

Reaction Enthalpies of Subsolidus Equilibria in Pelitic Rocks. Magnitude and Influence on Cretaceous Metamorphism of the Koralm Complex, Eastern Alps.

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With 6 figures

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Summary: The unusual high metamorphic grade of Eoalpine metamorphism in the Koralm Complex, Eastern Alps may, in principle, have contributions from three different heat sources. These include (i) conduction of heat from deeper crustal levels; (ii) advection of heat by fluids or magmas and (iii) internal heat production. We have shown elsewhere that heat conduction alone is unlikely to be the only important mechanism of heat transfer into the complex. The other potential heat sources need therefore to be evaluated. It is equally important to evaluate heat sinks and an integrated thermal model needs a careful comparison of the importance of heat sources and sinks during metamorphism. Here, we assess the importance of enthalpy production by metamorphic reaction to retrograde metamorphism of the Koralm complex and we speculate on alternative heat sources for the prograde path. In particular, we calculate the change of enthalpy content of assemblages with temperature for two pelitic bulk compositions representative of the Koralm complex. Our calculations confirm that the influence of enthalpies of reaction on the overall energy budget of the crust is small and that enthalpy changes across reactions may be well-approximated by an appropriate average heat capacity. For the two bulk compositions from the Koralm complex considered here, these are $cp = 1380 \text{ J kg}^{-1}\text{K}^{-1}$ and $cp = 1550 \text{ J kg}^{-1}\text{K}^{-1}$. Our results have two implications with particular relevance for the Koralm:

1. Since we show that heats of reaction have a negligible influence on the overall heat budget, other heat production mechanisms or advective processes are likely to have contributed to Cretaceous metamorphism. Indeed, the high average heat capacities appropriate to metapelites and the large amounts of pelitic rocks in the Koralm indicate that heat conduction is a particularly inefficient process in the complex. While we have not considered the influence of advective processes, we speculate that shear heating may form a substantial part of the overall heat budget.

2. It is argued that even small enthalpies of reaction may be recorded by the parageneses of metamorphic rocks by buffering effects which may force *PT* paths to converge locally, producing low variance assemblages. This may be seen in the Koralm complex where low variance assemblages are found unusually often.

Zusammenfassung: Reaktionswärme von Subsolidus Gleichgewichten in pelitischen Gesteinen. Größenordnung und möglicher Einfluß auf die Kretazische Metamorphose des Koralm Komplexes, Ostalpen. – Die ungewöhnlich hochgradige Eoalpine Metamorphose im Bereich der Koralm kann im Prinzip durch Beiträge von drei verschiedenen Wärmequellen verursacht worden sein. Dies sind (i) Wärmeleitung aus tieferen Krustenstockwerken; (ii) Wärmeduktion durch Fluide oder Magmen und (iii) interne Wärmeproduktion. In anderen Studien haben wir gezeigt, daß Wärmeleitung allein wahrscheinlich nicht der einzig wichtige Mechanismus des Wärmetransports in den Komplex ist. Es ist daher wichtig, die Größenordnungen anderer Wärmequellen abzuschätzen. In diesem Artikel diskutieren wir die Größenordnung von Wärmeproduktion durch metamorphe Reaktionen als Beitrag zur Eoalpinen Metamorphose in der Koralm. Andere Alternativen werden erwähnt. Insbesondere berechnen wir den Wärmeinhalt von Paragenesen in zwei verschiedenen, für die Koralm repräsentativen, pelitischen 'Bulk Compositions' als Funktion der Temperatur. Unsere Ergebnisse bestätigen die Ergebnisse anderer Autoren, daß der Einfluß der Reaktionswärme auf den Gesamtwärmehaushalt der Kruste klein ist. Für die zwei "Bulk compositions" der Koralm die hier verwendet wurden, kann der Einfluß daher gut durch mittlere Wärmekapazitäten von $cp = 1380 \text{ J kg}^{-1}\text{K}^{-1}$ beziehungsweise $cp = 1550 \text{ J kg}^{-1}\text{K}^{-1}$ angenähert werden. Die Rechnungen haben zwei wichtige Implikationen für die Koralm:

1. Nachdem Reaktionswärme einen vernachlässigbar kleinen Einfluß auf den Wärmehaushalt hat, ist es wahrscheinlich, daß andere Wärmequellen zur Metamorphose beigetragen haben. Diese Vermutung wird dadurch bestätigt, daß wir zeigen, daß pelitische Gesteine besonders hohe Wärmekapazitäten haben.

