Fluid-rock interaction in retrograde granulites of the Southern Marginal Zone, Limpopo high grade terrain, South Africa

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A B S T R A C T

Fluid infiltration into retrograde granulites of the Southern Marginal Zone (Limpopo high grade terrain) is exemplified by hydration reactions, shear zone hosted metasomatism, and lode gold mineralisation. Hydration reactions include the breakdown of cordierite and orthopyroxene to gedrite + kyanite, and anthophyllite, respectively. Metamorphic petrology, fluid inclusions, and field data indicate that a low H2O-activity carbon-saturated CO2-rich and a saline aqueous fluid infiltrated the Southern Marginal Zone during exhumation. The formation of anthophyllite after orthopyroxene established a regional retrograde fluid-rock interaction during thrust-controlled exhumation in the interval 2.69–2.62 Ga (Van Reenen et al., 2011). The limit of the regionally retrogressed granulite corresponds to a rarely described retrograde fluid-rock interaction during thrust-controlled exhumation in the interval 2.69–2.62 Ga (Van Reenen et al., 2011). The limit of the regionally retrogressed granulite corresponds to a rarely described retrograde fluid-rock interaction during thrust-controlled exhumation in the interval 2.69–2.62 Ga (Van Reenen et al., 2011).

1. Introduction

The Limpopo high-grade terrain in South Africa is well known for its classic exposures of regionally metamorphosed granulite-facies rocks. It is a late Archean ENE–WSW trending zone located between the granite-greenstone terrains of the Zimbabwe and Kaapvaal cratons (Fig. 1), subdivided into the Northern Marginal Zone, the Central Zone, and the Southern Marginal Zone (e.g., Van Reenen et al., 2011). The Northern and Southern Marginal Zones comprise high-grade granitoids and greenstone belt lithologies (e.g., Kreissig et al., 2001; Van Reenen et al., 2011), which are juxtaposed against the cratons as a result of compression-related exhumation in the interval ~2.69–2.62 Ga (Van Reenen et al., 2011).

The Southern Marginal Zone (SMZ) is particularly interesting as its metamorphic evolution is typical for subduction-related high-pressure granulites (clockwise P-T path), which also experienced ultrahigh-temperature conditions (Tsunogae et al., 2004; Belyanin et al., 2012). Granulites that show a clockwise P-T path and experienced both high-pressure and ultrahigh temperature conditions are not common (Touret and Huizenga, 2012). Further, the SMZ shows evidence of both near-peak and retrograde fluid-rock interaction during thrust-controlled exhumation in the interval 2.69–2.62 Ga (Van Reenen et al., 2011). The limit of the regionally retrogressed granulite corresponds to a rarely described retrograde
anthophyllite-in isograd (Van Reenen, 1986). The SMZ is thus an ideal terrain where the physico-chemical effects of fluid-rock interaction at deep- and mid-crustal levels can be studied.

The emphasis of this paper is to demonstrate the importance of an integrated approach of field mapping, mineralogy, fluid inclusion studies, and thermodynamic modelling in studying different aspects (i.e., P, T, fluid composition and redox state) of fluid-rock interaction in cooling granulites. We reviewed and reinterpreted mineralogical and fluid inclusions data from the literature, and applied thermodynamic model calculations within the C-O-H fluid system.

2. Geological setting of the Southern Marginal Zone

The SMZ is subdivided into a granulite zone (comprising garnet-orthopyroxene-cordierite-bearing metapelitic lithologies) in the north and a retrograde hydrated granulite zone (comprising garnet-biotite-plagioclase-anthophyllite/C6 gedrite/C6 kyanite-bearing lithologies) in the south (e.g., Van Reenen, 1986; Van Reenen et al., 2011) (Fig. 2). These two zones are chemically equivalent (Kreissig et al., 2000) and separated by the retrograde anthophyllite-in isograd (Van Reenen, 1986). Migmatitic pelitic rocks in the granulite zone show reaction textures that are associated with decompression and cooling from peak conditions at P > 10 kbar and T = ~1000 °C (e.g., Tsunogae et al., 2004; Van Reenen et al., 2011; Belyanin et al., 2012). They are characterised by the following four mineral assemblages: (1) orthopyroxene-plagioclase-biotite-quartz (±garnet, ±K-feldspar), (2) garnet-orthopyroxene-plagioclase-biotite-quartz (±K-feldspar), (3) garnet-orthopyroxene-cordierite-plagioclase-biotite-quartz (±K-feldspar), and (4) orthopyroxene-cordierite-plagioclase-biotite-quartz (±K-feldspar) (e.g., Van Reenen et al., 2011). Mineral assemblages (3) and (4) formed as a result of the reaction:

\[
2(\text{Fe, Mg})_3\text{Al}_2\text{Si}_3\text{O}_{12} + 3 \text{SiO}_2 \rightarrow 2(\text{Fe, Mg})_2\text{Si}_2\text{O}_6 + (\text{Fe, Mg})_2\text{Al}_4\text{Si}_5\text{O}_{18}
\]

