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On the importance of minding one's *P*s and *T*s: metamorphic processes and quantitative petrology

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ABSTRACT This Special Issue comprises a selection of the papers given at a two-day discussion meeting held at the University of Melbourne, Australia in June 2009 to celebrate Roger Powell's 60th birthday. At this milestone, it is fitting to review Roger's career to date. He has published ~200 scientific papers on topics that range from low- to high-grade metamorphism, from low- to ultrahigh-pressure (UHP) metamorphism, and from thermodynamics to kinetics. Most of Roger's papers are multi-authored and address important questions in the petrogenesis of metamorphic rocks. Roger is widely known for his work with Tim Holland to develop the most complete internally consistent dataset of thermodynamic properties of end members of phases necessary to undertake calculations on the conditions of formation and modification of metamorphic rocks. Additionally, Roger and Tim have developed activity–composition models for many of these phases, building on their important methodological developments in formulating such models. Roger is also responsible for the ongoing development of THERMOCALC, a thermodynamic calculation software package that may be used to undertake a wide range of phase diagram calculations, including *P–T* projections, *P–T*, *P–X* and *T–X*, compatibility diagrams and μ–μ diagrams. Together, Roger and Tim have changed the way we carry out quantitative phase equilibria studies. However, Roger's contributions to metamorphic petrology go well beyond the development of phase equilibria methods and mineral thermodynamics. He has contributed significantly to our understanding of a range of metamorphic processes, and with an extensive array of co-authors has shown how phase equilibria can be used to understand the evolution of metamorphic rocks in general terms as well as in specific terranes. The papers in this Special Issue cover the range from the stabilization of the continents to understanding the formation of orogenic gold deposits, from the stability of sapphirine–quartz-bearing assemblages to the crystallization of melt in migmatites, from the effects of ferric iron and sulphur on the stability of metamorphic mineral assemblages in general to the effects of ferric iron and H_2O on the stability of eclogite in particular, and to the quantification of UHP metamorphism. It is our hope that in reading these contributions, you will be stimulated to seek a better understanding of metamorphic processes and to improve our quantification of the variables in metamorphism.

Key words: continents; eclogite; migmatite; orogenic gold; phase equilibria.

PREAMBLE

It is our pleasure to introduce the papers in this Special Issue, which celebrates the 60th birthday of our editorial colleague, Roger Powell in June 2009. Figure 1 shows Roger relaxing a few weeks before the meeting. It is a good thing to relax from time to time after publishing close to 200 scientific papers and one of the more-readable books on thermodynamics (Equilibrium Thermodynamics in Petrology, London, Harper & Row, available as a pdf at: http://www.metamorph.geo.uni-mainz.de/thermocalc/).

In many respects, Roger's contributions can be summarized simply using data from the Web of Science. His scientific papers have accrued more than 10 000 cites, with 20 of these cited more than 100 times and two of those cited more than 1000 times. Roger has an h-index of 49 and his contributions were cited more than 1000 times in 2009. Not a bad achievement by one's 60th year! It will be interesting to review these data on the occasion of Roger's 70th birthday.

Most of Roger's papers are multi-authored and address important questions in the petrogenesis of metamorphic rocks. In particular, he has worked closely with Tim Holland in developing quantitative tools for petrological research. Although his work with Tim Holland has been at the core of Roger's phase equilibria endeavours, he has published papers with

