Experimental and petrological constraints on local-scale interaction of biotite-amphibole gneiss with H$_2$O-CO$_2$-(K, Na)Cl fluids at middle-crustal conditions: Example from the Limpopo Complex, South Africa

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Abstract Reaction textures and fluid inclusions in the ~2.0 Ga pyroxene-bearing dehydration zones within the Sand River biotite-hornblende orthogneisses (Central Zone of the Limpopo Complex) suggest that the formation of these zones is a result of close interplay between dehydration process along ductile shear zones triggered by H$_2$O-CO$_2$-salt fluids at 750–800 °C and 5.5–6.2 kbar, partial melting, and later exsolution of residual brine and H$_2$O-CO$_2$ fluids during melt crystallization at 650–700 °C. These processes caused local variations of water and alkali activity in the fluids, resulting in various mineral assemblages within the dehydration zone. The petrological observations are substantiated by experiments on the interaction of the Sand River gneiss with the H$_2$O-CO$_2$-(K, Na)Cl fluids at 750 and 800 °C and
1. Introduction

Ductile shear zones developed within high-grade metamorphic terrains are usually considered as effective pathways for external fluids (e.g., Newton, 1990; Aranovich et al., 2010). Localized over a scale of centimeters to a few meters orthopyroxene ± clinopyroxene and K-feldspar-bearing dehydration zones within biotite-hornblende(garnet) gneisses in various transitional amphibolite-to-granulite facies terrains are the best examples of such shear zones (Pichamuthu, 1960; Friend, 1981; Janardhan et al., 1982; Hansen et al., 1984, 1987; Stähle et al., 1987; Burton and O’Nions, 1990; Santosh et al., 1990; Milisenda et al., 1991; McGregor and Friend, 1992; Raith and Srikantappa, 1993; Dobmeier and Raith, 2000; Perchuk et al., 2000; Harlov and Förster, 2002; Rajesh, 2004; Ravindra-Kumar, 2004; Harlov et al., 2006; Rajesh et al., in press). Most researchers agree that the local dehydration of biotite- and hornblende-bearing gneisses to pyroxene-bearing assemblages is a result of the passage of low-εH2O fluid through the rocks at temperatures 700–800 °C and pressures 5–7 kbar. Instead of an H2O-CO2 fluid with high XCO2 (e.g., Friend, 1981; Janardhan et al., 1982; Newton, 1986), preference is lately given to more complex H2O-CO2-salt fluids (Hansen et al., 1995; Newton, 1995; Newton et al., 1998; Perchuk et al., 2000; Ravindra-Kumar, 2004; Harlov et al., 2006; Hansen and Harlov, 2009; Harlov, 2012; Tourret and Huizenga, 2012). This conclusion agrees with the data on activity of aqueous brines in many amphibolite and granulite terrains suggesting that this type of fluid is an important agent of high-grade metamorphism in the lower to middle crust (Tourret, 2009; Newton and Manning, 2010; Tourret and Huizenga, 2011). At granulite p-T conditions, aqueous brines are immiscible with CO2 (Schmulovich and Graham, 2004; Heinrich, 2007), resulting in coexistence of two fluids with contrast mobility (Watson and Brenan, 1987; Holness, 1997; Gilbert et al., 1998). Presence of supercritical brines coexisting with CO2-rich fluids explains in much better way textural, geochemical and thermodynamic characteristic of the rocks from the dehydration zones. Both coexisting fluids are characterized by low water activity at granulite p-T conditions (Aranovich and Newton, 1996, 1997, 1998), assisting to stabilization of anhydrous mineral assemblages. In addition, low water activity would prevent from the extensive partial melting (Aranovich and Newton, 1996). The relationships between passage of the low-water activity fluids (brines and CO2) and possible melting is still under hot debate. Using mass balance calculations and/or structural evidence, several studies on the dehydration zones proposed that formation of the pyroxene-bearing assemblages via metasomatism either preceded or was accompanied by partial melting (e.g., Stähle et al., 1987; Perchuk et al., 2000). Other groups of researchers argue for the dehydration induced by fluid infiltration only, without melting (e.g., Janardhan et al., 1982; Hansen et al., 1987; Santosh et al., 1990; Raith and Srikantappa, 1993; Harlov et al., 2006).

In addition to petrological and geochemical studies, the relations between dehydration induced by the complex H2O-CO2-salt fluids and partial melting could be resolved using experimental approach. Nevertheless, there are only few experimental studies available on dehydration processes for metamorphic rocks. Moreover, most of them are concentrated on the fluid-absent melting of rocks of diverse composition. Formation of orthopyroxene-bearing assemblages via dehydration melting of semi-pelitic rocks at pressures 5–7 kbar proceeded at temperatures above 800–850 °C (Nair and Chacko, 2002), while tonalitic rocks produced orthopyroxene-bearing assemblages at temperatures above 900 °C (Skjerlie and Johnston, 1993). Khodorevskaya (2004) performed experiments on “granitization” of amphibolite via infiltration of chloride-bearing aqueous solutions at 5 kbar and 750 °C. Harlov (2004) published results of an episodic study on interaction of tonalite biotite gneiss with KCl and NaCl-bearing fluids at 10 kbar and 900 °C and showed that chlorides stabilize orthopyroxene and clinopyroxene after biotite and plagioclase. Alkali feldspar microveins, characteristic for granulites and charnockites, were reproduced in these runs. However, p-T parameters of Harlov’s experiments are much higher than those for the dehydration zones in Precambrian complexes, i.e. temperatures below 850 °C at pressures 5–7 kbar (e.g. Nair and Chacko, 2002).

