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THERMODYNAMIC MODELLING OF METAMORPHIC PROCESSES: STATE OF THE ART IN PSEUDOSECTION APPROACH

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Understanding global-scale orogenic processes related to supercontinents, and their relationship to the secular evolution of the Earth's lithosphere, represent important challenges for Earth scientists today. The record of these processes is preserved in the microstructures, mineral assemblages and mineral compositions of lithospheric rocks exhumed to the Earth's surface. Given a well-characterized microstructural evolution, thermodynamic modelling is the key to quantifying changes in pressure and temperature, with the rate of these changes being provided by rock-forming and accessory mineral-based geochronology. Thus, metamorphic rocks provide Pressure–Temperature–time–deformation (P–T–t–d) data that help to parameterize orogenic processes.

Introduction

Equilibrium thermodynamics provides the formal mathematical framework that links measurable variables (whole rock or domainal compositions, mineral and fluid/melt inclusion compositions) with intensive variables (pressure, temperature and chemical potentials). This approach comprises the field of thermobarometry (e.g. Powell and Holland, 2008). Thermobarometry has evolved significantly in the last twenty-five years with the development of internally consistent thermodynamic datasets and sophisticated thermodynamic mixing models for phases of interest. These advances have enabled the calculation of equilibrium phase diagrams for complex chemical systems, close to those in nature, for a diversity of variables. Such diagrams are called pseudosections for the reasons given by Powell et al. (1998; 2005). Critically, inverse modelling using pseudosections allows using all available compositional information for both, the system and the individual minerals, which is not the case for conventional thermobarometry, where the chemical system is largely ignored. This development represents one of the most important advances of modern metamorphic petrology. The numerical modelling of phase relations requires a set of thermodynamic data for end-members, a description of the activity-composition (a-x) relations (the solid- or liquid-solution models) and a software to perform calculations.

The utility of pseudosection is that they permit natural observations, and interpretations from thin sections, to be explained in terms of the evolving P–T conditions, within the context of a structural evolution, and from place to place. When combined with petrologically-linked age data (i.e. petrochronology; cf. Kohn et al., 2017), the resulting P–T–t–d paths provide essential input into constraining the processes involved in mountain-build-

ing and the evolution of continental lithosphere (e.g. Brown, 2014; Fig. 1).

Despite these advances, there remain considerable uncertainties in both, the thermodynamic framework used (end-member thermodynamics and a-x models) and more importantly, in estimating the volume of equilibration and changes in rock composition during metamorphism. These issues require the approach to be used with care. Thus, the results of any calculations are best viewed as an independent theoretical framework in which to interpret a rock rather than an exact reproduction of its evolution (White et al., 2014).

Thermodynamic modelling of petrological systems is only a tool, but because the pseudosection approach uses the maximum amount of available information, it is extremely useful and, today is an essential tool in the parameterization of metamorphic histories.

From inverse to forward modelling: a short review

Knowledge on thermodynamics is a key to understand physicochemical changes occurring in Earth's lithosphere, producing metamorphic rocks. All systems naturally tend to the minimum energetic configuration, i.e. equilibrium. Chemical equilibrium implies no change over time. Thus, equilibration conditions attained by a mineral assemblage would preserve the characteristics of the phases involved in the system at a certain moment, e.g. the P–T formation conditions of a metamorphic rock. As soon as the conditions (e.g. P or T) change, the system will immediately tend to a new equilibrium state. However, since diffusion is involved, the scale at which the equilibrium will be achieved depends on the particular conditions (especially the temperature), on the character of the phases involved (e.g. diffusion in fluids is much faster than in solids), and on the available time.