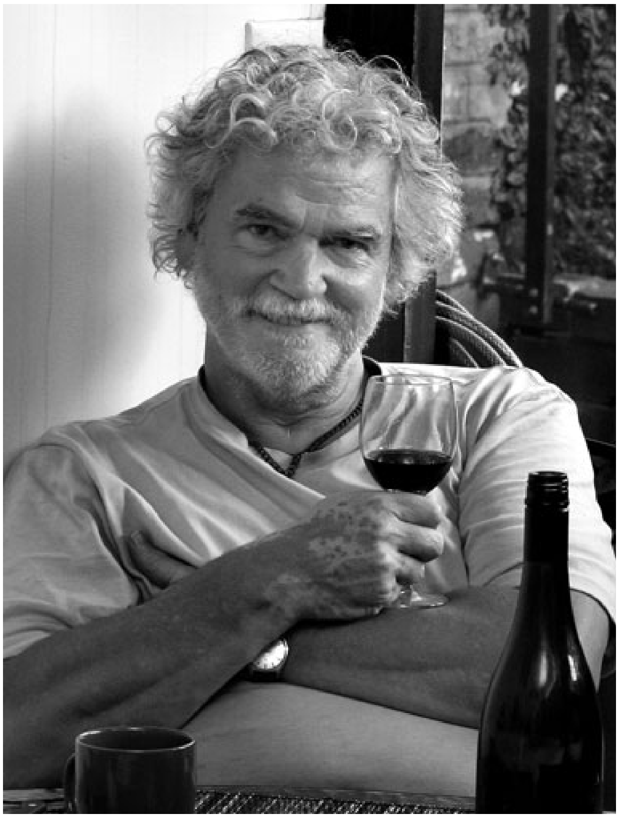

Fig. 1. Roger relaxing before the meeting in Melbourne in 2009.

close to 100 co-authors ranging from senior academics to students. Through his mentoring of honours and doctoral students, postdoctoral research associates and research visitors from around the world his impact extends far beyond the systematics of citation data. Those who have worked with Roger in Melbourne will remember fondly the many interesting and thought-provoking scientific discussions at lunch that were typically accompanied by an equally interesting and thought-provoking bottle of wine!

The papers in this issue reflect this collaborative approach to science. Roger is a co-author on six of the eight papers (with the co-authors ranging from honours student to senior academic), and he has published with the authors of the other two papers in the past. These eight papers cover the stabilization of the continents, the formation of orogenic gold deposits, the stability of sapphirine–quartz-bearing assemblages, the crystallization of melt in migmatites, the effect of ferric iron and sulphur on the stability of metamorphic mineral assemblages in general, the effects of ferric iron and H_2O on the stability of eclogite in particular, and the quantification of ultrahigh-pressure (UHP) metamorphism. These are all topics in which Roger has made a significant contribution, though they represent a small fraction of the various aspects of metamorphism in which Roger has worked. We hope that in reading them we will all take the time to think about what has been achieved in the past 40 years, and use this as a motivating force for what remains to be done.

ROGER AND QUANTITATIVE PHASE EQUILIBRIA STUDIES

Since completing his D.Phil at Oxford University in 1973, Roger has made an outstanding contribution to metamorphic petrology as attested to by the citation data quoted above. However, it is Roger's ongoing collaboration with Tim Holland, which began in the early 1980s, that has changed the way the rest of us carry out quantitative phase equilibria studies.

The collaboration with Tim has produced the most complete dataset of thermodynamic properties of end-members of the phases required to perform calculations on the conditions of formation of rocks and their interactions with fluids and melts. Such a dataset is a necessary first step in developing a quantitative understanding of chemical reaction among minerals, fluids and melts. The Holland & Powell (1998) dataset is internally consistent, meaning that all of the available information has been evaluated and combined statistically (in a least squares sense), yielding uncertainties and correlations. This allows the uncertainties on any thermodynamic calculations to be computed. However, quantitative phase equilibria studies require more than just an internally consistent thermodynamic dataset, and among several advances introduced by Roger and Tim the development of sophisticated thermodynamic models to treat non-ideal mixing properties of phases of interest stands out. A thermodynamic dataset and the activity–composition models must evolve or their usefulness will diminish. Roger and Tim have been indefatigable over the last two decades in increasing the range of entries in the dataset, refining the quality of the data and improving the activity–composition models.