Because of variable bulk and mineral composition of the rocks in the dehydration zones and diverse ranges of p-T-fluid conditions of their formation, it is hard to propose a global model for the fluid-induced dehydration process. However, such models can be created for specific examples of the dehydration zones accounting for their chemical and thermodynamic evolution deduced from petrological data. The present study is focused on dehydration zones within the Archean Sand River biotite-hornblende tonalite-trondhjemit-granodiorite orthogneisses (ca. 3.3–3.2 Ga; Kröner et al., 1999; Zeh et al., 2007) at the Causeway locality within the Central Zone of the Limpopo Complex, Southern Africa (Fig. 1). According to Jacek et al. (1997), the formation of these zones occurred during the latest Paleoproterozoic D3/M3 (~2.0 Ga) the metamorphic event in the Central Zone of the Limpopo Complex. Rajesh et al. (in press) describes in detail the geology, petrography and geochemistry of, as well as compositions of minerals and fluid inclusions of the rocks from the dehydration zones at the Causeway locality. In the present paper, we first use Rajesh’s et al. data to account for the various fluid-mineral reactions and p-T-fluid conditions during the dehydration process. The main focus of this study is on results of experiments on interaction of the Sand River...
is thin rims along grain boundaries. The second type is wide “veins” of K-feldspar enveloping large subhedral plagioclase crystals and anhedral quartz grains (Fig. 2A). This type of texture resembles a magmatic-like “monzonitic” texture. Myrmekites are locally developed along the contacts of plagioclase with K-feldspar.

According to Perchuk and Gerya (1992, 1993), K-feldspar microveins are products of plagioclase interaction with an alkali-bearing fluid

$$An_xAb + 0.5y(K_2O) = yKfs + An(x - y)Ab + 0.5y(Na_2O)$$  

(1)

This reaction indicates an increase in anorthite content in plagioclase resulting from the increase of the K activity in the fluid. Rajesh et al. (in press) described the local increase of the anorthite content of plagioclases by 2 mol%–3 mol% in contacts with the K-feldspar microveins in samples from all the three zones. The net transfer reaction (Perchuk et al., 2000):

$$nAn(1 - n)Ab + 4nQtz + (m + 2n)K_2O$$  

$$= (1 - n - m)Ab(m + 2n)Kfs + (nCaO + mNa_2O)$$  

(2)

indicates that the higher the activity of K in the fluid, the larger the amount of plagioclase is replaced by K-feldspar, while the plagioclase composition remains constant. Recently, Touret and Huizenga (2011) invoked reaction (2) to explain the conjugate development of K-feldspar microveins and myrmekites in charnockites and granulites.

In the partially dehydrated gneiss, K-feldspar microveins are accompanied by clinopyroxene (X$_{Mg}$ = 0.64–0.66; w(Al$_2$O$_3$) = 1.3%–1.7%) and subordinate orthopyroxene (X$_{Mg}$ = 0.50–0.51; w(Al$_2$O$_3$) = 0.8%–1.1%) (Fig. 2B). Appearance of the Cpx + Opx + Kfs coronas around biotite and/or hornblende seems to trace pathways within the partially dehydrated gneiss, presumably indicating infiltration of fluids along foliation or micro shear zones in the rock. It is texturally evident that the pyroxene-K-feldspar microassemblage is a product of biotite decomposition reactions (Fig. 2B). The formation of orthopyroxene and K-feldspar after phlogopite-annite biotite reflects the main charnockitic dehydration reaction

$$Bt + 3Qtz = 3Opx + Kfs + H_2O$$  

(3)

This reaction proceeds to the right via a decrease in the water activity. Nevertheless, orthopyroxene is subordinate in the reaction textures in the partially dehydrated gneiss. These textures predominantly consist of clinopyroxene and K-feldspar, whose growth after biotite corresponds to the reaction

$$Bt + 3An (in Pl) + 18Qtz + 3(K_2O) = 3Cpx + 7Kfs + (H_2O)$$  

(4)

It is the result of an increase in the K activity conjugate with a decrease in the water activity. There is no clear evidence for the participation of pargasite-edenite amphibole in these reactions. Its possible contribution to the formation of two-pyroxene + K-feldspar assemblage via interaction with an alkali-bearing fluid and a decrease in the water activity can be written as (Perchuk and Gerya, 1992):

$$Pr + 4Qtz + (0.5 K_2O) = Kfs + An(in Pl) + 3Opx + Cpx + (H_2O) + (0.5 Na_2O)$$  

(5)

Relationships between clinopyroxene, orthopyroxene and plagioclase in the presence of K-feldspar and quartz are regulated by the equilibrium (Safonov, 1998).
Equilibrium (6) indicates the prevalence of clinopyroxene over orthopyroxene in the partially dehydrated gneiss (Fig. 2B) corresponds to a higher K activity during the local formation of the two-pyroxene-K-feldspar coronitic assemblage in comparison to the formation of the orthopyroxene-K-feldspar assemblage in the charno-enderbitic vein, where clinopyroxene is absent. The increase of the anorthite content in plagioclase is not characteristic for its contacts with the pyroxene-K-feldspar coronas in the partially dehydrated gneiss, reflecting its consummation during the formation of clinopyroxene via simultaneously operating reactions (1), (2), (4)—(6).