Garnet Quartz Orthopyroxene Cordierite

during decompression and cooling (e.g., Van Reenen et al., 2011). Iron-rich rocks with a Mg/(Mg + Fe) mole ratio < 0.6 do not show any sign of reaction (1) whereas this reaction has run to completion in rocks with a Mg/(Mg + Fe) mole ratio > 0.7 (Van Reenen, 1986). Rocks with a Mg/(Mg + Fe) mole ratio between 0.6 and 0.7 show reaction (1) in progress (Fig. 3a) (Van Reenen, 1986).

The rare occurrence of primary mixed saline H2O-CO2 fluid inclusions in orthopyroxene (Touret and Huizenga, 2011) and in quartz inclusions in garnet (Van den Berg and Huizenga, 2001) indicates that granulite facies metamorphism occurred in the presence of a CO2 and a saline aqueous fluid (Van den Berg and Huizenga, 2001; Touret and Huizenga, 2011). These low-H2O activity fluids coexisted under conditions of immiscibility and are considered to be typical granulite facies fluids (e.g., Newton et al., 1998).

Post-peak grain-size scale metasomatism is exemplified by perthitic feldspar rims between quartz and garnet, which is the result of the reaction Garnet + Quartz + (K,Na)fluid → K-feldspar + Albite + Biotite (Touret and Huizenga, 2011). Large-scale, shear zone related metasomatism is shown by potassium alteration of tonalitic orthopyroxene-bearing gneisses in the Petronella Shear Zone (Fig. 2) (Smit and Van Reenen, 1997). Here, mesoperthite, perthite, and antiperthite are replacing precursor oligoclase (Smit and Van Reenen, 1997) while orthopyroxene remains stable. Whole-rock/garnet/quartz oxygen-isotope fractionation of the metasomatized rocks...
indicates that alteration took place at a temperature >800 °C (Hoernes et al., 1995; Smit and Van Reenen, 1997). Both the grain-size scale and large-scale metasomatic features indicate that a post-peak metamorphic high-salinity fluid was present.

3. Retrograde hydration and metasomatism in the southern part of the SMZ

Retrogradation of Mg-rich, K-poor pelitic and tonalitic granulites in the presence of H2O-bearing fluid phase resulted in hydration of cordierite and orthopyroxene (Van Reenen, 1986; Van Reenen et al., 2011). Orthopyroxene hydration established the retrograde anthophyllite-in isograd, which separates the hydrated zone from the granulite zone (Van Reenen, 1986). The hydrated zone occupies more than 4500 km² of crust in the hanging wall of the Hout River Shear Zone that bounds the SMZ in the south (Fig. 2) (e.g., Van Reenen et al., 2011).

3.1. Retrograde hydration: field observations and mineralogy

Cordierite hydration resulted in the formation of gedrite (comprising up to 2 wt.% Na₂O, Van Reenen, 1986) and kyanite. Hydration of cordierite can be expressed by the reaction (Van Reenen, 1986):

\[
3(Mg,Fe)_{2}Al_{4}Si_{5}O_{18} + 2 K_{2}O + H_{2}O \rightarrow (Mg,Fe)_{2}Al_{4}Si_{5}O_{22}(OH)_{2} + 4 K(Mg,Fe)_{2}AlSiO_{10}(OH)_{2} + 3 Al_{2}SiO_{5}
\]

which is probably not a completely true account of cordierite hydration as the Na₂O content of gedrite implies that a Na-bearing fluid phase was involved as a reactant. In the granulite zone, north of the anthophyllite-in isograd, hydration of cordierite is characterised by the inward growth of a fine-grained mixture of gedrite and kyanite at the cordierite edges and occurs while orthopyroxene remains stable (Fig. 3b). Cordierite hydration is most intense on and south of the anthophyllite-in isograd (Fig. 3c,d) where relatively coarse-grained gedrite-kyanite intergrowths pseudomorphically replace cordierite (Van Reenen, 1986). Cordierite hydration on the anthophyllite-in isograd is also associated with fine-grained euhedral garnet (Stevens, 1997), which is assumed to be related to the reaction:

\[
5(Mg,Fe)_{2}Al_{4}Si_{5}O_{18} + 2 H_{2}O \rightarrow 2(Mg,Fe)_{2}Al_{4}Si_{6}O_{22}(OH)_{2} + 6 Al_{2}SiO_{5} + 7 SiO_{2}
\]