Given the complex nature of phase equilibria calculations, the provision of the program THERMOCALC was critical to enable the rest of us to undertake these calculations with minimum training. The breadth of Roger's phase equilibria research interests has been central to the development of THERMOCALC, which has evolved from a tool with which to consider metamorphism in a largely theoretical way to a methodology that is far more directly applicable to rocks. THERMOCALC is a thermodynamic calculation software package that is used to undertake a wide range of phase diagram calculations, including P–T projections, P–T, P–X and T–X pseudosections, compatibility diagrams, and μ–μ diagrams. The large number of studies that now use quantitative phase diagrams to constrain peak P–T conditions, P–T paths, the interpretation of metamorphic microstructures and metamorphic processes is in large part due to the progress that Roger and his co-workers have made. It has been the simultaneous development of THERMOCALC, activity–composition relationships, different types of diagrams, application to metamorphic processes and the application to specific rocks that has made Roger's work so influential, and has enabled researchers throughout the world to make unprecedented advances in understanding the petrogenesis of metamorphic rocks.

METAMORPHIC PROCESSES AND QUANTITATIVE PETROLOGY: AN INTRODUCTION TO THE INDIVIDUAL PAPERS

In the light of his prodigious output on metamorphic phase equilibria studies, it is easy to forget that one of Roger's early papers, with his D.Phil supervisor Steve Richardson, focused on the thermal causes of metamorphism (Richardson & Powell, 1976). After moving to Australia in the 1980s, this theme was central to his collaboration with Mike Sandiford (e.g. Sandiford & Powell, 1986, 1990, 1991) who in the first paper asks 'Why are the continents just so...?' (Sandiford, 2010). This is important because the continents have not always been 'just so'. It has been argued that secular cooling of the Earth's mantle and the growth of the continental crust imply changes in the isostatic balance between continents and oceans, and that greater radiogenic crustal heat production and mantle heat flow during the Archean reduced the strength of the continental lithosphere, limiting crustal thickening (Sandiford, 1989; Flament *et al.*, 2008; Rey & Coltice, 2008). Indeed, it seems possible that during the Mesoarchean–Neoarchean as the continental lithosphere was stabilized, it passed through a rheological threshold, allowing for the development of one-sided subduction and significant topography (Rey & Coltice, 2008; Sizova *et al.*, 2010). Sandiford's paper explores the possibility that the emergence of a chemically, thermally and mechanically structured continental lithosphere reflects a set of thermally sensitive feedback relations that develop in response to plate tectonic forcing about an ambient stress state set by the mid-ocean ridge system. This paper follows on from earlier work with Sandra McLaren on tectonic feedback and the ordering of heat-producing elements within the continental lithosphere (Sandiford & McLaren, 2002), and links with even earlier ideas first developed with Roger that explored the role of gravitational potential energy in linking the thermal and mechanical evolution of metamorphic belts (Sandiford & Powell, 1991). It is likely that the continents have evolved to become 'just so' since the Neoarchean, in keeping with the emergence of one-sided subduction, as reflected in the development of paired metamorphic systems since the Neoarchean (Brown, 2006, 2007), and other significant changes to the Earth System across the Archean–Proterozoic boundary (e.g. Reddy & Evans, 2009).

Processes relating to crystallization of melt in veins in residual granulites and migmatites are not well understood, but have long been of interest to Roger (e.g. Powell, 1983a,b; Fig. 2). On the one hand, melt loss appears to be a requirement in many cases before final crystallization of the last dregs of liquid (e.g. Brown, 2002; White & Powell, 2002), but on the other hand, metamorphic core complexes in the Canadian Rockies provide evidence – in the form of uniformity of mineral $\delta^{18}O$ values – for recycling of hydrous fluid exsolved during melt ascent (Holk & Taylor, 2000). The role that diffusion, particularly of H_2O, may have in the formation and modification of migmatites was discussed by Roger in the early 1980s (Powell, 1983a), where diffusion between segregated melt and the residue would occur as a consequence of differences in $a(H_2O)$. In a recent paper, this type of process was raised by Rubatto *et al.* (2009), who argued for multiple fluid-induced melting events in migmatite leucosomes based on several episodes of short-lived zircon growth, each episode of zircon growth recording rapid crystallization of melt driven by gradients in $a(H_2O)$.