In some cases, monazite rims are clearly related to K-feldspar microveins enveloping fluorapatite in the charno-enderbitic vein (Fig. 2C). Similar rims were replicated experimentally by the reaction of a (Y + REE)-bearing fluorapatite with complex aqueous fluids involving H₂O, CO₂, KCl, HCl and H₂SO₄ as the result of coupled dissolution-re-precipitation (Harlov and Förster, 2003; Harlov et al., 2005; Harlov, 2011). Thus, the association of K-feldspar microveins with monazite rims on fluorapatite can serve as an evidence for reactions with complex fluids in the charno-enderbitic vein.

Retrogressive reaction textures are observed in all three rock types from the dehydration zone. Biotite with $X_{Mg} = 0.56–0.59$ and up to 0.6 f.u. of Ti forms symplectites with quartz replacing orthopyroxene (Bt-II in Fig. 3A) in the transition zone reflecting the shift of the equilibrium (1) to the left via an increasing water activity. Nevertheless, no K-feldspar is observed in the vicinity of the reaction textures. Although it should be suggested that K-feldspar is consumed by later re-hydration, the following reaction involving mobile K with increasing water activity can also serve as an explanation for this assemblage:

$$5\text{En} + \text{Mg} - \text{Ts(in Opx)} + (\text{K}_2\text{O}) + (\text{H}_2\text{O}) = 2\text{Phl (in Bt)}$$

A decrease in the Al-content of the orthopyroxene grains at the contact with biotite-quartz intergrowths supports this suggestion. The retrogressive textures developed in the core of the dehydration zone are replacement textures of orthopyroxene by paragasite-edenite amphibole (Fig. 3B). Composition of this amphibole is similar to the composition of amphibole from the partially dehydrated gneiss. However, it evolves toward actinolite at the rims of the grains. Thin amphibole rims are also locally observed around orthopyroxene grains in the transition zone, as well. These textures reflect the reaction

$$4\text{Opx} + 2\text{An (in Pl)} + \text{Qtz} + (\text{Na}_2\text{O}) + (\text{H}_2\text{O}) = \text{Prg (in Amp)} + \text{Ab (in Pl)}$$

operating at an increasing water and Na activity. In addition, orthopyroxene in both in the charno-enderbitic vein and the partially dehydrated gneiss is usually replaced by chlorite-
magnetite-calcite aggregates and locally with cummingtonite accompanied by magnetite.

3. Fluids in the dehydration zone

The progressive reaction textures indicate that formation of the pyroxene-K-feldspar-bearing assemblages within the dehydration zone is manifested by reactions governed by decrease of water activity and increase of alkali activity, notably potassium, in the fluids (Perchuk and Gerya, 1992, 1993). According to the equilibrium (6), formation of clinopyroxene-K-feldspar assemblages would correspond to higher alkali activity in the fluids with respect to orthopyroxene-K-feldspar assemblages. Reverse relations between water and alkali activities can be expected for supercritical aqueous solution (brines) with varying concentration of alkali salts (Aranovich and Newton, 1997). Formation of K-feldspar microveins (Fig. 2A–C) has been proposed as evidence for passage of such fluids along grain boundaries (Hansen et al., 1995; Franz and Harlov, 1998; Safonov, 1998; Perchuk et al., 2000; Harlov and Förster, 2002; Montanini and Harlov, 2006; Harlov, 2012; Tourret and Huizenga, 2012). Indeed, brine inclusions with salinity up to 29.2% of w(NaCl) are predominant type of fluid inclusions in quartz of the charno-enderbitic vein (Fig. 4; see also Rajesh et al., in press). They are usually accompanied by rare CO$_2$ inclusions (Fig. 4) with density up to 0.909−0.835 g/cm$^3$ corresponding to pressures up to 4.5−4.7 kbar. Primary-secondary brine inclusions with salinity 2.6%−10.5% of w(NaCl) are observed along healed cracks in quartz from the transition zone. Thus, fluid inclusion data suggest much higher salinity of the fluid in the charno-enderbitic vein of the dehydration zone in comparison to that in the transition zone. In addition, fluid inclusions indicate that the brine fluid operating in the core of the dehydration zone coexisted with CO$_2$-rich fluid, suggesting immiscibility of the fluids (Gilbert et al., 1998; Schmuelovich and Graham, 2004; Heinrich, 2007) and, thus, high salinity of the brine during the formation of the dehydration zone. The higher salinity of the fluid acting during evolution of the charno-enderbitic vein agrees with much higher chlorine content of apatites in this rock (0.4%−0.9%) in comparison to the apatites from the transition zone (0.3%−0.4%) (Rajesh et al., in press).

Chlorine partitioning coefficients between aqueous fluid and apatite coexisting with rhyolitic melt for 2 kbar and 900 °C (Webster et al., 2009) $K_{AP}^{fl}$ = 15.5−20.1, allow rough estimation of Cl content of the fluid that equilibrated with apatite from the charno-enderbitic vein. The calculated values 6.5%−12.0% of w(Cl) would correspond to 11%−19.5% of w(NaCl) in the aqueous fluid, which is within the range of salinity for fluid inclusions in quartz from the core vein and transition zone. Monazite rims in apatites enveloped by K-feldspar in the core of the dehydration zone (Fig. 2C) provide further evidence for interaction of the rocks the complex salt-bearing fluids (see Harlov, 2012).