3. Retrograde hydration and metasomatism in the southern part of the SMZ

Figure 2. Geological map of the Southern Marginal Zone of the Limpopo high-grade terrain (modified after Smit and Van Reenen, 1997). Black squares indicate sample localities of samples that were used for P-T reconstruction by Perchuk et al. (2000b) (sample localities: DR19, DV101, DV3) and Belyanin et al. (2012) (sample locality: Bln). White squares represent localities of samples that were used for fluid inclusion studies by Van Reenen and Hollister (1988) (sample localities: DR54, DR19, DR157, DV43), Du Toit (1994) (sample locality: DT), Mokgatla (1995) (sample locality: Mkg) and Van den Berg and Huizenga (2001) (sample locality: VdB&H). White circles indicate localities of samples of which fluid inclusion microphotographs/sketch are shown in Fig. 4 (sample localities: VdB&H, DV43, DR42).
occurs within a few hundred meters in the field and defines the anthophyllite-in isograd. The isograd cuts through lithological boundaries and major fold structures (Van Reenen, 1986). The Mg/(Mg + Fe) mole ratio of 0.60–0.70 for both anthophyllite and orthopyroxene confirms the univariant nature of this reaction implying that the fluid phase was externally buffered (Van Reenen, 1986). It is important to note that graphite is commonly associated with the products of the reactions (2), (3), and (4) (Van Reenen, 1986; Stevens, 1997). South of the anthophyllite-in isograd, pelitic rocks comprise gedrite, kyanite (occasionally sillimanite), garnet, biotite, and anthophyllite (Fig. 3d) whereas orthopyroxene and cordierite are absent (Van Reenen, 1986).

3.2. Metasomatism

Metasomatic features in the hydrated zone of the SMZ are restricted to shear zones and include potassium alteration (Klipbank Shear Zone, Fig. 2) (Smit and Van Reenen, 1997) and lode-gold deposits (e.g., Louis Moore, Osprey and Doornhoek gold deposits, see Figs. 1 and 2) (Van Reenen et al., 1994). Shear zone hosted metasomatism of tonalitic gneisses at Klipbank is characterised by an increase in K2O (from ~1.5 to ~4.5 wt.% and decreasing MgO, FeO, CaO and TiO2 whereas Al2O3 and SiO2 remain constant (Mokgatlha, 1995; Smit and Van Reenen, 1997). Typically, the most altered rocks show coarse-grained microcline (replacing oligoclase), Mn-rich garnet, and sillimanite (Hoernes et al., 1995; Mokgatlha, 1995; Smit and Van Reenen, 1997). Lode-gold mineralisation is characterised by arsenopyrite, quartz veining, carbonate and potassium alteration (Van Reenen et al., 1994).

3.3. Fluid inclusions

Fluid inclusion studies on non-hydrated and hydrated granulites were performed by a number of workers including Van Reenen and Hollister (1988), Du Toit (1994), Mokgatlha (1995) and Van den Berg and Huizenga (2001) (Table 1). Van Reenen and Hollister (1988) studied both non-hydrated (north of the anthophyllite-in isograd) and hydrated (south of the anthophyllite-in isograd) granulites (sample localities: DR54, DR19, DR157, DV43, see Fig. 2). Du Toit (1994) and Van den Berg and Huizenga (2001) studied samples from two deep crustal shear zones (Petronella and Annaskraal Shear Zones, respectively) in the granulite zone (sample localities DT and VdB&H, see Fig. 2). Lastly, Mokgatlha (1995) studied samples from the Klipbank Shear Zone that is situated south of the isograd (sample locality: Mkg, Fig. 2). With the exception of the study by Van den Berg and Huizenga (2001), all fluid inclusion studies focussed on the

