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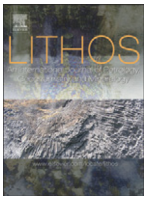

Discussion

Comments on “P–T record of two high-grade metamorphic events in the Central Zone of the Limpopo Complex, South Africa” by L. L. Perchuk, D. D. van Reenen, D. A. Varlamov, S. M. van Kal, Tabatabaeimanesh, R. Boshoff

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1. Introduction

In their latest paper Perchuk et al. (2007) conclude that the Central Zone (CZ) of the Limpopo Belt was subject to two distinct high-grade tectono-metamorphic events, during the Neoarchean at about 2.6 Ga (D2/M2) and during the Paleoroterozoic at 2.0 Ga (D3/M3), and that both events are reflected by different retrograde P–T paths, which can be distinguished on the basis of a petrological method presented by the authors. Based on their results Perchuk et al. (2007) conclude that all rocks throughout the CZ (an area more than 300 km long and 200 km wide) experienced a decompression-cooling path (DC1) from 900 °C/$P<9$ kbar to 600 °C/5 kbar during the Neoarchean, and then remained in the middle crust for the next 600 million years (from 2.6 Ga to 2.0 Ga). Subsequently, during the Paleoproterozoic, all these rocks underwent isothermal heating from 600 °C to 750–800 °C at 5.5–6 kbar followed by a second decompression-cooling path (DC2) from 800 °C/6 bar to 570–600 °C at 4.5–3.5 kbar. According to the authors these petrological results are in agreement with published structural, petrological and geochronological data. In our reply, we demonstrate that the tectono-metamorphic history presented by Perchuk et al. (2007) is oversimplified, based on incorrect assumptions, and ignores deviating data published by other working groups. Furthermore we show that the petrological method introduced by Perchuk et al. (2006, 2007), and in a number of previous papers (e.g. van Reenen et al., 2004; Boshoff et al., 2006; Hisada et al., 2005) is inadequate when constraining detailed retrograde metamorphic P–T paths for high-grade rocks.

2. Method

2.1. Estimation of reliable P–T–aH_2O conditions

The method used by Perchuk et al. (2006, 2007) is based on microstructural evidence and requires that P–T–aH_2O conditions can be inferred and calculated for a large number of local mineral equilibria, which were successively established during the retrograde P–T evolution in a certain mineral assemblage (e.g. Grt–Crd–Bt–Sill–Ksp–Qtz–H_2O, or Grt–Opx–Crd–Bt–Qtz–H_2O). The authors state: “we can confidently estimate the parameters at the beginning (equilibria of porphyroblast) and the end (mostly reaction textures) of a specific P–T path, while the uncertainties might be hidden in the rest of the path. However, using data from Table A4, we can calculate both the pressures and compositions of coexisting Fe–Mg minerals in the presence of garnet for a given local equilibrium at T and X_{Mg}^{Grt} (by using principles of classical equilibrium thermodynamics of solid solution). For example, many high-grade aluminous gneisses that belong to the system SiO_2–Al_2O_3–MgO–FeO–K_2O–H_2O are characterized by zoned garnet coexisting with biotite and cordierite…”. In order to estimate the P–T–X conditions at the beginning of the P–T evolution Perchuk et al. (2007) used two fundamental assumptions: (i) that garnet (cores), cordierite and biotite porphyroblasts formed an equilibrium assemblage at the beginning of the retrograde P–T history, and (ii) that the chemical equilibrium that existed among these three minerals at the metamorphic peak is still preserved in some of the investigated rocks (at least in the cores of the porphyroblasts).