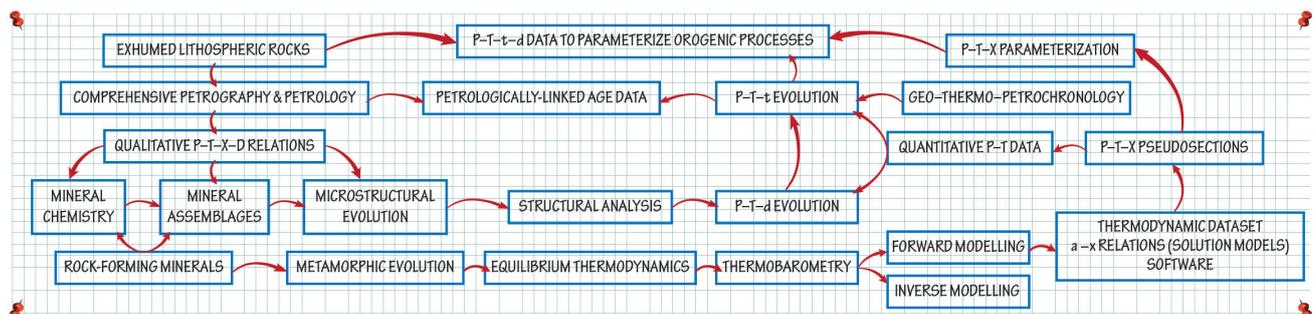


Fig. 1. Flow chart for P–T–t–d path calculations

If conditions change rapidly, the scale of equilibration will be small. However, it can be argued that even in this case the system will develop local equilibria – small domains where equilibrium is achieved or approached (e.g. Korzhinskii 1959; Thompson 1959). The equilibrium phase (mineral) assemblages and compositions can then be identified through a rigorous petrological analysis, and the principles of equilibrium thermodynamics may be applied in order to understand the rock, and determine its conditions of formation (cf. Powell, 1978; Pitra, 2011).

The first to apply the concept of chemical equilibrium in metamorphic rocks was Goldschmidt (1911), suggesting through his research that thermodynamics was an essential tool for the study of metamorphism. He also pointed that the development of distinctive minerals in each type of metamorphic rock could be influenced by variations in depth (pressure), temperature and changes in the bulk rock chemical composition. For long, it has only been possible to infer qualitative comparisons on the P–T formation conditions of metamorphic rocks through the presence of index minerals, or based on the assemblages resulting by the metamorphism of a wide range of protoliths under a particular facies.

Chemical thermodynamics is the formal mathematical framework that links measurable variables (i.e. mineral composition) with those that cannot be directly measured (i.e. chemical potential, pressure, temperature or fluid composition; e.g. Wood and Fraser, 1977; Powell, 1978), using mathematical expressions based on the application of three laws: the ideal gas equation, and the first two laws of thermodynamics. This enables deciphering the P–T history of metamorphic rocks, which is the main aim of geothermobarometry.

Experimentally determined phase equilibrium lie at the heart of nearly all thermobarometric methods. The experimental calibration of metamorphic reactions is the so-called conventional or classical inverse modelling thermobarometry, and was the only numerical method used until the late 80s for the quantification of the P–T formation conditions in a metamorphic rock (e.g. Hodges, 1991; Spear, 1993). It involves the use of two (end-members) mineral reactions, ideally one highly pressure-dependent (geobarometer) and another strongly dependent on temperature (geothermometer). The simultaneous solution of both reactions in the P–T space provides a quantitative estimation to be valid only if minerals are in equilibrium.

Although this technique may provide reasonable results, likewise requires important simplifications and show several limitations (errors derived from thermodynamic consistency, from the experimental calibrations or from the assumed equilibrium condition; e.g. Holland and Powell, 1985; Berman, 1991). One of the most important limitations is the use of single sets of equilibria to calculate the P–T conditions under which a rock equilibrated.

A rock contains multiple minerals and is affected by several reactions. Then, increasing these information increases the accuracy on the estimations. Thus, to overcome these issues, and allow calculation of all equilibria between a set of not only mineral end-member data, but also to activity-composition data (together with calorimetric or heat capacity and volume data among others), thermodynamic databases were created (e.g. Powell and Holland, 2008).

The so-called multi-equilibrium thermobarometry begins to develop during the 90s for this purpose. It involves the use of internally consistent thermodynamic datasets for a wide range of minerals and chemical systems, implying a breakthrough on the research of phase relationship for mineral assemblages. These datasets are known as internally consistent because the thermodynamic parameters regressed for each phase depend on the others to produce equilibria which best fit the experimental determinations. The two most commonly used internally consistent databases in metamorphic petrology are those compiled by Holland and Powell

(1985; 1990; 1998 updated 2003; 2011) and Berman (1988; 1991; 2007). Currently, several thermodynamic calculation software use internally consistent datasets for modelling phase equilibrium in petrological systems. THERMOCALC (Powell and Holland, 1988), Perple_X (Connolly, 1990) and Theriak-Domino (de Capitani and Brown, 1987) are most common in metamorphic petrology.

Thermodynamic calculation software

At their heart, these computer programs are an internally consistent thermodynamic datasets that allows using thermodynamic data in a variety of ways, solving how to handle multiple dimensions represented in two.