Table 1

| Calculation results for \( \log_{10} f^{\text{fluid}}_{\text{O}_2} \) assuming \( X_{\text{H}_2\text{O}}/(X_{\text{H}_2\text{O}} + X_{\text{CO}_2} + X_{\text{CH}_4}) = 0.1 \). \( c_{\text{carbon}} = 1 (P = 6 \text{ kbar}, T = 610 \text{ °C}) \). See text for discussion. |
| --- | --- | --- | --- |
| \( X_{\text{H}_2\text{O}} \) | \( \log_{10} f^{\text{fluid}}_{\text{O}_2} \) | \( \log_{10} f^{\text{fluid}}_{\text{O}_2} - \log_{10} f^{\text{FMQ}}_{\text{O}_2} \) | \( X_{\text{CO}_2}/(X_{\text{CO}_2} + X_{\text{CH}_4}) \) |
| 0.1 | -18.9 | +0.6 | 1 |
| 0.3 | -19.0 | +0.5 | 1 |
secondary (trail-bound) fluid inclusions only with inferences on either hydration and/or metasomatic processes that post-date the peak of metamorphism.

Microthermometry was performed on doubly polished thick sections (~200 µm) using a Chaixmeca (Van Reenen and Hollister, 1988), USGS (Du Toit, 1994; Mokgatlha, 1995), and Linkam heating-freezing stages (Van den Berg and Huizenga, 2001). The precision for the microthermometric measurements (<31 °C) is ~0.5 °C.

The above mentioned studies illustrate that both the granulites and the hydrated granulites have similar fluid inclusion assemblages. These include trail-bound CO2-rich (Fig. 4a) and trail-bound aqueous inclusions with variable salinity.

### 3.3.1. CO2-rich fluid inclusions

Melting of the CO2–rich inclusions typically occurs near or at the triple point of pure CO2 (~56.6 to −57.0 °C). Van den Berg and Huizenga (2001) reported on a few CO2-rich inclusions in granulites north of the anthophyllite-in isograd that had significantly lower melting points (down to ~58.5 °C) caused by the presence of CH4 (up to ~10 mol%). Although H2O is not visible in the CO2-rich fluid inclusions (Fig. 4a,b), it has in a few cases been detected by means of clathrate melting (Van Reenen and Hollister, 1988). This implies that the inclusions may contain up to 20 vol.% H2O as this is optically not visible (e.g., Bakker and Diamond, 2006), particularly in small inclusions.

Homogenisation temperatures (Th) of CO2-rich fluid inclusions are characterised by the disappearance of the vapour phase (liquid + vapour → liquid). Each trail typically shows a Th range of 10 °C or less. Van Reenen and Hollister (1988) identified relatively small and relatively low-density (Th = ±12 to ±26 °C) CO2–rich fluid inclusions in short trails diverging from larger, higher density (Th = −4 °C) CO2–rich fluid inclusions trails. Van den Berg and Huizenga (2001) described high-density trails of CO2–rich fluid inclusions that are intersected by low-density CO2–rich fluid inclusion trails (Fig. 4c). These textures show that the low-density inclusions formed later than the high-density ones. Further, it can be argued that some of the low-density inclusion trails were derived from decrepitated higher density CO2-rich inclusions (Van Reenen and Hollister, 1988).

The Th bar plots show that all samples, hydrated or not, comprise low-density CO2–rich fluid inclusions with a Th between +20 and +31 °C (Fig. 5a–g). Higher density inclusions (Th < +10 °C) are rarely present in the hydrated samples (Fig. 5e–g) whereas granulites north of the anthophyllite-in isograd contain inclusions with Th values as low as −30 °C (Fig. 5c).

### 3.3.2. Saline aqueous inclusions

Trails of aqueous inclusions have been described in all samples but are relatively rare. Therefore, a chronological relationship between the saline aqueous and the CO2-rich trail-bound inclusions could not be established. In numerous aqueous inclusions salt cubes could be identified (Van Reenen and Hollister, 1988). Initial melting temperatures are variable with values as low as −55 °C, which indicates the presence of Ca²⁺ and Mg²⁺ in addition to Na⁺ and probably K⁺. Final ice melting temperatures range between −30 and 0 °C (Van Reenen and Hollister, 1988) indicating salinities ranging between ~30 and 0 wt.% NaCl equivalent.