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In their first assumption Perchuk et al. (2007) state that the peak metamorphic assemblage in most of their samples was Grt–Bt–Crd–Sill–Ksp–Pl–Qtz (sample TOV13 — Mount Shanzi; 06-19 — Campbell; T18, T73 — Baklykraal). However, cordierite was observed as primary inclusions in garnet porphyroblasts only in the opx-bearing, Mg-rich (MgO = 17.90 wt.%) sample JC1. Thus, the assumption that cordierite belongs to the peak metamorphic mineral assemblage of opx free, Mg-poor samples such as TOV13 (MgO = 4.30 wt.%), T18 (MgO = 1.43 wt.%), T73 (MgO = 5.44 wt.%) and 06-19 (MgO = 7.30 wt.%) is not supported by microstructural evidence, and therefore it is likely that cordierite in these rocks was not present at the metamorphic peak but formed during the retrograde *P–T* evolution. This, for example, is demonstrated by Zeh et al. (2004) and more recently by Millonig et al. (2008), who investigated metapelitic rocks (of similar composition) from different parts of the Limpopo Belt by using quantitative phase diagrams (i.e. *P–T* pseudosections) to explain mineral assemblages, modes and compositions (see Fig. 9 and 10 in Zeh et al., 2004, and Fig. 7 in Millonig et al., 2008). In fact, the application of the "*P–T* pseudosection method" well demonstrates that the upper limit of the cordierite stability depends on the bulk rock composition, mainly on X_{Mg} = (Mg/Mg + Fe). In metapelitic rocks with high X_{Mg} cordierite forms at higher pressures (and coexisting cordierite and garnet have higher X_{Mg}) than in those rocks with lower X_{Mg}, even if the final assemblage is identical (e.g. Grt–Bt–Crd–Sill–Ksp–Pl–Qtz). In fact, such a correlation is well reflected by the samples investigated by Perchuk et al. (2007). For example, the authors get different starting *P–T* conditions for the metapelite sample TOV13 from Mount Shanzi (P = 8.2 kbar, T = 856 °C; X^{Grt}_{Mg} = 0.53, X^{Crd}_{Mg} = 0.84) and sample 06-19 from the Campbell structure (P = 4.99 kbar, T = 697 °C, X^{Grt}_{Mg} = 0.27 X^{Crd}_{Mg} = 0.72), which are located only a few kilometres apart. Thus, instead of polymetamorphism, as pertained by the authors based on the *P–T* paths obtained from Mount Shanzi and the Campbell structure, the different *P–T* vectors rather reflect the situation that due to variations in the bulk rock composition retrograde cordierite formation in these rocks started at different *P–T* conditions during one and the same retrograde *P–T* evolution. In this context, it must furthermore be pointed out that the bulk composition presented by Perchuk et al. (2007) for the Mount Shanzi sample (TOV13) cannot be representative for the thin section investigated from the same sample (see Table 1, in Perchuk et al., 2007). The reason being that the "cores" of all the Fe–Mg minerals (cordierite, biotite and garnet) investigated from sample TOV13 have X_{Mg} values that are larger than that of the bulk rock (bulk rock X_{Mg} = 0.5; X^{Crd}_{Mg} = 0.84–0.85; X^{Grt}_{Mg} = 0.51–0.53; X^{Bt}_{Mg} = 0.691–0.71, see Tables 1 and 2, in Perchuk et al., 2007). That cannot be the case when assuming that all three minerals were in a chemical equilibrium at peak metamorphic conditions.

Their second assumption claiming a chemical equilibrium between all Fe–Mg porphyroblast cores is also unlikely. Even if the mineral assemblage Grt–Crd–Bt–Sill–Bt–Ksp–Qtz was present at the metamorphic peak, the Fe–Mg composition of biotite must have changed during the retrograde evolution, due to diffusive Fe–Mg exchange between garnet-(rims), cordierite and biotite, and due to mass balance constraints. Since the diffusivity of Fe–Mg couples in biotite is much faster than in garnet and cordierite ($D^{Bt}_{FeMg-1} \gg D^{Crd}_{FeMg-1} > D^{Grt}_{FeMg-1}$; see Spear, 1993; page 612), compositional zoning of individual biotite flakes and adjacent biotite crystals will be smoothed out quickly (in particular at high-grade metamorphic conditions), whereas garnet will develop a pronounced retrograde zoning. These facts are well known and described in detailed by Spear (1989, 1993); Florence and Spear (1991); Spear and Florence (1992); Zeh et al. (1997). These authors also show that the X_{Mg} of biotite inclusions in garnet will also be reset, and cannot be used to obtain metamorphic peak conditions, as done by Perchuk et al. (2007). In fact, the minerals in the rocks investigated by Perchuk et al. (2007) have indeed undergone "differential" diffusion as is reflected by the relatively small variations of $X^{Biotite}_{Mg}$ (and $X^{Cordierite}_{Mg}$) in contrast to X^{Garnet}_{Mg} (see Tables 2, 3; and Figs. 8 and 9). Therefore, the calculated pressure and aH$_2$O in Tables 2 and 3 of Perchuk et al. (2007) simply reflect the change of X^{Grt}_{Mg} of the garnet zoning.