The retrogressive reactions are products of joint increase of CO$_2$ and H$_2$O activities, as well as oxygen fugacity during the later stage of evolution of the dehydration zone. Reaction textures resulted from these reactions are observed in all three rock types of the dehydration zone, being more abundant in the charno-enderbitic vein, suggesting that the vein initially contained much higher concentration of fluids in comparison to the surrounding rocks. Presence of secondary low-salinity aqueous fluid inclusions

![Figure 3](image1.png) Retrogressive reaction textures in the rocks of the dehydration zone. (A) Biotite (Bt-I) and biotite-quartz symplectites (Bt-II) developed after large orthopyroxene grains in the transition zone; note rarity of K-feldspar; (B) Partial replacement of orthopyroxene with the secondary pargasite-edenite amphibole in the charno-enderbitic vein.

![Figure 4](image2.png) Brine and CO$_2$ fluid inclusions in quartz from the charno-enderbitic vein of the dehydration zone.
in the charno-enderbitic vein and transition zone indicate that fluid system in the dehydration zone evolved from brines + CO₂ at the earlier stages toward the later less saline aqueous or aqueous-carbonic fluids. Nevertheless, reaction (8) resulting in formation of pargasite-enstatite-tremolite amphibole after orthopyroxene (Fig. 3B), as well as reverse reaction (2) responsible for formation of myrmecites after K-feldspar indicates that the late reactions could also be governed by activities of dissolved salts in the supercritical fluids.

4. p-T-aH₂O conditions within the dehydration zone

Application of the hornblende-plagioclase-quartz thermobarometer (e.g. Holland and Blundy, 1994) to the primary assemblage amphibole + biotite + plagioclase + quartz in the partially dehydrated gneiss gives pressure-temperature conditions of 730–790 °C and 5.6–6.2 kbar. The two-pyroxene-K-feldspar textures in this sample indicate the localized later dehydration of the primary assemblage related to the formation of the orthopyroxene-bearing veins. Using the version 2.3 of the winTWQ software, we calculated temperatures from the two-pyroxene Fe⁵⁺-Mg exchange equilibrium within the range of 670 ± 40 °C. Application of the equilibrium Ca-Ts (in Cpx) + quartz = An (in Pl) resulted in a wide range of pressures values, from about 2.5 up to 9 kbar, because of uncertainties in determination of Al in the M1 and T sites of low-Al clinopyroxene, which, in turn, depends on errors in the electron microprobe determination of silica and estimation of Fe³⁺. Nevertheless, a statistical maximum within this range of pressure values points to 5.8 ± 0.4 kbar. Application of the Fe⁵⁺-Mg exchange equilibria of biotite with both orthopyroxene and clinopyroxene for the partially dehydrated gneiss gave unreasonable values above 950 °C reflecting disequilibrium between biotite and new locally formed pyroxenes in the rock. Thus, mineral equilibria in the partially dehydrated gneiss show that the assemblage Cpx ± Opx ± Kfs was formed at lower temperature in comparison to the initial gneissic assemblage Amph + Bt + Pl + Qtz at constant or slightly decreasing pressure at the retrograde metamorphism.

The transition zone does not contain relics of primary gneissic assemblage. Nevertheless two textural and compositional generations of biotite in this rock (Bt-I and Bt-II in Fig. 3A) allow determination of the temperature evolution of the sample from 765 ± 20 °C to 700 ± 10 °C. Orthopyroxene-biotite exchange equilibrium for compositions of the minerals from the charno-enderbitic vein gives the range of temperatures of 730–850 °C without distinct statistical maximum. This wide range of values would reflect the fact that not all biotite in the vein was in equilibrium with orthopyroxene. Composition of rare biotites and orthopyroxenes in contact in the vein gave temperature values of 811 ± 6 °C. These biotites, orthopyroxenes, and associated K-feldspars in the vein gave an opportunity to estimate the water activity (using winTWQ software) in the range of 0.28–0.26. Such low water activity is imposed by coexisting aqueous brine and CO₂-rich fluids. Following the equations by Aranovich and Newton (1997) for water activity in the KCl-NaCl-H₂O brine, this activity would correspond to about 55 mol%–56 mol% of salts in the aqueous brine for pressure 6 kbar. Nevertheless, it must be kept in mind that this concentrated brine would characterize separate domains Opx + Bt + Kfs + Pl + Qtz in the charno-enderbitic vein related to later formation of K-feldspar microveins and, locally, biotite. Initial water activity in the fluid that interacted with the gneiss along the shear zone is unknown and could be much higher. It does not rule out that the influx of these fluids was accompanied by melting (Perchuk et al., 2000). In fact, oblique position of the orthopyroxene-bearing vein with respect to the host gneiss and the transition zone (Fig. 1), variations in bulk composition and trace element pattern in the charno-enderbitic vein (Rajesh et al., in press), as well as magmatic-like (monzonitic) textures of separate domains within the vein (Fig. 2A) support this assumption. Following to Ebadi and Johannes (1991) and Aranovich and Newton (1996), minimum haplogranite melting at temperatures of 750–800 °C and pressure about 6 kbar could occur at aH₂O above 0.4 both in the presence of H₂O-CO₂ and H₂O-NaCl fluids.