### 3.4. P-T-fluid constraints on retrograde hydration and metasomatism in the SMZ

Oxygen-isotope thermometry of a rock sample that comprises cordierite without any sign of hydration (sample P19C, Venneman and Smith, 1992; Hoernes et al., 1995) points at an equilibrium temperature of ~670 °C. The orthopyroxene hydration temperature is calculated to be 610 °C from the garnet-biotite geothermometry (Kaneko and Miyano, 2004) using samples on the anthophyllite-in isograd comprising coexisting...
Figure 5. Bar plots (bar width is 2 °C) for Th for CO₂-rich trail-bound fluid inclusions measured in samples from different localities in the Southern Marginal Zone (see Fig. 2 for sample localities). Source of data: a, d–f: Van Reenen and Hollister (1988); b: Du Toit (1994); c: Van den Berg and Huizenga (2001); g: Mokgalatla (1995).
orthopyroxene and anthophyllite (Van Reenen, 1986). Whole-rock/mineral oxygen isotope fractionation of anthophyllite-bearing (orthopyroxene-absent) and metasomatized rocks (Klipbank Shear Zone) indicate fluid infiltration at ~600 °C (Hoernes et al., 1995). Based on the P-T path by Perchuk et al. (2000b) (Fig. 6), the pressure of orthopyroxene hydration should be slightly below 6 kbar rather than at least 6 kbar as previously suggested (Van Reenen, 1986).

So far, several authors have assumed that orthopyroxene hydration was caused by a low H2O–activity fluid (afliH2O = ~0.2) (Van Reenen, 1986; Newton, 1994; Van Reenen et al., 2011). This is based on the fact that lowering afliH2O from unity to ~0.2 lowers the temperature for reaction (4) from ~800 to ~610 °C, assuming Mg end-members for both orthopyroxene and anthophyllite (Fig. 6) (Van Reenen, 1986; Newton, 1994; Van Reenen et al., 2011). However, orthopyroxene and anthophyllite do comprise significant amounts of Fe (Van Reenen, 1986). Using the Wood and Banno (1973) orthopyroxene activity–composition model and the orthopyroxene compositions from Van Reenen (1986), the average enstatite orthopyroxene is ~0.39. Evaluation of the orthopyroxene hydration reaction using the spreadsheet PTGibbs (Brandelik and Massonne, 2004) in conjunction with Holland and Powell’s (1998) dataset shows that the Fe content in anthophyllite and afliH2O have opposite effects on the temperature of reaction (4). An increase in the Fe content of anthophyllite can be compensated by an increase of afliH2O (i.e., greater than 0.2) in order to maintain the temperature of orthopyroxene hydration at 610 °C. Therefore, afliH2O of ~0.2 represents a minimum value for the hydrating fluid.

There is little doubt that the low afliH2O fluid in the SMZ is a carbon-saturated CO2-rich fluid. Evidence for this includes: (1) the occurrence of graphite associated with the hydration reaction products, (2) carbonation reactions that occur in ultramafic rocks in the hydrated part of the SMZ, i.e. the transformation of olivine into magnesite and orthopyroxene according to the reaction olivine + CO2 → orthopyroxene + magnesite (Van Schalkwyk and Van Reenen, 1992), and (3) the presence of secondary CO2-rich fluid inclusion trails.

The minimum afliH2O value of ~0.2 corresponds to a minimum XH2O value of ~0.1 in a CO2-rich fluid (Aranovich and Newton, 1996). The upper XH2O limit in a CO2-rich fluid can be established from the lower temperature limit of melting at ~800 °C (Smit and Van Reenen, 1997). This temperature corresponds with the solidus (Qz-Ab-Or-H2O-CO2 system) for XH2O = ~0.3 (Fig. 6), i.e. XH2O was ≤0.3. Therefore, XH2O of the hydrating fluid in the SMZ ranged between 0.1 and 0.3, which is in good agreement with the observed CO2-rich fluid inclusions without any visible H2O. Using the software by Bakker (2003) (i.e., BULK), XH2O values of 0.1 and 0.3 correspond to a water volume fractions of ~<5 and ~<15 vol.%, respectively, which is hardly visible.

The temperature of metasomatism in the Klipbank Shear Zone was constrained from (1) whole-rock/Grt/Qz oxygen-isotope fractionation and found to be ~600 °C (Hoernes et al., 1995). This temperature has also been established for gold mineralisation based on the alteration assemblage (Van Reenen et al., 1994). The alkali mobility exemplified by metasomatism requires the presence of a saline fluid in addition to the CO2–rich fluid. The secondary trail-bound saline aqueous fluid inclusions may represent this fluid. Considering the variation in the salt content of these fluids, it is likely that the fluid trapped in these inclusions resulted from mixing between two fluids with contrasting salinities (e.g., Wilkinson, 2001). In that case, the fluid inclusions with the highest salinity (i.e., ~30 wt.% NaCl equivalent) represent the saline aqueous fluid that is responsible for potassium alteration and gold mineralisation whereas the low-salinity fluid is probably meteoric in origin (e.g., Yardley et al., 2000).