Der große Anteil von pelitischen Gesteinen in der Koralm zeigt daher, daß dort Wärmeleitung ein besonders ineffizienter Prozess der Metamorphose ist. Wir denken an Erwärmung durch metamorphe Fluide oder durch Reibungswärme während der Deformation als mögliche zusätzliche Beiträge. Beides wird kurz diskutiert.

2. Es ist möglich, daß der qualitative Mineralbestand eines Gesteines auch durch kleine Reaktionsenthalpien beeinflusst wird, indem thermische Pufferprozesse wirksam werden. Zum Beispiel ist es möglich, daß *PT* Pfade zu invarianten Punkten hin konvergieren. Solche Prozesse würden es erlauben, mehr niedrigvariante Paragenesen zu erzeugen als man erwarten würde. Wie in vielen anderen metamorphen Terrains auch, findet man in der Koralmpe erstaunlich oft uni- und invariante Paragenesen und es kann sein, daß dies das Ergebnis eines solchen Prozesses ist.

1. Introduction

Eoalpine metamorphism in the Koralm complex reached amphibolite and eclogite facies metamorphic grade around 700° C and 14–17 kbar (e.g. THÖNI & JAGOUTZ, 1992; STÜWE & POWELL, 1995; EHLERS et al., 1994; FRANK et al., 1983). Even for the large depths indicated by the high metamorphic pressures these temperatures are unusually high and cooling rate (EHLERS et al., 1994) as well as overall estimates of the energy budget (STÜWE & SANDIFORD, 1994; STÜWE, 1996) indicate that heat conduction alone may not be sufficient to explain this metamorphism. The importance of other heat sources as contributors to the energy budget must therefore be discussed. Of a number of alternative heat sources, we focus in *this* study on the magnitude of contributions from enthalpy consumed or released in metamorphic reactions. Order of magnitude estimates by a number of authors have shown that its influence on the overall energy budget of metamorphic terrains is small (e.g. solid-solid reactions: THOMPSON & ENGLAND, 1984; PEACOCK, 1987; CONNOLLY & THOMPSON, 1989; BARR & DAHLEN, 1989; PEACOCK, 1989; melting reaction: STEFAN, 1891; STÜWE, 1995). However, no studies have calculated reaction enthalpies of individual uni-, di- and tri-variant reactions on petrogenetic grids relevant to certain bulk compositions. Such a study may be relevant for areas like the Koralm complex, where rocks of pelitic bulk compositions constitute large vertical sections of the Austroalpine nappe pile. In order to evaluate the enthalpy changes of metamorphic assemblages quantitatively, the calculation of reaction enthalpy has been implemented as an additional output to the software THERMOCALC (POWELL & HOLLAND, 1988). Though this facility is new to the software THERMOCALC, we focus in this study on results of relevance to the Koralm Complex. The method of calculation is summarised in the Appendix and a general discussion of this new facility will follow elsewhere (STÜWE & POWELL, in prep.).

2. Results

According to the bulk composition of the majority of rock types in the Koralm complex, we have calculated the enthalpies of the mineral assemblages in two representative pelitic bulk compositions, involving the phases chlorite, staurolite, garnet, potassium feldspar, aluminosilicate, biotite, muscovite, quartz and H₂O. *Bulk 1* is the bulk composition of parts of the Plattengneis shear zone and has the oxide proportions K₂O:FeO:MgO:Al₂O₃:SiO₂:H₂O = 3.4:5.1:3.4:9.35:63.75:15 on a molar basis. A petrogenetic pseudosection for this bulk composition has been discussed by STÜWE & POWELL 1995 and STÜWE 1995 (Fig. 1 this study; Fig. 3a of STÜWE & POWELL 1995). The amount of H₂O chosen allows about 2% of free H₂O to be present at 500°C. In AFM, the Al/(Fe+Mg) of *bulk 1* is below garnet-chlorite. *Bulk 2* is above garnet-chlorite and corresponds therefore to many ky-bearing rocks of the Koralm complex (Fig. 2 this study ; Fig. 8a of XU et al. 1994). It is characterised by the oxide proportions