In order to investigate the possibility for melting and evolution of mineral assemblages in the charno-enderbitic vein, we modeled (using the PERPLEX software; Connolly, 2005) phase assemblages in the vein in dependence on temperature at constant average pressure of 5.6 kbar for the bulk composition w(SiO₂)−64.41%, w(Al₂O₃)−16.92%, w(Fe₂O₃)−4.54%, w(MgO)−1.38%, w(CaO)−4.72%, w(Na₂O)−4.09%, w(K₂O)−1.27%, w(TiO₂)−0.12%, w(P₂O₅)−0.25%, w(MnO)−0.12% reported by Rajesh et al. (in press), assuming 2% of w(H₂O + CO₂) in the system and 10 mol% of NaCl in the fluid (Fig. 5). This volatile content implies a fluid-saturated system, i.e. the presence of a free fluid phase along with hydrous minerals. Mixing models for Ti-bearing biotite, orthopyroxene, Ca-Na-amphibole, ternary feldspar, as well as for the silicate melt recommended in PERPLEX were used in the calculations. The calculated relations are in a good qualitative agreement with the sequence of mineral assemblages in the charno-enderbitic vein, while the temperature ranges of stability of these assemblages suits well with the results of thermobarometric calculations. Biotite appears via re-hydration of orthopyroxene below 780–800 °C, whereas Ca-Na-amphibole joins the assemblages below 740 °C (Fig. 5). Both minerals coexist with the partial melt, which is stable down to about 710 °C within the

![Figure 5 Phase assemblages at 5.6 kbar in dependence on the bulk w(H₂O)/w(H₂O + CO₂) ratio calculated for the bulk composition of the charno-enderbitic vein (Rajesh et al., in press) using energy minimization procedure via PERPLEX software. Dashed line indicates appearance of the melt in the system. In addition to the shown phases, all assemblages contain feldspars (ternary feldspars or sanidines), quartz, and ilmenite.](image-url)
range of H$_2$O/(H$_2$O + CO$_2$) weight ratio in the system above 30%. The melt content in the system increases with temperature, but even at temperatures about 800 °C, i.e. at the average peak temperature during the dehydration process, it does not exceed 30% in the presence of a water-rich fluid. Although at higher content of CO$_2$ in the system (assuming CO$_2$-rich fluid) temperature of melting gradually increases up to 790 °C, this range is well within the temperatures estimated for the dehydration zone (Fig. 5).

5. Experimental study of interaction of the Sand River gneiss with the H$_2$O-CO$_2$-(K, Na)Cl fluids

Petrological and fluid inclusion data showed that a key factor for formation of the dehydration zone in the Sand River biotite-amphibole gneisses was a streaming of the (K, Na)Cl-bearing H$_2$O-CO$_2$ fluid at temperatures of 750–800 °C. In order to reproduce the above fluid-mineral reactions proceeding in the dehydration zone, as well as to show a possibility of partial melting during the dehydration process, the experiments on interaction of the Sand River gneiss with H$_2$O-CO$_2$, H$_2$O-CO$_2$-KCl, and H$_2$O-CO$_2$-(K, Na)Cl fluids were performed at 750 and 800 °C and 5.5 kbar. Cylindrical pieces of the gneiss (produced from the gneiss sample using diamond tube drill) were placed into the gold capsules of 3 mm in diameter, 0.2 mm of wall thickness, and 40 mm in length filled with a homogeneous mixture of oxalic acid and KCl or (KCl + NaCl) with a variable chloride/(H$_2$O + CO$_2$) weight ratios. The experiments were carried out using the internally heated high gas pressure vessel. Duration of all experiments was 10 d each. After experiments, the gneiss pieces recovered from the capsule, were cut along the vertical axis and polished. All samples were mapped in order to identify the places affected by the fluid and their position with respect to the source of the fluid in the capsule.

5.1. Experiments at 750 °C

The chloride-free CO$_2$-H$_2$O fluid produced insignificant changes in composition of biotite at 750 °C, while no clear reaction textures were identified. Addition of KCl into the fluid resulted in formation of spectacular reaction intergrowths of K-feldspar with clinopyroxene corresponding to the reaction (4). The higher KCl content in the starting fluid resulted in more intensive development of the reaction textures after biotite and amphibole, especially within the peripheral areas of the run samples (Fig. 6A). Usually, the clinopyroxene-K-feldspar textures are accompanied by either ilmenite or Ti-bearing magnetite or sphene (Fig. 6A). Run sample produced at KCl/(CO$_2$+H$_2$O) = 0.033 contains films of glass at the contacts of hornblende and quartz (Fig. 6B). The major characteristic of this quenched melt is low content of glass at the contacts of hornblende and quartz (Fig. 6B). The melt content in the system increases with temperature, but even at temperatures about 800 °C, i.e. at the average peak temperature during the dehydration process, it does not exceed 30% in the presence of a water-rich fluid. Although at higher content of CO$_2$ in the system (assuming CO$_2$-rich fluid) temperature of melting gradually increases up to 790 °C, this range is well within the temperatures estimated for the dehydration zone (Fig. 5).

In contrast to KCl-bearing runs, all samples interacted with the mixed KCl-NaCl-bearing fluids at 750 °C show pockets of glass (Fig. 6C), implying that addition of NaCl into the fluid intensifies melting of the gneiss. This glass shows much higher w(Al$_2$O$_3$) content and w(Na$_2$O/K$_2$O) ratio, while the w(Cl) content reaches 1% (Table 1). Newly formed K-feldspar in the KCl-NaCl-bearing runs forms microveins only in the “metasomatic” zones, which do not contain glass. In contact with biotite and amphibole grains, these microveins are accompanied by clinopyroxene. In the intensely molten zones of the run samples, clinopyroxene appear as numerous euhedral crystals in the glass sporadically accompanied by ilmenite (Fig. 6C). Euhedral plagioclase crystals were found in glass in the runs with the mixed KCl-NaCl-bearing fluid. Amphibole containing up to 2.5% of w(Na$_2$O) and about 1.3% of w(K$_2$O) crystallizes from the melt along with clinopyroxene and plagioclase in the run with the ratio (KCl + NaCl)/(CO$_2$+H$_2$O) = 0.02 (Fig. 6D).