4. C-O-H fluid modelling

4.1. Equilibrium calculations

In this study, C-O-H model calculations are used to constrain the redox state of the fluid–rock system, and for testing whether fluid inclusion data and fluid compositions determined from metamorphic reactions are in agreement. Aspects of C-O-H fluid calculations have been addressed by numerous authors (French, 1966; Ohmoto and Kerrick, 1977; Huizenga, 2001 and references therein). A C-O-H fluid system has seven unknowns at a fixed fluid pressure and temperature: XH2O, XCO2, XCH4, XH2, XCO, afliH2O, and afliCarbon, i.e. the mole fractions of H2O, CO2, CH4, H2, CO, the fluid oxygen fugacity and the fluid carbon activity, respectively. Four independent equilibria can be written (e.g., French, 1966; Ohmoto and Kerrick, 1977) for the C-O-H fluid system: CO + ½ O2 ⇋ CO2, H2 + ½ O2 ⇋ H2O, CH4 + 2 O2 ⇋ CO2 + 2H2O, and C + O2 ⇋ CO2. The mass balance constraint yields (ignoring the very small value of XH2) XH2O + XCO2 + XCH4 + XCO + XH2 = 1. Having defined five equations for the C-O-H system, two compositional parameters need to be specified in order to calculate the remaining five variables. One can choose any two compositional parameters (e.g., single-molecule fractions, mole fraction ratios, atomic ratios, a fixed afliCarbon of 1 if graphite is present, see Huizenga, 2001) to solve this system. However, the choice of these two parameters obviously depends on what data are available.

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**Figure 6.** Pressure-temperature diagram illustrating the partial prograde and retrograde P-T paths of the Southern Marginal Zone, and the P-T conditions for the cordierite and orthopyroxene hydration reactions (blue box). Solidus curves (Qz-Ab-Or-H2O-CO2 system) labelled for different XH2O values are indicated (black curves) (Ebadi and Johannes, 1991). The dashed P-T loop is after Belyanin et al. (2012) (see Fig. 2 for sample locality). The retrograde P-T path (solid grey arrow) is the average for samples DR19, DV101 and DV3 (see Fig. 2 for sample localities) as calculated by Perchuk et al. (2000b). The orange curves represent the enstatite-anthophyllite (Mg end-members) stability curve for a afliH2O of 1 (dashed curve) and 0.2 (solid curve). The subdivision of the granulite facies into different P-T regimes is after Brown (2007): HT – high temperature; UHT – ultrahigh temperature; HP – high pressure. The Al-silicate system (red curves) is after Holdaway (1971).
We used the following constraints for the calculations: (1) $P$ and $T$ conditions were set at 6 kbar and 610 °C, respectively, (2) $d_{\text{fluid}}$ was set at unity assuming carbon saturation ($d_{\text{fluid}} = 1$), and (3) the $X_{H_2O}/(X_{CO_2} + X_{CH_4})$ ratio was 0.1. The first constraint is based on the $P$-$T$ hydration conditions of orthopyroxene. The second constraint is based on the presence of graphite associated with the hydration reaction products. The last constraint is based on the presence of CH$_4$ in the CO$_2$-rich inclusions near triple point of CO$_2$. However, the melting point of CH$_4$ is lower than the triple point of CO$_2$. The results for $680$ km show that $X_{CH_4}$ is in accordance with the estimated hydration conditions of orthopyroxene.

An updated version of the spreadsheet COH (Huizenga, 2005) was used to perform the calculations. Thermodynamic data for the fluid species and graphite for calculating equilibrium constants for reactions in the fluid phase were taken from Holland and Powell (1988). Fugacity coefficients for the fluid species were calculated from the equations of state by Shi (2005) assuming ideal mixing. Note that the calculated results for $f_{\text{CO}_2}^{\text{fluid}}$ are reported as absolute values and as values relative to $f_{\text{H}_2O}$ buffered by the fayalite-magnetite-quartz (FMQ) buffer ($f_{\text{FMQ}}^{\text{fluid}}$) calculated from the equation (Ohmoto and Kerrick, 1977): $\log_{10} f_{\text{FMQ}}^{\text{fluid}} = -25738/T + 9.00 + 0.092(P - 1)/T$ ($T$ in kelvin, $P$ in atmosphere).

