Experimental studies and thermodynamic modelling have advanced our understanding of partial melting in the crust and have provided a framework for the interpretation of migmatites, residual granulites and granites. Each approach has advantages and pitfalls, and each is more appropriate than the other for investigating particular aspects of the melting process. A comparison of these two approaches may be useful because, together, they potentially give more information. A comparison of a small number of experiments with model calculations using equivalent bulk compositions shows important consistencies between the results, especially regarding the overall topologies of key melting equilibria. Despite this, several significant differences between the two approaches remain, though the sources of these differences are difficult to determine.

**KEYWORDS:** melting, experiments, phase diagrams, thermodynamics

**INTRODUCTION**

The study of migmatites provides information on partial melting of the crust. Granulate facies migmatites are particularly important for understanding the origin of high-temperature, H₂O-undersaturated granitic magmas that are capable of ascending into the upper crust and, potentially, erupting. However, studies of natural rocks are limited by the fact that they are the end product of a range of metamorphic and deformation processes that operate during long-lived residence in the deep continental crust. This allows deformation and recrystallization to modify the rock and mineral textures produced by melting and for elements to be redistributed between melt and residuum-rich portions of the rock. Experimental petrology and thermodynamic modelling allow us to generate a “snap shot” of anatetic processes and provide us with a framework within which we can interpret many of the features encountered in high-grade rocks, thus contributing considerably to our understanding of partial melting and recycling of the crust.

Partial melting has been a significant focus of experimental studies for many decades. Such studies provided the first constraints on the melting process (e.g. Tuttle and Bowen 1958; Wylie 1977), estimates of melt fertility of different rocks (e.g. Patiño Douce and Beard 1995; Johannes and Holtz 1996) and constraints on the reactions that control melt production (e.g. Vielzeuf and Holloway 1988). Experimental studies of partial melting range from single-component (unary) melting to experiments on a large range of chemical systems. These include the unary melting relationships for end-member phases, binary and ternary systems, and larger systems such as K₂O–Al₂O₃–SiO₂–H₂O (KASH) and K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O (KFMAH). These experiments, particularly those with a small number of components, are particularly useful for deriving the thermodynamic properties of minerals and silicate melt end-members (e.g. Burnham 1975; Berman and Brown 1987; Ghiorso and Sack 1995; Holland and Powell 1998, 2001; White et al. 2001, 2007). However, the compositional spaces of such systems commonly lie well away from those of rocks, so the results of such experiments are difficult to directly relate to partial melting in the crust. The second type of experiments includes those concerned with very large chemical systems, such as natural compositions. The main aim of these experiments is to investigate mineral assemblage development and partial melting, as may occur within the particular rock types being investigated. As they concern large chemical systems, it is more difficult to use such experiments to derive the thermodynamic properties of mineral and melt end-members, though these experiments have been utilised to derive melt models (e.g. Ghiorso and Sack 1995). Regardless, these experiments do provide useful constraints on the appropriateness of the models derived from experiments in simpler systems, and are of use in expanding such models to larger chemical systems.

Experimental studies on partial melting along with the geometrical analysis of phase relationships (e.g. Grant 1985; Vielzeuf and Holloway 1988) have long provided a reasonable understanding of the underlying melting relationships in rocks. However, fully quantitative thermodynamic calculations on melting using large, internally consistent datasets and complex activity models have evolved mostly over the last fifteen years as more sophisticated activity models for both minerals and melt have been developed. The melt end-members for the haplogranitic system were first included in the internally consistent dataset of Holland and Powell (1998), with the activity-composition relationships for melt presented in Holland and Powell (2001) and extended in White et al. (2001). These developments allowed quantitative thermodynamic calculations on melting using large, internally consistent datasets and complex activity models have evolved mostly over the last fifteen years as more sophisticated activity models for both minerals and melt have been developed. The melt end-members for the haplogranitic system were first included in the internally consistent dataset of Holland and Powell (1998), with the activity-composition relationships for melt presented in Holland and Powell (2001) and extended in White et al. (2001). These developments allowed quantitative thermodynamic calculations on melting using large, internally consistent datasets and complex activity models have evolved mostly over the last fifteen years as more sophisticated activity models for both minerals and melt have been developed.

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Application of these models to melting processes in general, and to specific rocks via pseudosections (phase diagrams drawn for a fixed rock composition), has become relatively common since.