5.2. Experiments at 800 °C

Heating of the biotite-amphibole gneiss at 800 °C without any fluid did not have any influence on the phase assemblage. However, when the sample interacted with the salt-free H$_2$O-CO$_2$ fluid at 800 °C shows distinct glass areas along the contacts of plagioclase and quartz with biotite and amphibole. Glass includes euhedral orthopyroxene and Ti-magnetite crystallites (Fig. 7A). The w(Al$_2$O$_3$) content in the orthopyroxene varies from 1.5% to 2.5%. Melting of the gneiss in presence of the H$_2$O-CO$_2$ fluid at 800 °C produces dactitic melt containing 4%–6% of w(K$_2$O + Na$_2$O) with prevalence of K$_2$O over Na$_2$O (Table 1). It is evident that alkalis in this melt are inherited from the precursor biotite and plagioclase. Voids in the glass formed by fluid bubbles contain quartz, CaCO$_3$, and rare MgCO$_3$ grains imply saturation of the fluid coexisting with the melt with silica and carbonates.

In contrast to 750 °C experiments, melting is extensive in the gneiss upon interaction with H$_2$O-CO$_2$-KCl fluid at 800 °C. Depending on the KCl/(H$_2$O + CO$_2$) ratio in the starting fluid, there is a regular change in mineral assemblages coexisting with the melt. At KCl/(H$_2$O + CO$_2$) below 0.01, pargasite-edenite amphibole (w(Na$_2$O) = 1.4%–1.8% and w(K$_2$O) = 1.0%–1.3%) appears along with orthopyroxene (Fig. 7B). In comparison to the orthopyroxene from the run sample produced with the H$_2$O-CO$_2$ fluid (Fig. 7A), the orthopyroxene coexisting with amphibole (Fig. 7B) shows lower w(Al$_2$O$_3$) content, 0.7%–1.5%, suggesting influence of both alkalis in the fluid/melt (Perchuk and Gerya, 1992, 1993) and amphibole as a concentrator of Al$_2$O$_3$. Both Ti-magnetite and ilmenite are present in the orthopyroxene-amphibole-melt reaction textures in this run sample. At KCl/(H$_2$O + CO$_2$) = 0.014, amphibole and Ti-magnetite disappears from the reaction assemblage, and orthopyroxene coexists with clinopyroxene and ilmenite. Clinopyroxene prevails over orthopyroxene in these reaction textures. At the higher KCl content in the fluid, assemblage clinopyroxene + K-feldspar + ilmenite coexist with the granitic melt (w(SiO$_2$) = 68%–72% and w(Al$_2$O$_3$) = 6%–10%) (Fig. 7C; Table 1). The K$_2$O content in this melt is positively dependent on the KCl content in the starting fluid mixture (Table 1). The K$_2$O/Na$_2$O ratio in the melt varies from 5 to 9 (Table 1), resulting from a strong K-Na exchange between the melt and KCl-rich fluid. In addition to K-feldspar crystallizing directly from the melt, the run samples at 800 °C show extensive K-feldsparization of the contacting plagioclase (Fig. 7C). In contact with biotite and amphibole grains, these K-
feldsparized zones in plagioclase contain clinopyroxene crystals, suggesting that clinopyroxene and K-feldspar can be formed both from the melt and metasomatically. At KCl/(CO₂ + H₂O) ≈ 0.1, intensively K-feldsparized zones of plagioclases along cracks contain minute crystals of kalsilite, Ca-garnet, and calcite assuming low SiO₂ activity in this strongly metasomatized portions of the run samples.

Sequence of the mineral assemblages produced during interaction of the gneiss with the H₂O-CO₂-(K, Na)Cl fluids at 750 °C. Phases formed in the experiments are italicized. (A) Large euhedral crystals of clinopyroxene and K-feldspar formed after biotite and hornblende; sphene appears as minute crystals in the products of biotite decomposition; (B) Localized melting in contacts between hornblende and quartz with formation of potassium-rich melt, clinopyroxene and K-feldspar (small euhedral crystals in the glass); large rounded voids in the glass indicate coexistence of the melt with a free fluid; (C) Extensive melting of the gneiss with formation of K-Na granitic melt, clinopyroxene, plagioclase, and ilmenite (bright acicular crystallites); (D) Na-K-rich amphibole, clinopyroxene, plagioclase crystallizing from the melt formed from interaction of the gneiss with (K, Na)Cl-bearing fluid.

Figure 6  Phase assemblages produced via interaction of the Sand River biotite-amphibole gneiss with the H₂O-CO₂-(K, Na)Cl fluids at 5.5 kbar and 750 °C. Phases formed in the experiments are italicized. (A) Large euhedral crystals of clinopyroxene and K-feldspar formed after biotite and hornblende; sphene appears as minute crystals in the products of biotite decomposition; (B) Localized melting in contacts between hornblende and quartz with formation of potassium-rich melt, clinopyroxene and K-feldspar (small euhedral crystals in the glass); large rounded voids in the glass indicate coexistence of the melt with a free fluid; (C) Extensive melting of the gneiss with formation of K-Na granitic melt, clinopyroxene, plagioclase, and ilmenite (bright acicular crystallites); (D) Na-K-rich amphibole, clinopyroxene, plagioclase crystallizing from the melt formed from interaction of the gneiss with (K, Na)Cl-bearing fluid.

amphibole + ilmenite + melt has been produced at (NaCl + KCl)/(CO₂ + H₂O) = 0.02, while clinopyroxene + ilmenite coexists with a melt at the higher (NaCl + KCl)/(CO₂ + H₂O) ratios.