In addition to the diffusive overprint, the composition of biotite and cordierite must have changed during the retrograde *P–T* evolution due to mass balance constraints. In fact, garnet will be resorbed (consumed) during the retrograde *P–T* evolution (see Figs 4, 7 and 8 in Perchuk et al., 2007), whereas biotite and cordierite are formed (produced). Since $X^{Crd}_{Mg} > X^{Bio}_{Mg} > X^{Grt}_{Mg}$, the garnet resorption causes the newly formed biotite and cordierite to successively obtain a lower X_{Mg}. Furthermore the Fe–Mg diffusivity in biotite is fast, thus the Fe–Mg exchange with previously formed (peak metamorphic) cordierite and biotite will occur quickly. It is thus highly unlikely that either matrix biotite or biotite inclusions in garnet have preserved peak metamorphic compositions as suggested for the investigated rocks (see Perchuk et al., 2007).

In addition to biotite, also the core composition of garnet porphyroblasts can be modified by diffusion processes, depending on the garnet size, cooling rates and some other parameters, which are summarized in the Dodson equation (see Dodson, 1973; Florence and Spear, 1991; Ehlers et al., 1994; Zeh et al., 1997). Commonly, modified garnet cores show round X_{Mg} zoning profiles and the absence of a pronounced compositional plateau (as is shown by the profile in Fig. 5e, Perchuk et al., 2007). Consequently, if the garnet core compositions are used to constrain peak metamorphic conditions, it must be shown that garnet does not contain relics of a prograde growth zoning, as was observed for garnet from some of the high-grade metapelite rocks from the Central Zone in the Messina area (Zeh et al., 2004).

2.2. Estimation of the retrograde P–T path using zoned minerals

As a prerequisite for the calculation of their retrograde *P–T* paths, Perchuk et al. (2007) assumed that zoned garnet coexists with biotite and cordierite. However, the problems associated with this approach are that (i) garnet will be consumed during the retrograde *P–T* evolution (see contour *P–T* diagrams in Zeh et al., 2004, Fig. 10) while biotite and cordierite are formed, and (ii) that the biotite/cordierite and garnet zoning have different origins. In fact, cordierite and biotite may produce a retrograde growth zoning pattern (if not erased quickly by volume diffusion), whereas garnet develops a diffusion zoning pattern, which is always characterized by decreasing X_{Mg} toward the garnet rim (indicative for decreasing temperatures; see Fig. 9 in Perchuk et al., 2007). In addition, Perchuk et al. (2007) do not take into account that during volume diffusion, only the outermost garnet rim is in equilibrium with the surrounding matrix (e.g. with cordierite and biotite), whereas the rest of the garnet porphyroblast is always in disequilibrium and, thus, its composition cannot be used to constrain retrograde *P–T* conditions. In fact, a garnet zoning profile produced by diffusion is an integral product of diffusive Fe–Mg exchange between garnet and surrounding Fe–Mg minerals (e.g. biotite, cordierite) over the whole time of diffusive overprint, which starts after garnet growth ceased (may be at the metamorphic peak) and proceeds down to ca. 400 °C, the blocking temperature for Fe–Mg diffusion in garnet (c.f. Florence and Spear, 1991). Since the retrograde garnet zoning profile results from kinetic effects, the "principles of classic thermodynamics" cannot be used to derive *P–T* paths or calculate equilibrium mineral compositions, as done by Perchuk et al. (2006, 2007). In general, each X_{Mg} garnet diffusion zoning will reflect decreasing temperature. However, the form of the garnet diffusion zoning is relatively independent of the pressure evolution, but strongly depends on the cooling history, the garnet size, and the modal amounts of garnet and biotite in the respective rock (see Robl et al., 2007). Thus, pressures and aH$_2$O calculated on the basis of measured X^{Grt}_{Mg} diffusion zoning profiles (Tables 2, and 3) are meaningless according to thermodynamic principles.

The shape (slope) of the retrograde *P–T* paths presented by Perchuk et al. (2007) strongly depends on the final *P–T* point, which always reflects the lowest *P–T* conditions. The authors postulate that these minimum *P–T* conditions can be obtained from the composition