Perple_X is a command-line-driven software package that performs Gibbs energy minimization to create phase diagrams and pseudosections.

Theriak-Domino is a suite of programs to calculate and plot thermodynamic functions, equilibrium assemblages and rock-specific equilibrium assemblage diagrams (i.e. pseudosections).

Straightforward application is granted by both Perple_X and Theriak-Domino, which are based on fast computing algorithms and has the ability to calculate and plot “ready to use” phase diagrams in reasonably short times without user intervention, performing calculations with a wide range of thermodynamic databases.

On the other hand, THERMOCALC uses a nonlinear equation solver to calculate user-specified equilibria via only its own internally consistent thermodynamic dataset (Holland and Powell, 1985; 1990; 1998 updated 2003; 2011). It handles mineral equilibria through inverse modelling (geobarometry/thermometry using average P–T), and forward modelling (calculating phase diagrams for model systems, i.e. P–T–X– μ pseudosections). The average P–T method of THERMOCALC considers an independent set of equilibria (from which all the other possible equilibria can be calculated) and a robust statistical treatment to indicate quantitatively the uncertainty on the result (Powell and Holland 1994; Powell and Holland 2008). Create a diagram in THERMOCALC is laborious as curves must be built up one by one and manually combined, and can be extremely time-consuming without granting success. On the other hand, it allows understanding how phase diagrams are calculated (user monitors the Phase Rule, Schreinemaker’s analysis, and how variance changes across field boundaries).

Summarizing, numerical modelling of phase relations requires a set of thermodynamic data for mineral end-members, a description of the activity-composition relations and a software to perform the calculations.

Among the most frequent software implemented in metamorphic petrology, the rapidity and relative easiness of use, together with the possibility of using multiple datasets, make Perple_X and Theriak-Domino interesting alternatives for calculating phase diagrams in relatively simple chemical systems. Calculating diagrams in complex chemical systems requires considerable understanding on the operation of both. THERMOCALC may be the best choice for calculating accurate phase diagrams in complex chemical systems, or with phases requiring complex mixing models (López-Carmona, 2015; see example in Fig. 2).

Pseudosection approach

The advantage of multi-equilibrium thermodynamic calculation programs resides in their ability to generate pseudosections.

After the pioneering work of Hensen (1971), and subsequent inquiries by some isolated workers (e.g. Hudson 1980), it was the development of the internally-consistent thermodynamic datasets and the software THERMOCALC at the end of the 1980s, what allowed the widespread use of pseudosections for metamorphic rocks (Powell and Holland 1985; 1988; Guiraud et al. 1990; Powell and Holland 1990).

Pseudosections are phase diagrams that show stability fields of different equilibrium mineral assemblages for a particular bulk-rock composition (e.g. Powell and Holland, 1988). Considering the rock chemical composition (X) provides added constraints unavailable in conventional thermobarometry, such as phase's coexistence, when phases (minerals, fluids or liquids) in the mineral assemblage are no longer stable, or when additional phases join the mineral assemblage. Through the comparison between the natural observations and the results of the numerical model, pseudosections allow understanding the metamorphic evolution of a specific rock as P, T and X change. Pseudosections have the power to provide valuable additional thermobarometric information and do not depend on measurements of

mineral composition. Likewise, even partly preserved assemblages (e.g. inclusions or partly pseudomorphed minerals) may be useful to infer segments of the P–T path of a rock, before and after the main equilibration stage (e.g. López-Carmona et al., 2011; 2013; 2014).

Moreover, at each point of a pseudosection, the composition and proportion of all phases may be calculated. Then, pseudosections allow estimating specific equilibria by calculating the P–T stability of particular mineral compositions with respect to the bulk rock composition, i.e. allows calculating mineral composition (and proportion), expressed in relative molar abundance) isopleths. The value set for the isopleth compositional variable derives from the EPMA analysis of that particular mineral in a specific sample (cf. Evans, 2004^{a,b}).