6. Comparison of the experimental results with the petrological data on the dehydration zone

Experiments demonstrate that interaction of biotite-amphibole gneiss with the H₂O-CO₂-(K, Na)Cl fluids at 750–800 °C is able to produce various mineral assemblages depending on temperature, chloride/(H₂O + CO₂) and KCl/NaCl ratios in the fluid. They additionally prove that partial melting of the Sand River gneiss is...
Table 1: Average compositions of the melts formed during interaction of the Sand River gneiss with H2O-CO2-\((K, Na)Cl\) fluids at 5.5 kbar.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>H2O-CO2</th>
<th>H2O-CO2-(Na, KCl)</th>
<th>H2O-CO2-(Na, KCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>750</td>
<td>800</td>
<td>750</td>
</tr>
<tr>
<td>Chloride/H2O + CO2</td>
<td>0.033</td>
<td>0.014</td>
<td>0.025</td>
</tr>
<tr>
<td>Coexisting phases</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Opx + Ti-Mt</td>
<td>67.78</td>
<td>66.86</td>
<td>66.41</td>
</tr>
<tr>
<td>Opx + Amp + Cpx</td>
<td>7.18</td>
<td>7.18</td>
<td>7.18</td>
</tr>
<tr>
<td>Cpx + Kfs + Ilm</td>
<td>25.05</td>
<td>26.99</td>
<td>27.58</td>
</tr>
<tr>
<td>Total</td>
<td>90.21</td>
<td>91.58</td>
<td>96.56</td>
</tr>
</tbody>
</table>

Increase of temperature up to 800 °C does produce neither dehydration nor partial melting. This observation is consistent with the data by Škjerlie and Johnston (1993), which indicate that the dehydration melting of the tonalitic gneiss with formation of orthopyroxene-bearing assemblages begins above 900 °C.

Resulting mineral assemblages and progress of the partial melting in the gneiss in presence of the H2O-CO2-(K, Na)Cl fluids significantly depends on fluid composition. The KCl-bearing fluids suppress melting, whereas addition of NaCl significantly intensifies this process. There are several possible reasons for this effect of NaCl. Probably, NaCl more actively interacts with biotite in contrast to KCl. Because of local dehydration, such interaction produces more additional water in the fluid increasing its activity and assisting to melting. Moreover, KCl has larger suppressing effect on water activity than NaCl (Aranovich and Newton, 1997).

Melts produced during interaction of the gneiss with the mixed KCl-NaCl fluids are characterized by higher Na2O and Al2O3 contents (Table 1), which surely assist to higher solubility of Cl in the melts (Webster, 1997) and to a progress of the melting process. Different effects of KCl and NaCl on the melting process would assume that initial stages of formation of the dehydration zone within the Sand River biotite-hornblende gneisses manifested by the partial melting were triggered by KCl-NaCl mixed fluids, whereas later metasomatic reactions with formation of the clinopyroxene-K-feldspar coronas in the partially dehydrated gneiss were driven by essentially KCl-rich fluids. Indeed, textural features of the clinopyroxene-K-feldspar assemblage in the gneiss samples interacted with the H2O-CO2-KCl fluids at 750 °C (Fig. 7A), reproducing reaction (4), are remarkably similar to those in the partially dehydrated gneiss in the dehydration zone (Fig. 2B). Thermobarometric data on the clinopyroxene-K-feldspar textures show that they were formed metasomatically at temperatures below 750 °C at higher alkali activity (notably, potassium) in a fluid in comparison to the charno-endibite vein.

Our experiments prove that clinopyroxene-bearing assemblages are characteristic either for temperatures 750 °C (and, possibly, lower) or for high salt concentrations in a fluid. At high KCl content in the fluids they form in absence of a melt (Fig. 7A). In contrast, orthopyroxene-bearing assemblages form at temperature 800 °C in presence of the partial melt and at lower concentrations of salts in the H2O-CO2 fluid (Fig. 7A, B). This conclusion also is in line both with the thermobarometry and the PERPLEX modeling of the charno-endibite vein from the dehydration zone (Fig. 5), which show that the vein was formed at temperatures up to 800 °C during partial melting caused by the H2O-CO2-salt fluid. Textural relations allow assumption that K-feldspar microveins in the charno-endibite vein could represent both metasomatic textures and products of the melt crystallization (Fig. 2A, C). Experiments also show that crystallization of K-feldspar from the melt is accompanied by “metasomatic” replacement of plagioclase (Fig. 7C). Further, PERPLEX modeling of the charno-endibitic vein (Fig. 5) predicts a possibility for coexistence of orthopyroxene and pargasite-edenite amphibole with the partial melt. Present experiments reproduced the orthopyroxene + amphibole assemblage (Fig. 7B) and showed that it was stable with the partial melt at relatively low concentrations of salts in a fluid. Nevertheless, this assemblage did not form in presence of the salt-free H2O-CO2 fluid suggesting that alkalies were determining components in crystallization of the amphibole. This conclusion agrees with the reaction (8) indicating the formation of amphibole in presence of alkali-bearing fluids.
Thus, the present experimental results closely reproduce most of the petrologic data obtained for the dehydration zone within the Sand River gneiss. Therefore, these results could serve as an additional basis for the model for formation of the dehydration zone.