### 4. Results

The calculation results (Table 1) show that the $\log_{10} f_{\text{CO}_2}^{\text{fluid}}$ is 0.5--0.6 log units higher than $\log_{10} f_{\text{FMQ}}^{\text{fluid}}$. The calculations also show that $X_{CO_2}/(X_{CO_2} + X_{CH_4})$ is 1, which is generally in good agreement with melting temperatures of most of the CO$_2$-rich fluid inclusions near triple point of CO$_2$. However, the melting point of some of these inclusions below the triple point of CO$_2$ (i.e., $\sim 57$ °C) is most likely due to some CH$_4$ (up to 5 mol%). Thiéry et al. (1994) as graphite is present in the hydrous rocks. The calculated $X_{CO_2}/(X_{CO_2} + X_{CH_4})$ value of 1 indicates that CH$_4$ was not a primary species in the CO$_2$-rich fluid but resulted from post-trapping changes (Hall and Bodnar, 1990).

In order to confirm the secondary origin of CH$_4$ in the CO$_2$-rich fluid another calculation was done using a different compositional constraint. Instead of defining $X_{H_2O}/(X_{H_2O} + X_{CO_2} + X_{CH_4})$ we fixed $X_{CO_2}/(X_{CO_2} + X_{CH_4})$ at 0.99 (Table 2). The calculated $X_{H_2O}/(X_{H_2O} + X_{CO_2} + X_{CH_4})$ is $0.99$ and $f_{\text{fluid}}^{\text{fluid}}$. The calculated $X_{H_2O}/(X_{H_2O} + X_{CO_2} + X_{CH_4})$ can be compared with the $X_{H_2O}$ of the CO$_2$-rich fluid (i.e., between 0.1 and 0.3). The results show that a fluid with $X_{CO_2}/(X_{CO_2} + X_{CH_4})$ between 0.99 and 0.95 should have had a $X_{H_2O}/(X_{H_2O} + X_{CO_2} + X_{CH_4})$ value between 0.6 and 0.8, respectively, and $f_{\text{fluid}}^{\text{fluid}}$ near FMQ (Table 2). This result is unrealistic as the relatively high $X_{H_2O}$ value implies that orthopyroxene hydration would have occurred at a temperature higher than 610 °C. Therefore, the presence of CH$_4$ in the CO$_2$-rich inclusions can only be explained by H$_2$ diffusion into the inclusions (Hall and Bodnar, 1990).

Summarising, the C-O-H calculations demonstrate that: (1) the presence of carbon-saturated CO$_2$-rich fluids requires a $f_{\text{CO}_2}^{\text{fluid}}$ that is 0.5--0.6 log units above FMQ and (2) the carbonic component was pure CO$_2$.

### 5. Discussion and conclusions

#### 5.1. Source of the CO$_2$-rich and saline aqueous fluids

Both CO$_2$-rich and aqueous saline fluids (~$30$ wt.\% NaCl equivalent) infiltrated the granulites during cooling at $P$-$T$ of hydration 6 kbar and 610 °C, respectively. This is illustrated by (1) the occurrence of anthophyllite, gedrite, kyanite and graphite, (2) the involvement of Na and K in reactions (2) and (3), respectively, (3) shear zone hosted metasomatism (Klipbank shear Zone), and (4) the presence of CO$_2$-rich and saline aqueous fluid inclusions. The pervasive nature of fluid infiltration is inferred from the widespread occurrence of the hydrated mineral phases. Whole-rock/mineral oxygen isotope fractionation patterns indicate an external fluid source (Hoernes et al., 1995). Although there is no direct fluid inclusion evidence, it is likely that both fluids were immiscible.

Two potential sources for the CO$_2$-rich fluid have been suggested in previous studies, namely devolatilization reactions within the underlying greenstone belt rocks (Van Reenen and Hollister, 1988) and a deep mantle source (Van Reenen et al., 1994). A mantle source was suggested based on the $\delta^{13}C$ signature ($-5$ to $-6\%$) of magnesite in hydrated ultramafic rocks (Van Schalkwyk and Van Reenen, 1992). However, these values do not conclusively point to a mantle source (Kerrick, 1987). Therefore, prograde devolatilization reactions in the underlying greenstone belt rocks from the Kaapvaal Craton footwall are the most plausible source for CO$_2$-rich fluids. This is supported by the fact that underthrusted mica schist from the Sutherland/Giyani greenstone belt (Fig. 1) reached peak $P$-$T$ conditions ($\sim 600$ °C and 5--5.5 kbar, Fig. 7) (Perchuk et al., 2000a) at $\sim 2.69$ Ga (Kreissig et al., 2001), which is contemporaneous with the early stage of SMZ exhumation.
In both cases, the permeability of the rocks will increase (e.g., Oliver, 1996; Putnis, 2009; Putnis and Austrheim, 2013).