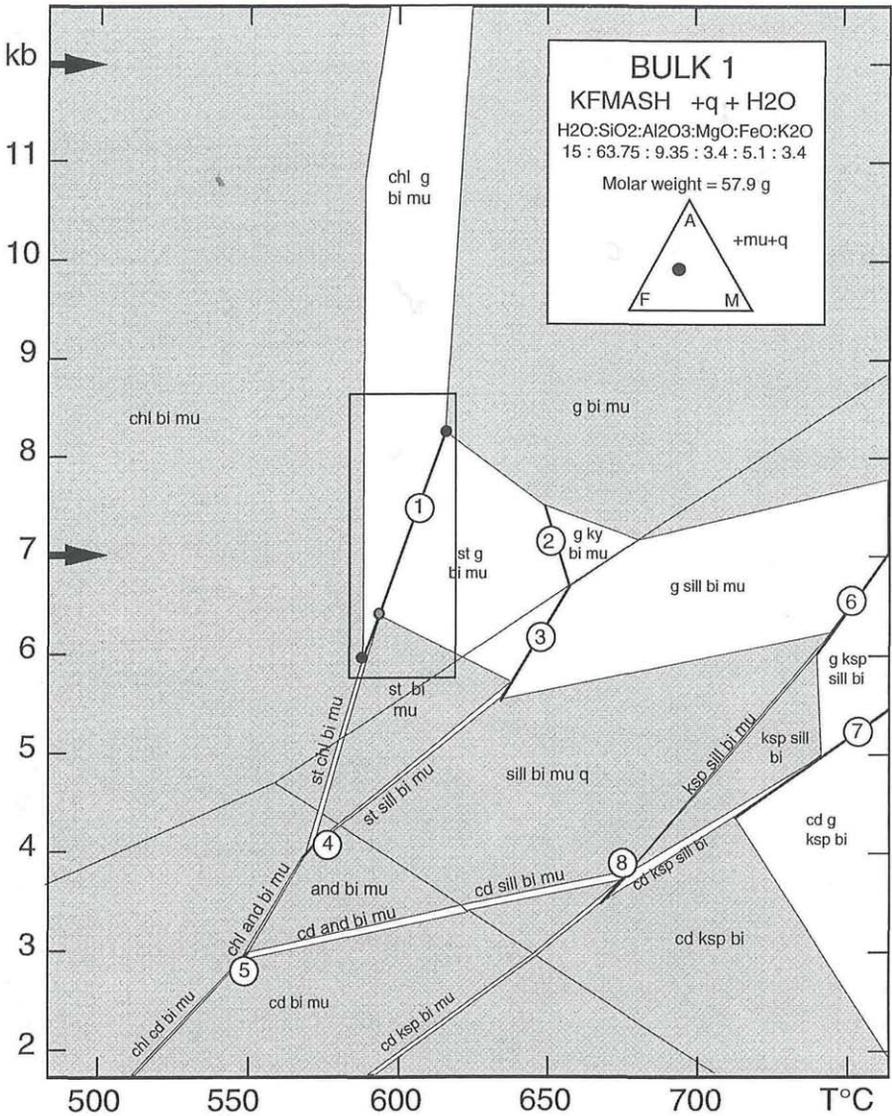


Fig. 1: Pseudosection of the pelitic bulk composition „bulk 1“ in the system KFMASH. The chosen bulk composition is that of the Plattengneis (STÜWE & POWELL, 1995) with 15% H₂O in the system. Thick arrows show the locations of the *H-T* sections shown in Fig. 3. Black dots along the staurolite isograd indicate the terminations of the ‘visible’ part of the reaction where modal and enthalpy changes go to zero. The grey dot indicates the locus of maximum mode and enthalpy change along the reaction. The rectangle shows the part of the diagram which is reproduced in Fig. 4a. Divariant fields are white, trivariant fields are shaded.