7. Model for formation of the dehydration zone

Petrologic data show that the local dehydration of the Sand River gneisses via channeled fluid migration along shear zones occurred at the retrograde (D3/M3) stage of regional metamorphism in the Central Zone of the Limpopo Complex at about 2.0 Ga. The $p$-$T$ parameters obtained both for the partially dehydrated gneiss GAB-7 (760 ± 30 °C), the transition zone GAB-8 (765 ± 20 °C), and the charno-enderbritic vein (811 ± 6 °C) show that formation of the shear zones, the fluid flux along them and the formation of the charno-enderbritic veins manifested the beginning of this stage (Perchuk et al., 2008; Smit et al., 2011). Fluid inclusion in minerals of the charno-enderbritic vein shows that the fluids streamed through the shear zones contained H$_2$O, CO$_2$ and salt components. Heterogeneous trapping of CO$_2$ and brine inclusions in quartz (Fig. 4) suggests that this fluid consisted of two coexisting phases, CO$_2$-rich fluid and aqueous brine. Coexistence of two fluids, as well as high temperature metasomatism (recorded in K-feldspar microveining) during metamorphism of the Central Zone during both D2/M2 and D3/M3 stages has been previously documented for the rocks from the different areas of the Central Zone (e.g. Hisada et al., 2005; Huizenga et al., 2011).
Following the oblique position of the charno-enderbitic vein with respect to the host rocks (Fig. 1), magmatic-like “monzonitic” textures in the charno-enderbitic vein (Fig. 2A), PERPLEX modeling (Fig. 5), and the experimental results (Fig. 7A–C), we assume that the fluid-rock interaction along the shear zones resulted in formation of the partial melt coexisting with orthopyroxene at temperatures about 800 °C. This melt dissolving aqueous brine left less soluble CO2, which seems to be very inert during this process.

Subsequent cooling from 800 °C down to 700–670 °C at near constant or slightly decreasing pressure 5.4–6.2 kbar resulted in formation of diverse mineral assemblages within the different portions of the dehydration zone. In the charno-enderbitic vein and transition zone, the cooling has been expressed in formation of biotite and/or pargasite-edenite amphibole after orthopyroxene (Fig. 5). In contrast, at the periphery of the dehydration zone this stage is recorded in the formation of localized two-pyroxene-K-feldspar assemblage (670 ± 40 °C). Such outstanding variations in mineral assemblages at close temperatures can be explained only by strong variability of activities of species in fluids circulating within the dehydration zone during the cooling stage. Probably, this variability of fluids was regulated by crystallizing the fluid-saturated granitic melt, which exsolved residual brine and H2O-CO2 fluids. The first portions of the fluid exsolved from the melt at the beginning of crystallization must be saline (Kilink and Burnham, 1972; Webster, 1997). It resulted in formation of a network of K-feldspar microveins and, locally, biotite and amphibole in the charno-enderbitic vein. This saline fluid coexisted with CO2 insoluble in the granitic melt. Mobility of these fluid portions in the gneiss was very different (Watson and Brennan, 1987; Gilbert et al., 1998): the brine fluid would infiltrate the gneiss over larger distances with respect to the CO2-rich fluids. In fact, dense CO2-rich inclusions are usual for the charno-enderbitic vein, but rare or absent in the transition zone and surrounding gneiss. Saline fluid penetrated deep into the gneiss provoked further dehydration under higher alkali activity with the localized formation of the two-pyroxene-K-feldspar assemblage (670 ± 40 °C), while relatively immobile CO2 remained in the close vicinity of the melt vein. Further cooling drove composition of the aqueous fluid toward lower salinity assisting the better mixing with carbonic fluids. Low salinity H2O-CO2 fluid (preserved as secondary fluid inclusions both in the vein and the transition zone) was responsible for formation of the chlorite + calcite + magnetite, cummingtonite (+magnetite) both inside and outside the charno-enderbitic vein below 600 °C.

8. Conclusion

The described dehydration zone within the Sand River gneisses is a wonderful example of local variations of activities of water and alkalis in the course of channelled fluid flux along shear zones. These variations are interplay of the retrograde p-T evolution, fluid heterogeneity of the H2O-CO2-salt fluids, different mobility of brine and CO2-rich fluids in the crystalline matrix, partial melting, and different solubility of fluid species in the melt. As a result, mineral assemblages ranging from granitic (Bt + Kfs + Pl + Qtz) through charno-enderbitic (Opx + Kfs + Pl + Qtz) to monzonitic (Cpx ± Opx + Kfs + Pl ± Qtz) form within the localized zone over centimeter-to-meter volume of rocks. No doubt, that these variations in fluid activity could appear in rocks both on local scale, as observed in the studied dehydration zone, and on regional scale.

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Abbreviations

| Ab  | albite |
| Amp | amphibole |
| An  | anorthite |
| Ap  | apatite |
| Bt  | biotite |
| Ca-Ts | Ca-Tschermack molecule |
| Cpx | clinopyroxene |
| Ed  | edenite |
| Ilm | ilmenite |
| Kfs | K-feldspar |
| Mg-Ts | Mg-Tschermack molecule |
| Mnz | monazite |
| Mt  | magnetite |
| Opx | orthopyroxene |
| Phl | phlogopite |
| Pl  | plagioclase |
| Prg | pargasite |
| Qtz | quartz |
| Sph | sphene |

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