Another possible driving force for fluid flow includes grain-size scale porosity (e.g., Oliver, 1996) as exemplified by trails comprising CO2-rich fluid inclusions. Here, permeability is created by overpressured fluids causing micro-hydrofracturing (e.g., Touret and Huizenga, 2012). Considering the relatively flat slope of isochores for CO2-rich fluids in P-T space, hydrofracturing is only possible if the retrograde P-T path is dominated by decomposition rather than cooling. So, in the case for the SMZ, this mechanism is not relevant for cooling between 800 and 600 °C where the retrograde P-T path is approximately parallel to the isochores for the CO2-rich fluids (Fig. 7).

The expected Th range for CO2-rich fluid inclusions, which are trapped during retrograde hydration (between ~670 and ~600 °C), is between ~20 and ~10 °C (Fig. 7). However, such CO2-rich fluid inclusions have not been found (Fig. 5d–g). The relatively low density of the CO2-rich inclusions can be explained by (1) the fact that some of the low-density inclusions comprise the CO2-rich fluid that was liberated from originally higher density CO2 fluid inclusions that decrepitated during decompression (Van Reenen and Hollister, 1988), and (2) trapping of the fluid at a pressure between the lithostatic and hydrostatic pressure. The latter is expected to occur in a strike slip environment as mentioned above (Roering et al., 1995) and also where hydration reactions have increased the permeability of the rocks.

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References


(Kreissig et al., 2001). In other words, prograde metamorphism in footwall greenstone belts is caused by thrusting of SMZ granulites over the Kaapvaal Craton along the bounding Hout River Shear Zone (e.g., Roering et al., 1992; Van Reenen et al., 2011). Greenstone belt fluids produced during prograde metamorphism are typically aqueous-carbonic in composition (Powell et al., 1991). This fluid may become CO2 rich if (1) T > 500 °C (Powell et al., 1991), (2) the greenstone belt is dominated by (ultra)mafic lithologies (Powell et al., 1991), or (3) the fluid interacts with graphite in a relatively oxidised environment.

The source of the saline aqueous fluid remains hypothetical. It could either be inherited from granulites, or derived from underlying greenstone belts. Greenstone belts are known to contain evaporitic brines (e.g. Westall et al., 2002) and connate saline waters (Classly et al., 2010).

5.2. Fluid-rock redox state during hydration

The oxygen fugacity of the CO2-rich fluid is 0.5–0.6 log10 units higher than fO2,FMQ. The pervasive nature of fluid infiltration implies that the fluid phase and host-rock were in redox equilibrium (i.e., fluid = rock). Considering the fact that graphite is part of the hydration mineral assemblages, oxidation of the host rocks must have occurred during retrograde hydration as a result of graphite precipitation according to the reaction CO2 + C + O2. In other words, graphite precipitation was driven by the redox difference of the oxidised and the relatively reduced host rock and redox equilibrium was reached during graphite precipitation (e.g., Huizenga and Touret, 2012). Local redox variations (i.e., more oxidised) in the host rock explain the absence of graphite in some of the hydrated rocks.

5.3. Fluid migration in the lower and middle crust

Whereas a saline aqueous fluid is highly mobile, a CO2-rich fluid is considered to be immobile in the continental crust because of its wetting angle characteristics (Watson and Brennan, 1987). Flow of the CO2-rich fluid along grain boundaries is, therefore, not feasible. Other factors must have played a role such as fluid flow along deep-to mid-crustal shear zones, volume changes associated with hydration reactions, and fluid-induced micro fracturing.

Firstly, the relatively high spatial density of shear zones south of the isograd compared to the northern part is noteworthy (Fig. 2) and indicates a structural control on the fluid flow. In particular strike slip faults, where the fluid pressure is expected to be less than the lithostatic pressure, will be preferred sites for focussed fluid flow (Roering et al., 1995).

Second, volume changes associated with retrograde hydration reactions in the SMZ were significant (Table 3) and did probably contribute to an increase in the permeability of the rocks (e.g., Jantveit, 2010). A volume increase (i.e., reactions (3) and (4), Table 3) may cause fracturing whereas a volume decrease associated with the replacement of cordierite by gedrite, kyanite and quartz (reaction (2), Table 3) will cause an increase in the porosity.


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