In the second paper in this Special Issue, White & Powell (2010) investigate in a quantitative manner the

Fig. 2. Roger at a 1-day symposium on 'Fluids in Metamorphism' in 1982. From left to right the individuals in the photograph are: John M. Ferry, Kenneth R. Grieg, Bruce W.D. Yardley, Colin M. Graham, Doug Rumble, Arny E. Sveinbjornsdottir, Michael Brown, Roger Powell, Jacques Touret, Vic J. Wall, Bernard E. Leake and Alan B. Thompson.

development of gradients in chemical potential between melt-rich domains and host residue as considered qualitatively in Powell (1983a). In particular, as temperature declines, the chemical potential of H_2O becomes higher in the melt-rich domains than in the host, particularly when biotite enters the assemblage in the host. This promotes diffusion of H_2O from the melt to the host, which in turn drives crystallization of anhydrous products from the melt and hydrous products in the host. Diffusion of H_2O into the residue may be in part responsible for the commonly anhydrous nature of leucosomes, especially in granulite facies migmatites. If H_2O can diffuse between the melt-rich domains and the entire host, then formation of a selvedge between the two is unlikely. Alternatively, if diffusion of H_2O between melt-rich domains and the host is spatially limited, then a selvedge may form. Finally, White & Powell (2010) posit that crystallization of melt via the diffusion of H_2O into the host may drive melt-bearing horizons in orogenic belts across a critical rheological transition expelling any remaining melt from the system.

The importance of oxidation state to mineral stability has been known for a long time (e.g. Chinner, 1960; Ganguly, 1968, 1969, 1971; Caporuscio & Morse, 1978; Hensen, 1986; Clarke *et al.*, 1989; White *et al.*, 2000), and the need to develop phase equilibria methods that consider ferric iron explicitly has long been of interest to Roger. However, ferric iron is commonly not determined during routine analysis of rocks and minerals, and indeed it requires considerable effort to obtain precise and accurate analyses for ferric iron in both cases. For this reason, ferric iron either is commonly ignored or it is included in thermobarometric calculations and phase equilibria modelling by assigning some proportion of the total iron in the bulk composition as ferric or by assessing the proportion of ferric iron in a mineral analysis by charge balance as part of a recalculation protocol.

In the first of three papers that address the effects of ferric iron on mineral equilibria, Diener & Powell (2010) undertake calculations in the Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O–TiO_2–O (NCKFMASHTO) chemical system for mafic and pelitic rock compositions that explicitly account for ferric iron and examine its effect on phase relations in rocks. In principle, their results may be inverted to estimate the oxidation state of rocks. In a novel application, these authors show that ferric iron significantly increases the stability of corundum + quartz to lower *P–T*, making it possible for this assemblage to exist in oxidized rocks of appropriate composition at crustal conditions.

Based on phase relations in the FeO–MgO–Al_2O_3–SiO_2 (FMAS) chemical system (e.g. Bertrand *et al.*, 1991; Harley & Motoyoshi, 2000), coexisting sapphirine + quartz in granulites increasingly has become regarded as a definitive assemblage characteristic of ultrahigh-temperature metamorphic conditions (UHTM) – by convention >900 °C – in spite of a

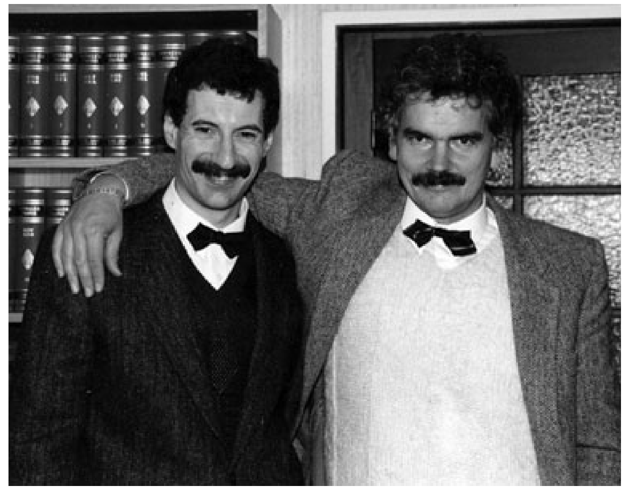

Fig. 3. Michel Guiraud and Roger during Michel's habilitation celebration in Paris in 1990.

cautionary note about the effect of ferric iron on the stability of this assemblage in Baldwin *et al.* (2005). Indeed, it is well known that high oxygen fugacity increases the stability of sapphirine + quartz to lower *P–T* (e.g. Caporuscio & Morse, 1978; Hensen, 1986; Powell & Sandiford, 1988).