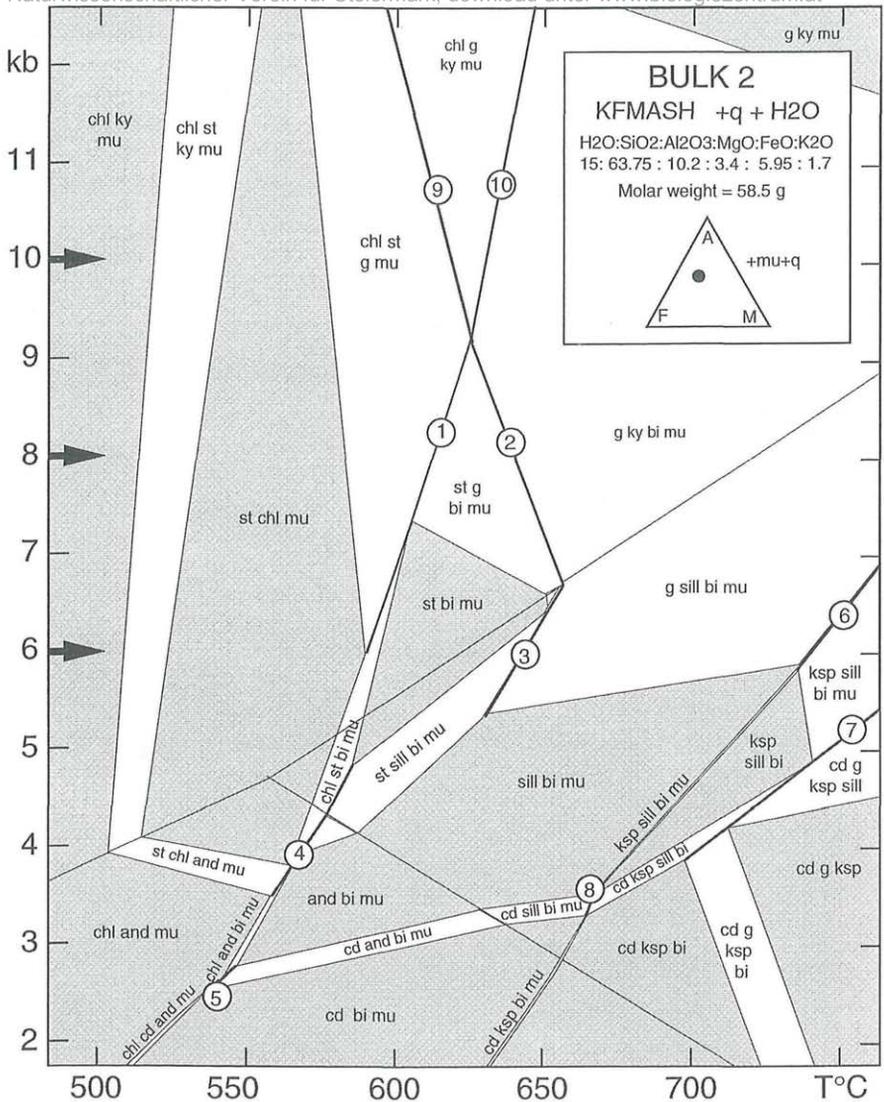


Fig. 2: Pseudosection of the pelitic bulk composition „bulk 2“ in the system KFMASH. The chosen bulk composition is that of XU et al. 1994 Fig. 8b, with 15% H₂O in the system. Thick arrows indicate locations of the *H-T* sections shown in Fig. 3. In the region between 550°C and 600°C and 3–4 kbar the shown pseudosection is simplified. A series of small divariant fields joining degenerate univariants should appear in this region. The difference of the shown pseudosection to that of XU et al. 1994 arises from the use of a newer version of the thermodynamic dataset, except for the absence of the divariant fields at low *T* (see text). Divariant fields are white, trivariant fields are shaded.