Comparing the results of modelling with those of experimental studies is challenging. However, much interest exists within the petrological community for understanding the accuracy of modelling of assemblage stability within partially melted rocks and for extending these techniques to the evolution of magmatic systems (e.g. Villaros et al. 2009). Comparison is difficult because significant limitations exist in the application of both techniques; yet, as detailed below, these limitations are different in the two approaches and the techniques are thus far more complementary than many researchers may realize. This contribution discusses the virtues and pitfalls of both modelling and experimental studies for understanding partial melting of the crust. It compares experimental and modelling results in the Na2O–CaO–K2O–FeO–MgO–Al2O3–SiO2–H2O (NCKFMASH) system. This is a sufficiently complex chemical system to permit realistic investigation of crustal melting, but it lacks the minor components (Ti, F, Cl, Fe3+) that influence mica and amphibole stability. These components are difficult to include in the models, though much progress has been made in considering some of these (e.g. Ti and Fe3+; White et al. 2000).

ADVANTAGES AND PITFALLS OF EXPERIMENTAL AND THERMODYNAMIC MODELS

Neither experiments nor thermodynamic models can accurately represent the reality of partial melting of the crust. Partial melting is a dynamic process, generally characterized by a material flux as melt and residuum separate, and involves a complexly evolving thermal system. Modelling can deal with this to some degree, but conventional partial melting experiments generally do not consider compositional change in the bulk system. Importantly, the sources of uncertainty and the problems with each method are very different. This constitutes a major hurdle for undertaking a direct comparison of the two approaches. More importantly, regardless of how well or poorly the approaches agree, is either an adequate representation of what occurs in nature?

Experiments

Advantages An experimental approach to investigating crustal anatexis has several inherent advantages. Experiments have the potential to provide direct constraints on P–T conditions, melt fertility and melt composition, as experiments can deal with the full chemical complexity of rocks. This has great value due to the large influence that some minor elements have on the stability of different phases, especially mica and amphibole, during partial melting. Carefully planned experiments using synthetic minerals could isolate and investigate the influence of each of these variables, allowing their effects to be better modelled. Experiments can be used to investigate the full range of compositions, pressures and temperatures appropriate to crustal rock processes, including metamorphism and melting in subduction zones, though experiments at the lower-temperature end of this range become difficult. For example, tonalite–trondhjemite–granodiorite genesis and the origin of the Archean crust have largely come to be understood through a combination of studies of the geochemistry of the granitoids (e.g. Martin and Moyen 2002) and experimental studies on the partial melting of mafic rocks (e.g. Beard and Lofgren 1991; Angel and Watson 1995). Kinetic factors that may influence partial melting in nature are incorporated into experiments, as their results are indications that diffusion, nucleation and crystal growth in melt have occurred. These processes are scalable, if mineral mixtures are used, as the diffusion length scales necessary to achieve equilibrium are a function of the grain size of the starting-material powders. Experiments also had tremendous value in investigating the flux of components from subducting crust into the mantle (e.g. Schmidt et al. 2004) and the behaviour of trace elements in minerals, melts and fluids (e.g. Rubatto and Hermann 2007).

Pitfalls Despite the versatility of an experimental approach to partial melting, there are also distinct challenges. Experiments are time consuming, with fluid-absent experiments commonly requiring two to three weeks to equilibrate at the lower range of melting temperatures. Consequently, it is laborious to perform sufficient experiments to derive the underlying topology of the phase relations within a significant P–T window. A significant problem also exists with attempts to bracket melting reactions by experimental reversal, because melt in crystallization experiments commonly persists to considerably lower temperatures than the solidus temperature established during melting experiments. In general, this behaviour is attributed to the slow kinetics of reaction between the experimentally grown phases during cooling. Redistribution of elements within the charge may also be important, retarding retrograde re-equilibration. For example, once H2O is concentrated in the melt, the relevant solids for that domain in the charge is much closer to the wet granite solidus than, for example, the biotite melting reaction that produced the melt. Thus, the rates at which biotite can grow and melt can crystallize are limited by the rate of the diffusion of elements through the melt. In general, heating experiments are considered to more accurately constrain the position of incongruent melting reactions. However, in the case of fluid-absent studies, overstepping of the melting reaction may be particularly important to consider because in the subsolidus assemblage there is no fluid to facilitate diffusion between crystals and promote equilibration. Fluid-absent conditions are most relevant to partial melting of the lower continental crust. Yet under these conditions the oxidation state cannot be directly controlled in experiments. Consequently, hydrogen loss from capsules may result in variations in the proportion of Fe3+ within individual charges and between the results of different experiments. This effect commonly manifests itself as a rind of oxide minerals at the capsule wall, particularly in experiments conducted in gas vessels. The effects of oxidation of the charge must have consequences for the experimental results through a reduction of the amount of water, the conversion of ferrous to ferric iron and the growth of oxide phases.