In the second of these three papers, Taylor-Jones & Powell (2010) develop a new thermodynamic model for sapphirine that includes Fe_2O_3. Using calculated phase diagrams for quartz-saturated systems in the FeO–MgO–Al_2O_3–SiO_2–O (FMASO) and FeO–MgO–Al_2O_3–SiO_2–TiO_2–O (FMASTO) chemical systems, Taylor-Jones & Powell (2010) show that Fe_2O_3 and TiO_2 have a considerable effect on the phase relations relative to the simpler FMAS chemical system. In oxidized systems, the stability field of sapphirine + quartz assemblages may extend down temperature to as low as 850 °C. Thus, in the absence of any qualification concerning the oxidation state of a rock, the sapphirine + quartz assemblage is not necessarily diagnostic of UHTM conditions.

The role of fluids has been a long-standing interest of Roger's (Fig. 2) and the range of behaviour relating to the preservation of peak mineral assemblages for fluid-undersaturated *v.* fluid-saturated conditions was a topic addressed by Michel Guiraud and Gisella Rebay together with Roger at the turn of the millennium (Guiraud *et al.*, 2001). Figure 3 shows Michel Guiraud with Roger, his doctoral advisor, celebrating Michel's successful habilitation in 1990 in Paris.

In the third paper of this group, Rebay *et al.* (2010) consider the effect of ferric iron and H_2O content on the stability of common low-temperature eclogite (garnet + omphacite $>70\%$ of the mode; <600 °C). These authors use calculated phase equilibria for a single MORB bulk rock composition in the NCKFMASHTO chemical system to see under what conditions of pressure (*P*), temperature (*T*), H_2O

Fig. 4. Geoff Clarke, Chunjing Wei and Roger in the Dabieshan in 2004.

content and oxidation state common eclogite is predicted to occur. These authors show that although oxidation state does have a strong effect on mineral assemblage stability, the key controls on developing the predominantly garnet + omphacite assemblage typical of common low-temperature eclogite are temperature and H_2O content. For the predominantly garnet + omphacite assemblage typical of common low-temperature eclogite (< 600 °C) the H_2O content must be less or much less than that required for H_2O saturation. For much of the eclogite stability field at < 600 °C and pressures less than coesite stability, lawsonite eclogites and common low-temperature eclogites are mutually exclusive with regard to H_2O content with the lower-temperature lawsonite eclogites requiring higher H_2O contents.

Since the first reports of coesite as inclusions in garnet and omphacite in eclogite from the Dabieshan in the late 1980s (Okay *et al*., 1989; Wang *et al*., 1989), the metamorphic evolution and the mechanism of exhumation of these rocks have been foci for research. Indeed, to demonstrate that he is not as tied to his computer as some people think, Roger visited the Dabieshan with Geoff Clarke at the invitation of Chunjing Wei (Fig. 4). In this issue, Wei *et al*. (2010) investigate the metamorphic evolution of glaucophane-bearing UHP eclogites from the western Dabieshan terrane using a combination of petrographic observations and pseudosections calculated in the Na_2O–CaO–K_2O–MnO–FeO–MgO–Al_2O_3–SiO_2–H_2O–TiO_2–O (NCKMnFMASHO) chemical system. These authors consider the metamorphic evolution in four stages. The prograde stage, which is dominated by the release of ~27% of the H_2O bound in hydrate minerals, is characterized by an early *P–T* path segment dominated by heating with only a slight increase in pressure before evolving to a segment dominated by an increase in pressure with only slight heating, suggesting an evolution from slower to faster subduction. The assemblage around the peak stage is garnet + omphacite + lawsonite + talc + phengite + coesite ± glaucophane ± kyanite, which yields peak *P–T* conditions of 2.8–3.2 GPa at ~610 °C. An early decompression stage is characterized by breakdown of lawsonite, releasing ~70–90% of the H_2O bound in the peak hydrate minerals, which results in growth of glaucophane and epidote. And a later retrograde stage is characterized by the development of hornblende + epidote + albite/oligoclase + quartz assemblages at the margins of eclogite blocks owing to fluid infiltration at *P–T* conditions of 0.5–1.0 GPa at 500–580 °C.