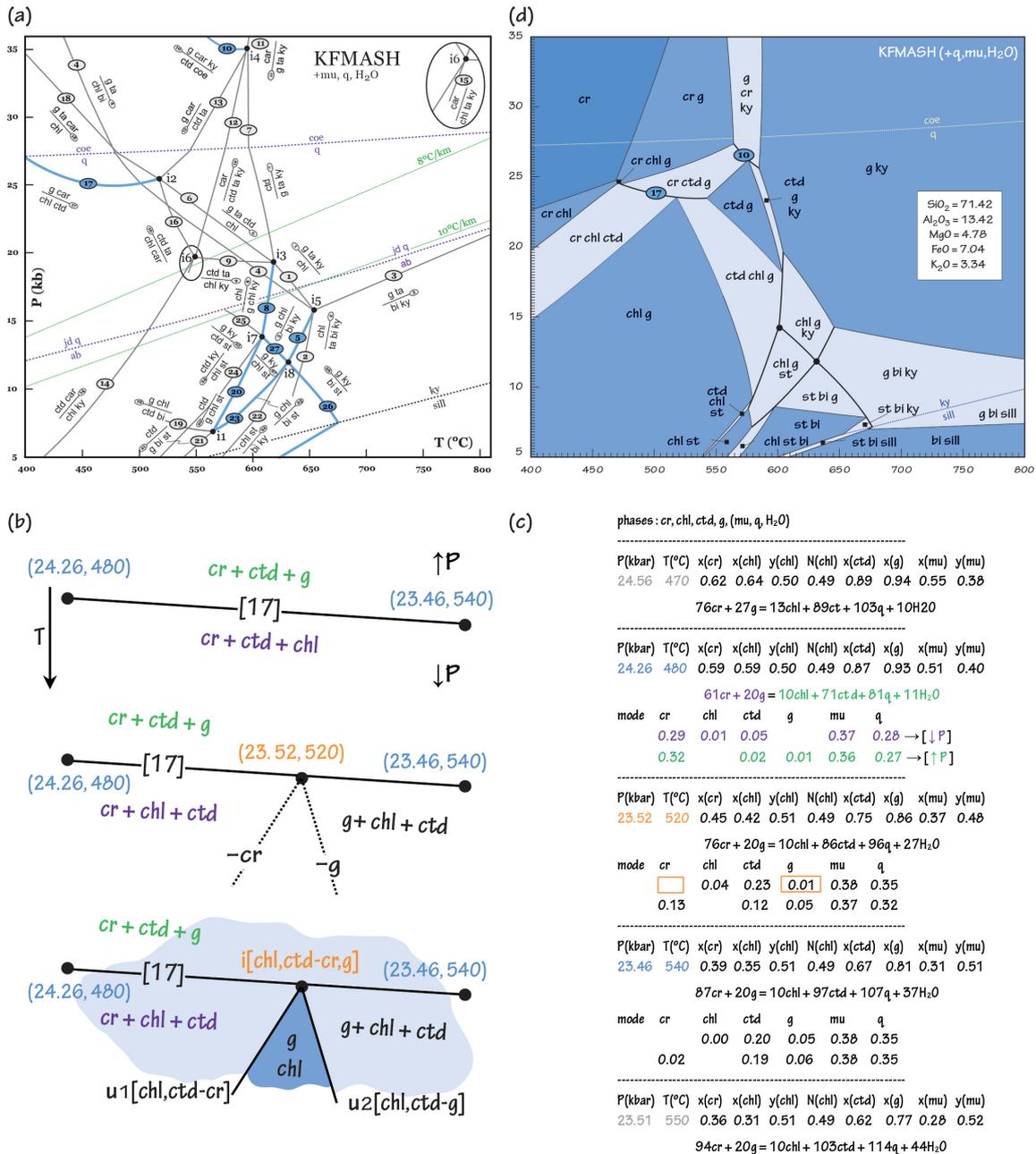


Fig. 2. (a) Petrogenetic grid for various high-pressure metapelites. Black dots and blue lines represent the invariant points and univariant reactions "seen" by sample BS, used as an example composition. Modified after Wei and Powell (2003); (b) user's draft for reaction [17]; (c) thermocalc "output" for reaction [17]; (d) P–T pseudosection in the KFMASH system for sample BS. Black dots and highlighted black lines represent the invariant points and univariant reactions "seen" by the BS composition. Modified after López-Carmona et al. (2010; 2015)

Isopleths then are used to further constrain equilibration conditions. Isopleths are particularly useful when applied on understanding chemical zoning of minerals. These isolines allow to quantitatively investigate the effects of crystal fractionation on phase stability. Therefore, applying pseudosections to real rocks provides P–T estimates at which particular minerals grew within a rock. However, pseudosections are not fool proof and show certain drawbacks that are shortly addressed below.