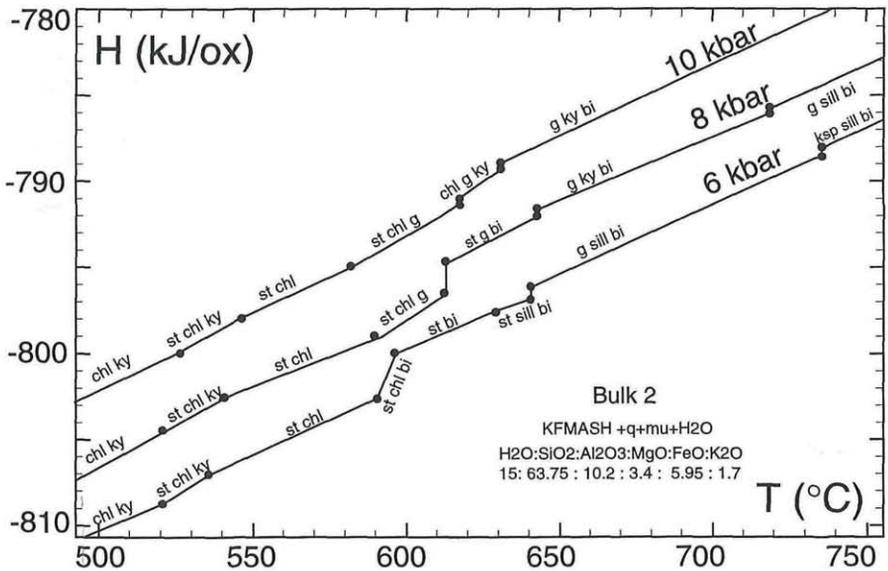
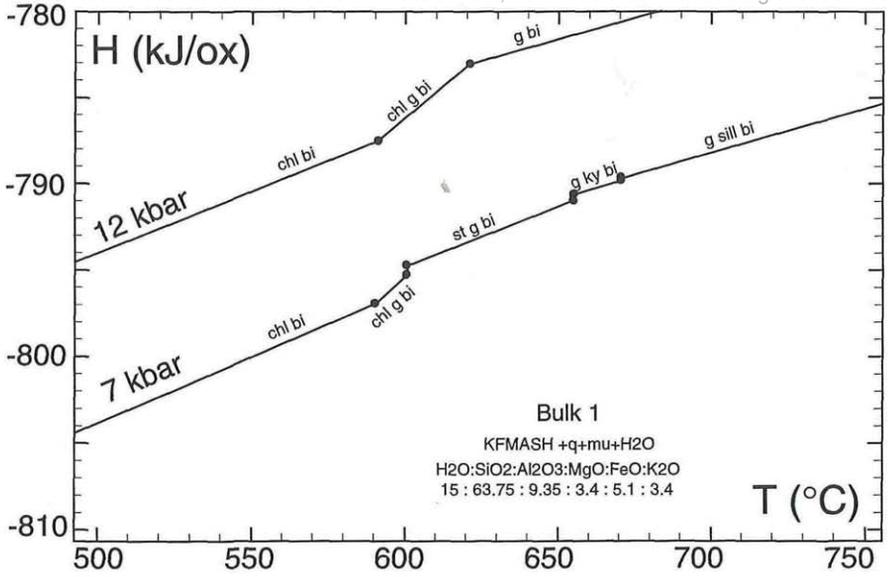


Fig. 3: Heat (H) vs temperature (T) sections through Figures 1 and 2. The enthalpy content is given in kJ mole^{-1} normalised to one oxide. This is 57.9 g of assemblage for *bulk 1* and 58.5 g assemblage for *bulk 2*. Enthalpy content per gram of assemblage is therefore given by dividing the H values by the respective weights.

$K_2O:FeO:MgO:Al_2O_3:SiO_2:H_2O = 1.7:5.95:3.4:10.2:63.75:15$. For both bulk compositions, thermodynamic pseudosections were calculated in the range between 480°C and 760°C and 2 to 13 kbar covering the majority of the *PT* range of interest to the Koralm (Fig. 1, 2). Minor differences of the absolute positions of the fields between this and the other quoted studies arise from the use of a newer version of the thermodynamic dataset in the present study. Ten univariant reactions appear within the *PT* range of interest:

- (1) chl + g + mu = st + bi + q + H₂O
- (2) st + bi + q = g + ky + mu + H₂O
- (3) st + bi + q = g + sill + mu + H₂O
- (4) chl + st + mu = and + bi + q + H₂O
- (5) chl + mu + q = cd + bi + and + H₂O
- (6) q + mu = g + ksp + sill + bi + H₂O
- (7) sill + bi + q = cd + g + ksp + H₂O
- (8) cd + mu + q = ksp + sill + bi + H₂O
- (9) chl + st + q = g + ky + H₂O
- (10) chl + mu = g + ky + bi + q + H₂O

This numbering is used to label the reactions in Figures 1–2. Of the reactions, reaction (1) is the staurolite isograd, reactions (2) and (3) are equivalent except for the aluminosilicate polymorph change and reaction (6) is the muscovite breakdown reaction. It should be noted that the stoichiometry of reactions (2), (3) and (9) is given by THERMOCALC but does not correspond to observations in the Koralm. The stoichiometry of these reactions as shown requires the X_{Mg} of garnet to be larger than that of staurolite which is not observed. Fortunately, this does not influence the subsequent discussion because: (a) We will show below that the heat of reaction released or consumed at univariant reactions is largely a function of the amount of H₂O released. This is largely independent of the relative X_{Mg} of garnet and staurolite and therefore of the topology of this reaction. (b) A comparison of Figures 1 and 2 with the *PT* path of THÖNI & JAGOUTZ (1992) and STÜWE & POWELL (1995) shows that the *PT* path of the Koralm crosses few univariant reactions. Reaction enthalpies of di- and trivariant equilibria are overall much more important than those of univariants. (c) The topology of all other equilibria in the grid remains unchanged for different stoichiometries of these reactions.

With the enthalpy calculation facility in THERMOCALC, the pseudosections of Figures 1–2 can, in principle, be contoured for enthalpy. However, such a plot is very cluttered and may even be misleading as it would include the adiabatic enthalpy changes that occur during pressure change. For clarity, a series of isobaric *H-T* sections were constructed through the pseudosections of Figures 1–2 (Fig. 3). The most important feature of Fig. 3 is that the curves are largely parallel and that the enthalpy content steps at univariant reactions are small compared to the enthalpy changes in divariant and trivariant fields. The slope of each curve is the heat capacity of the assemblage. The enthalpy change across a univariant reaction changes along the reaction, akin to modal changes (Fig. 4). These changes, for a given bulk composition, are zero where the reaction terminates in a trivariant assemblage (black dots on the staurolite isograd on Figs. 1, 4). Within each part of the univariant reaction, bounded by the same divariant fields, enthalpy and mode changes are effectively linear. Despite the absolute changes of enthalpy production along the univariants, the enthalpy change per mode change is constant along the entire reaction. Along the staurolite isograd shown in Fig. 4, the enthalpy change per gram of released H₂O is 2.8 kJg⁻¹ H₂O. This value is representative of many other full system reactions, and it can be used as a representative value for the enthalpy change associated with univariant reactions in the pelitic system. Thus, a good approximation of the enthalpy change across a dehydration reaction may be obtained by plotting the modal change of H₂O across the reaction and combining this with the 2.8 kJ g⁻¹ H₂O

