (2007) at the University of California. We can foresee that these results will change significantly our perception of lower crustal processes in the near future.

Lower Crust–Mantle Connection

Fluid inclusions identical to those found in granulites have also been found in upper mantle rocks that occur as xenoliths in basalts. Pure CO₂ inclusions were first discovered by E. Roedder (1965) in mantle xenoliths from Hawaii basalts. His findings were later confirmed when similar inclusions were found in xenoliths within many other alkali basalts. The density of these inclusions corresponds to a depth of formation of ~30 km. However, this result does not relate to the formation conditions but rather reflects the maximum internal pressure (~10 kb) that an inclusion can resist while embedded in hot lava during eruption. This implies, as discussed in detail elsewhere (Touret, 2010; Touret et al., 2010), that the level at which free CO₂ occurs may be much deeper, most likely at a pressure of ~20 kbar at which the mineral phases have equilibrated. In fact, the only fluid inclusions formed at mantle conditions that can survive uplift are those that occur in diamonds. Minute fluid inclusions are abundant in some (cloudy) diamonds, but their small size and physical properties make their study difficult. Nevertheless, O. Navon and co-workers at the Hebrew University of Jerusalem found an impressive list of high-density fluids that show a continuous compositional range between carbonatitic and saline end members (e.g., Izraeli et al., 2001, 2004). Furthermore, alkali chlorides have been found in kimberlites, either as mineral phases or in melt inclusions (Kamenetsky et al., 2004, 2009; Maas et al., 2005). A close relationship also exists between brines and carbonatites, which is indicated by the common occurrence of immiscible brines in primary carbonatite minerals such as apatite (e.g., Morogan and Lindblom, 1995). Although carbonatites and kimberlites are relatively rare at the Earth's surface, the widespread evidence of mantle metasomatism, assumed by most workers to be caused by carbonatite melts (e.g., Coltorti and Grégoire, 2008), indicates that they are probably common in the mantle. In support of this, experiments have shown that carbonatitic melts do have a great potential to metasomatize the mantle owing to their high mobility (Hammouda and Laporte, 2000). The breakdown of carbonate mineral phases, liberating the CO₂ found in inclusions, depends on the pressure, temperature, and oxygen fugacity and may thus vary locally within the mantle (e.g., Dalton and Wood, 1995).

CONCLUSIONS

We believe that these mantle fluids, CO₂ and brines, are the major source of granulite fluids. As we have mentioned previously, the situation is more complicated for brines, for which not only the density but also the composition changes continuously during rock evolution. Together with the findings of alkali chlorides in kimberlites, carbonatites, and diamonds it is now clear that both fluids play a very important role in the lower crust and mantle. Clearly, finding adequate chemical tracers (e.g., Cl stable isotopes) is a major challenge for present-day geochemistry.

Both CO₂ and chlorine were probably introduced into the lower crust and mantle through plate tectonic processes since the

Archean (e.g., Santosh and Omori, 2008). With respect to CO₂, this option was discussed in detail and shown to be viable by Santosh and Omori (2008). A complete discussion would be beyond the scope of this chapter, but generally it can be argued that our findings agree with a scenario first envisaged by Menzies et al. (1985), more recently by Santosh and Omori (2008), and further expressed to us by R.C. Newton (June 2009, personal commun.). The subducted carbonate-rich sediments can either release CO₂ into the lower crust from decarbonation reactions during subduction and/or react with mantle peridotite in the shelf region of the carbonated solidus. The resulting carbonatite magmas, which are enriched in H₂O, alkalis, and halogens, metasomatize the overlying mantle wedge, creating enriched mantle. This material is intrinsically unstable, being rich in hyperfusibles and, probably, radioactivity. It will eventually melt to form alkaline basalts, outgassing early, being rich in CO₂ and Cl, and stall out in the lower crust. There, these mantle fluids may mix with other internally derived fluids, which are produced by prograde metamorphic reactions and modified by fluid-rock interaction, or (for CO₂) expelled from saturated granitic melts. The “dry” lower crust is without doubt a place where extensive fluid-dominated processes have taken place.

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