Commonly, melting experiments dealing with natural rock systems cover a temperature range from fluid-absent subsolidus conditions to 1000 °C or higher, i.e. a range of some 200–300 °C. Over much of this range, the assemblages produced in typical metapelites and metagreywackes contain melt volumes in excess of 15 to 20%, and at the highest temperatures melt volumes of 50% or more are common. Granulites do not follow such an evolution, and efficient deformation-driven melt loss produces a residual chemistry and also preserves the high-temperature assemblage. Consequently, while such experiments have relevance for identifying the initial fluid-absent melting reactions by which the granulites melted, they do not mimic the melting behaviour of such granulites. Maintaining all the melt in the system, as occurs in experiments, results in greater melt production than would occur naturally, where the removal of more hydrous melt, at lower temperature, can be efficient.
**Thermodynamic Modelling**

Advantages Compared to experiments, thermodynamic calculations on melting relationships can be undertaken relatively quickly and easily. This provides the opportunity to investigate a range of compositions – within the scope of the calibration limits of the models – and more easily constrain the melting reactions. In addition, such calculations can be undertaken to investigate a range of physical and chemical processes, such as the fractionation of components into porphyroblastic phases and the loss of melt from the rocks. Importantly, calculated phase diagrams give a more comprehensive and coherent view of the underlying phase relationships in rocks than can be extracted from the limited number of experimental runs in a typical experimental study. For example, the number of fields in a calculated pseudosection will typically far exceed the number of experiments that can be undertaken within a reasonable time frame. The ability to undertake calculations in a range of chemical systems and to be able to produce complete phase diagrams has been important to our current understanding of high-temperature phase relationships and the core equilibria that control melt production and the formation of the mineral assemblages diagnostic of the granulite facies. For the application to natural residual rocks, it is also possible, via thermodynamic modelling, to re-integrate melt back into the composition to create an approximate protolith (e.g. White et al. 2004) and to investigate the interaction between melt and residuum on a range of scales (e.g. White and Powell 2010).

**Pitfalls**

Despite the many advantages of calculated phase petrology, there are also many pitfalls and sources of uncertainty. The most important of these is our limited understanding of the thermodynamic properties of minerals and melts (end-member thermodynamics and activity–composition relationships, in particular). Any calculation can only be as good as the input thermodynamic data. While some reasonable estimate of uncertainty can be considered for some of these properties, such as the enthalpy of formation of the end-members, the uncertainties associated with other properties, such as the activity–composition relationships, are essentially unknown.

Much of the assessment of the appropriateness of a given model calculation can only be done in a rather simplistic and comparative way, such as through a comparison of mineral modes (abundances) and compositions with available natural and experimental examples. Other important constraints in the application of mineral equilibria modelling to melting are the inherent limits in the chemical systems that can be considered with the currently available models and the limits in the \( P-T-x \) (where \( x \) denotes composition) range for which these existing models can be considered reasonably appropriate. While calculations can be undertaken in increasingly large chemical systems, such as NCKFMASHTO (\( \text{Na}_2\text{O}–\text{CaO}–\text{K}_2\text{O}–\text{FeO}–\text{MgO}–\text{Al}_2\text{O}_3–\text{SiO}_2–\text{H}_2\text{O}–\text{TiO}_2–\text{Fe}_2\text{O}_3 \)), such systems are still a significant simplification of nature and the effects of other components on the phase equilibria are unconstrained.

**HOW DO THE APPROACHES COMPARE?**

To date relatively few studies have attempted to model the results of experiments on synthetic or natural compositions (e.g. Johnson et al. 2008; Tajčmanová et al. 2009; Grant 2009). A direct comparison of thermodynamic modelling and experiments can be undertaken where the experimental composition used is in the same system as the composition used in the modelling (e.g. KFMASH or NCKFMASH). A greater challenge arises where the composition used in the experiments is a natural rock powder that contains many components not accounted for in the modelling. Here, constraining which of a large number of potential sources is responsible for any difference is difficult. Important questions are, what aspects of experimental studies and thermodynamic modelling can be compared and what types of phase diagrams are the most appropriate? While the results of many experiments are interpreted in terms of the location of reactions and the resulting underlying phase diagram, such interpretations are generally not unique, and instead, the basic results (assemblages, mineral proportions and mineral compositions) represent more reliable criteria for comparison. As experiments are undertaken on material of a known composition over a range of \( P-T \) conditions, they are most akin to \( P-T \) pseudo-

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**FIGURE 1** Calculated pseudosections for two bulk rock compositions used in the experiments of Stevens et al. (1997).