The final two papers in this issue concern fluids and gold deposits, topics that have attracted Roger's attention on and off over the years (e.g. Powell, 1983a; Powell *et al*., 1991; Phillips & Powell, 1993; Guiraud *et al*., 2001; White *et al*., 2003). Evans *et al*. (2010) are concerned with the effects of sulphur on mineral stabilities under greenschist facies conditions. Sulphur is ubiquitous in the Earth, and it has multiple valence states that allow it to participate in many geochemical processes; in crustal rocks, it is common as sulphide or sulphate minerals. To advance thermodynamic modelling of geochemical processes involving sulphur, Evans *et al*. (2010) have augmented the Holland & Powell (1998) dataset to include thermodynamic data for sulphides, anhydrite, H_2S, elemental S and S_2 gas. Using the new dataset, these authors construct pseudosections for mafic greenschist facies rocks from the Golden Mile, Kalgoorlie, Western Australia. The observed sequence of mineral assemblages, including the sulphide and oxide phases, in rocks affected by interaction with an infiltrating fluid is predicted to be stable at increasing $X(CO_2)$ as the degree of hydrothermal alteration increases. Increasing $X(CO_2)$ stabilizes successively pyrite–magnetite, pyrite–hematite and anhydrite–pyrite, and magnetite–pyrrhotite is predicted at temperatures greater than 410 °C. For a rock of fixed bulk composition, the prediction of a variety of sulphide and oxide phases as a function of changes in fluid composition and temperature is of particular interest because it refutes the proposal that such variation is produced by the infiltration of multiple fluids with contrasting redox state (see also Evans *et al*., 2006; Evans, 2010).

In the last paper, Phillips & Powell (2010; see also Phillips & Powell, 2009) consider the enrichment, segregation, timing, distribution and character of many goldfields, such as those found in Archean greenstone belts, to be explained by a model in which metamorphic devolatilization of hydrated and carbonated greenschist facies metabasic rocks across the greenschist–amphibolite facies boundary extracts H_2O, CO_2, S and Au. Elevated gold in solution is achieved by complexing with reduced sulphur and by buffering near the optimal fluid pH for gold solubility (Phillips & Evans, 2004).

Migration of this syn-metamorphic fluid occurs via shear zones and/or hydraulic fracture systems, where the geometry of the system determines the degree of fluid focusing into volumes small enough to form economic accumulations of gold. Gold deposition is facilitated by reduction of the fluid by contact with appropriate host rocks and/or by sulphidization of wall rocks, and is commonly accompanied by alteration where the host rock is of suitable bulk composition (e.g. White *et al.*, 2003). The correlation of major gold deposits with rock type, even where the gold is primarily in veins, argues for rock-dominated, not fluid-dominated, depositional systems (Evans *et al.*, 2006). As a consequence, a general role for mixing of multiple fluids, or temperature and/or fluid pressure decrease and boiling is unlikely (Evans *et al.*, 2010).

FINAL REMARKS

It has been our enjoyable task to edit this Special Issue of the *Journal of Metamorphic Geology* in celebration of the Roger Powell's 60th birthday last year. Roger has made a significant contribution not only to metamorphic geology in general, but specifically to the *Journal of Metamorphic Geology*, through his extensive publications and his efforts as a reviewer and editor. We end with two wishes. First, that Roger continues to publish stimulating papers that advance both the methodologies available to us in our studies of metamorphic rocks and the understanding of metamorphic processes. Second, that this set of papers stimulates a continued resurgence of metamorphic studies, for without information about the burial, residence at depth and exhumation of rocks we cannot constrain orogenic processes.

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