When calculated using a thermodynamic dataset, pseudosections represent the result of a forward numerical modelling, and are independent on the petrographic observations in the specific rock. An important restriction when using multi-equilibrium tools is implicit in the internally consistent thermodynamic dataset. Knowledge on the thermodynamic parameters for mineral phases used in thermobarometry has largely improved since databases appeared, but there is still much to be done. Occasionally, the use of provisional data in the internally consistent database is subject to unknown errors that can slightly alter phase's stability, and thus the P–T estimates. Nevertheless, even the best software cannot overcome problems arising from missing or unconfident thermodynamic data.

Two crucial elections have to be carefully considered before start working with THERMOCALC: choosing the chemical system, and the right bulk rock composition. The chosen chemical system must be as close as possible to nature. Ignoring a phase component (such as e.g. apatite) can artificially modify the bulk rock composition. This can be solved applying the appropriate corrections (e.g. Ca in apatite correction $\text{CaO} = \text{CaO} - 3.33 \cdot \text{P}_2\text{O}_5$). The available chemical system usually depends on the accessible solid solution models. In general, simpler systems may be used to forward modelling theoretical scenarios, whereas inverse modelling requires larger systems. However, complex systems imply complex mixing models for solid-solution phases that may be a source of additional errors. Choosing the right bulk rock composition (expressed in mol %) is decisive since the pseudosection would be only valid for such election. Nevertheless, as many minor elements are systematically ignored (e.g. P_2O_5 or BO_3), bulk rock compositions in THERMOCALC are always (reliable) approximations to real rocks. The effects of overlooking these components depend on the sensitivity with which the adjustments on the bulk composition have been done, which relies on the petrographic user-knowledge of the sample considered. THERMOCALC manages the so-called effective bulk rock composition, which is that available to the reacting assemblage of phases (see Stüwe, 1997). Metamorphic rocks are commonly heterogeneous; this effective composition then may change throughout the history of metamorphic recrystallization, and largely depends on the equilibration volumes. Two mechanisms can alter the effective bulk-composition of a rock during metamorphism, the open system behaviour (e.g. deformation or fluid effects) and the successive (re)equilibrations. The occurrence of chemically zoned phases (typically garnet) in a sample implies crystal fractionation. Thus, the chemical reservoir from which minerals are growing (whole-rock composition before garnet crystallization) would change into a new rock composition devoid of the components that reacted while the zoned crystal was growing (effective rock composition after garnet crystallization; cf. Hollister, 1966; Atherton, 1968; Spear, 1991).

Accordingly, the effective bulk-composition of a rock through its metamorphic history may be characterised by a multitude of relatively small equilibration volumes (e.g. Stüwe, 1997; Tinkham and Ghent, 2005; Pitra, 2011). Currently two main approaches are used to obtain the effective-bulk composition, but the method used depends on the scale and accuracy of the problem to be solved. Small compositional domains may be analysed by quantitative X-ray mapping with an EPMA over a selected area of the sample (e.g. Clarke et al., 2001; Marmo et al., 2002).

This method allows both, the possibility to selectively eliminate individual phases that are interpreted not to have been reacting during recrystallization of surrounding phases, and the chance to eliminate compositional domains that are distinctly different from that of the region of primary interest in compositionally layered samples (see Tinkham and Ghent, 2005). Equilibrium is generally thought to be attained at the hand-sample scale if no clear evidence to the contrary is found (Chernoff and Carlson, 1997; Hirsch et al., 2003). Theoretically, if the compositional domains of interest are about 1 cm wide or greater, up to hand-sample scale, individual domains can be separated and analysed with X-ray fluorescence spectroscopy (XRF). THERMOCALC is provided of a facility (the rbi “read bulk info” code) that allows defining or changing a bulk rock composition through the mode and composition of phases. This application can be used to investigate the internal buffering of fluids or the fractionation of bulk rock compositions due to porphyroblast growth, as well as to assess the loss of melt from a bulk rock composition or to make an approximate protolith composition from a melt depleted rock.

Finally, the difficulty to determine the proportion of significant components such as H_2O and Fe_2O_3 (“O” in THERMOCALC) in the bulk composition, by routine analytical techniques, raises important uncertainties when modelling phase equilibria, and can largely influence phase relations and hence, P–T estimates. The amount of H_2O has to generally be guessed, if not in excess, whereas the Fe_2O_3 can be determined. Total iron (expressed as $\text{Fe}_2\text{O}_{3(T)}$) can be measured by XRF and FeO can be analysed by wet chemical titration. Then, the amount of Fe_2O_3 is calculated stoichiometrically.

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