**FIGURE 1A** was calculated for the metagreywacke composition B; **FIGURE 1B** was calculated for the metapelitic composition AS. The \( P-T \) conditions of the experiments are shown as filled circles and the experimental products for each point are labelled in red. The mineral abbreviations are after Kretz (1983), except that the first letters are not capitalized.
sections. Importantly, in any comparison between assemblages, mineral proportions and mineral compositions, the fact that these are correlated must be taken into consideration (i.e. any differences in mineral compositions between the models and the experimental results will inevitably lead to some differences in mineral modes and possibly assemblages due to mass balance requirements for a fixed rock composition).

In experiments, there is also the problem of differences between the nominal and actual chemical system used. For example, the inclusion of small seeds of natural garnet in experiments potentially adds some MnO to the composition. In addition, the activity of oxygen is commonly not constrained, such that an experimental composition nominally in NCKFMASH, for example, will contain an indeterminate amount of ferric iron and actually be in the NCKFMASHO system. Furthermore, the presence of unreacted cores in an experiment also means that the composition of the volume of equilibration is different from that of the whole experimental charge.

In the following, we compare the results of partial melting experiments and thermodynamic modelling for two synthetic NCKFMASH compositions – a metagreywacke and a metapelite – from Stevens et al. (1997). As the experimental compositions were synthetic and located in a nominal chemical system for which modelling can be undertaken, a direct comparison is possible.

**FIGURE 1** shows calculated P–T pseudosections for the experimental greywacke composition B (Fig. 1a) and the pelite composition AS (Fig. 1b) of Stevens et al. (1997). The P–T conditions of the experimental runs and the resulting experimental products are also shown. For the metagreywacke composition, the results from the two approaches are similar, especially at 10 kbar. At 5 kbar, the model predicts the appearance of orthopyroxene (opx) and the disappearance of biotite (bt) coexisting with melt at temperatures approximately 50 °C lower than observed in the experiments. Furthermore, the model predicts a wide stability field for cordierite (crd), whereas the mineral is present in only two of the experimental runs.

A comparison of the metapelite experiments with the model also reveals similarities and differences. Again, biotite persists to higher temperatures (20–50 °C) in the experiments than predicted by the model calculations. In addition, the presence of cordierite in the experiments at 10 kbar is not replicated in the model. However, as with the metagreywacke composition, there are important similarities between the results of the two approaches. At 5 kbar, both methods show the appearance of spinel (spl) and the loss of garnet (grt) at high temperatures.

Comparing the overall assemblages and the mineral modes allows a better assessment of the significance of any differences in assemblages. For example, if a mineral is present in the model and absent from the experiments, or vice versa, but the mode of that mineral is rather small, then the apparent difference is likely to be of limited significance; it could be the result of small uncertainties in the model, reflect nucleation issues, or be due to the presence of an unidentified minor phase in the experiments.

**FIGURE 2** shows a comparison of the modes of the phases in the experiments and models discussed above. The T–mode plots for the experimental runs (Fig. 2a–d) are modified from Stevens et al. (1997) in which the modes of K-feldspar (kfs), plagioclase (pl) and quartz (qtz) were not differentiated. For the calculated modes (Fig. 2e–h), these minerals are differentiated but are coloured the same to allow an easier comparison with those of the experiments. In addition, the calculated T–mode diagrams extend to lower temperatures than those of the experimental runs to accommodate the fact that the calculations predict the key equilibria at slightly lower temperatures.

The T–mode diagrams for the metagreywacke composition (Fig. 2a, b, e, f) show a number of important similarities, particularly at higher T. The proportions of melt (liq), garnet and orthopyroxene at higher T are similar in both, and both approaches infer the rapid consumption of biotite over a relatively small temperature range, although the absolute temperature does differ. The differences in modes for the metapelitic composition (Fig. 2c, d, g, h) are more profound. At 5 kbar, the modelling predicts more
A comparison of mineral/phase compositions can also be made, considering that there are uncertainties in both the calculated compositions and the analyses, particularly those of the experimental glasses. Figure 3 shows the measured compositions of the experimental products (squares and circles) and the calculated compositions (lines) for melt/glass, garnet, orthopyroxene and cordierite. The match in mineral compositions ranges from close [e.g. Mg# in orthopyroxene and K/(K + Na) in melt] to rather different [e.g. Mg# in cordierite and the trends defined by Al/(Ca + Na + K) in melt for the AS composition at 5 kbar].

**Source of the Differences**

The main sources of uncertainty in the experimental studies revolve around whether equilibrium was attained on the scale of the charge and whether the assemblage produced is the stable one as opposed to a metastable one. In addition there are uncertainties in the analysis of the phases, compounded by the small grain size and the inherent difficulties in analysing hydrous and Na-bearing aluminosilicate glasses. The model calculations are affected by uncertainties in the end-member thermodynamics and the activity–composition models used.

While the origin of a particular difference between the two approaches is commonly difficult to determine, in some cases it can be determined from other experimental studies and/or from consideration of phase relations determined from rocks. If we take, for example, the presence of cordierite in the experiments on the pelite composition AS at 10 kbar and its absence in the model, potential reasons for the difference range from problems with the thermodynamic data to issues arising from the experiments. From the modelling, the coexistence of garnet and cordierite (with quartz, K-feldspar and melt) is metastable at 10 kbar; whereas this assemblage should only be stable on the low-pressure side of the multivariant field equivalent to the KFMASH reaction

\[
\text{garnet} + \text{cordierite} = \text{orthopyroxene} + \text{sillimanite},
\]

which limits coexisting garnet and cordierite to below about 9 kbar over the temperature range considered (White et al. 2007). Whereas it could be argued that the position of this equilibrium as determined from the modelling is grossly incorrect, it is also well constrained via experimental studies (e.g. Carrington and Harley 1995) – albeit in the smaller KFMASH system compared to NCKFMASH modelled here – to be close to where it occurs in the models. Hence, in this example it would appear that the source of the problem lies in the metastability of the experimental assemblage developed.

The modelling results give melt compositions with a higher A/CNK for composition AS at 5 kbar than those reported in the experiments of Stevens et al. (1997) (FIG. 3a) and other experiments on similar compositions. This difference probably reflects problems with the model, especially when the model is applied to assemblages that have lost quartz and K-feldspar.

While the source of some of the differences, such as for cordierite (above), can be constrained, on the whole it is more difficult for most. It would be unwise, for example, to attempt to adapt the models to fit perfectly with a single experimental study as there are typically some inconsistencies between different experimental studies. However, the many experimental studies available do provide important constraints on the existing strengths and weaknesses of thermodynamic models. Although a number of outstanding differences between the two approaches remain, there are, encouragingly, a greater number of similarities. Importantly, the general topologies generated by the calculations and inferred from the experiments are similar.

**CAN WE RECONCILE EXPERIMENTS AND MODELLING WITH NATURE?**

Regardless of how the two approaches compare, the most important question is, how well does either approach inform us about melting in nature? Both models and experiments are merely simplified proxies for natural systems. However, despite these caveats, the results of both methods broadly replicate what is inferred from the study of migmatites. Importantly, the general similarities in topology between what can be calculated, interpreted from experiments and inferred from rocks tell a consistent story about the partial melting process. Central to this is

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**Figure 3** Comparison of measured and calculated compositions for the major phases. The experimental results are given as squares and circles and the model compositions as lines. (A) Comparison of the Mg number [Mg# = 100Mg/(Mg + Fe)] of cordierite, orthopyroxene and garnet. (B) Comparison of K/(K + Na) and Al/(Ca + Na + K), indicated as A/CNK, for the experimental glasses and modelled melt compositions.
the relationship between the breakdown of hydrous phases and the production of melt. Such observations allow us, for example, to confidently infer the production and loss of melt from anhydrous granulites even if direct evidence for this is absent. In addition, the experimental and thermodynamic approaches both allow estimates of the P–T conditions of melting and the proportion and composition of that melt, features necessary for understanding large-scale geotectonic differentiation. However, assuming either approach to be a perfect representation of nature would be naïve at best.

FUTURE NEEDS

We need to develop better thermodynamic models for minerals and melt in increasingly complex systems, by both extending the compositional space of evaluated phases and constraining the mixing properties of existing models (see Powell and Holland 2010 for a more detailed discussion). For partial melting modelling studies, the key progress to be made is in extending and refining the mineral and melt models to make them applicable to a greater range of compositions, such as metabasic rocks and to a wider range of P–T conditions, such as subduction settings. The extension and refinement of melt and mineral models are dependent on good experimental and natural data. In particular, experiments that investigate the role of minor components in isolation (Ti, F, Mn, etc.) in compositionally well-constrained systems [synthetic mixes in NCKFMASH(O), for example] are likely to be more useful to the development of thermodynamic models than experiments on natural compositions, where it is more difficult to isolate and differentiate the effects of each of the multitude of minor components present.

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