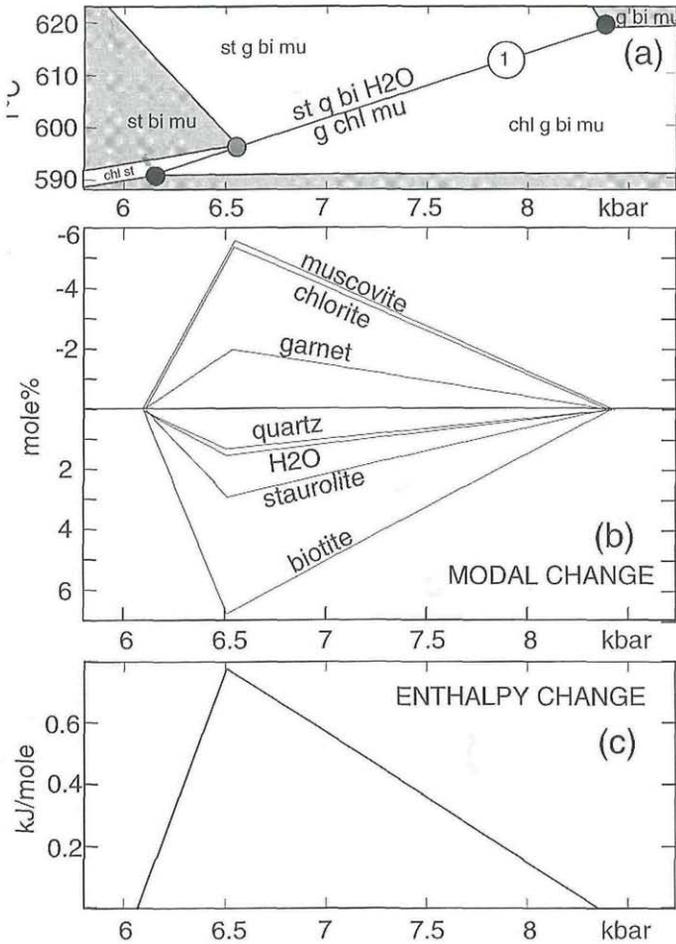


Fig. 4: Modal and enthalpy change along the staurolite isograd for the bulk composition *bulk 1*. (a) shows a section of the *PT* pseudosection also shown in Fig. 1, with the axes reversed. Shaded areas are trivariant fields, white areas are divariant fields. For this bulk composition the staurolite isograd is seen between 6.1 and 8.3 kbar. (b) Modal changes of phases across the staurolite isograd in an up-temperature direction. (c) Enthalpy change across the staurolite isograd in an up-temperature direction. If the enthalpy production is normalised to the modal change of H₂O, the staurolite isograd produces 2.8 kJ g⁻¹ H₂O. This is found by dividing the enthalpy change by the mode change of H₂O multiplied by its molar weight (18 g mole⁻¹).

value derived from Fig. 5. The amount of H₂O released across the ten different univariant reactions “seen” by *bulk 2* is plotted in Fig. 5. For the range of H₂O release of between 0 and 6 mole% H₂O (Fig. 5) (0–18.4 g H₂O kg⁻¹ assemblage) and 2.8 kJ g⁻¹ H₂O enthalpy change across each reaction, there is an enthalpy change of up to 51.5 kJ kg⁻¹ assemblage associated with the univariant reactions important to the pelitic rocks of the Koralm complex.

3. Discussion

3.1 The shape of H-T curves and thermal implications

The calculations presented above show that enthalpy changes associated with the univariant reactions are small compared to the overall enthalpy changes associated with the continuous reactions during temperature increase (Fig. 3). Therefore, it is possible to approximate the H changes during T increase with an average heat capacity as given by the average slope of the H - T curves on Fig. 3. For the curves shown on Fig. 3, this is about $cp_{bulk1} = 1380 \text{ J kg}^{-1}\text{K}^{-1}$ and $cp_{bulk2} = 1550 \text{ J kg}^{-1}\text{K}^{-1}$. These values may be considered as representative values for the heat capacity of pelitic rocks in general but it is noted that they are significantly higher than the average values for the crust generally used in the thermal modeling literature ($cp = 1000 \text{ J kg}^{-1}\text{K}^{-1}$) (e.g. WELLS, 1980; ENGLAND & THOMPSON, 1984). This is not unexpected, because pelitic sediments are more hydrated than many other rocks and heat consumed during the prograde path is therefore likely to be larger than that of the average crust. However, it indicates that in areas like the Koralm, where large vertical sections of the crust are made up of hydrated sediments, care must be taken that not too conservative values for the heat capacity are used. The large volumes of pelitic rocks in the Koralm suggest therefore that it may be particularly difficult to heat the rocks by conductive energy transfer from lower crustal levels.

3.2 Thermal buffering of PT Paths

In order to evaluate the thermal buffering effects of reaction enthalpy on the thermal evolution of PT paths in general, and the PT path of the Koralm in particular, a thermal model may, in principle, be coupled with a thermodynamic pseudosection and the H - T relationships of Fig. 3. However the small magnitude of the enthalpy changes across

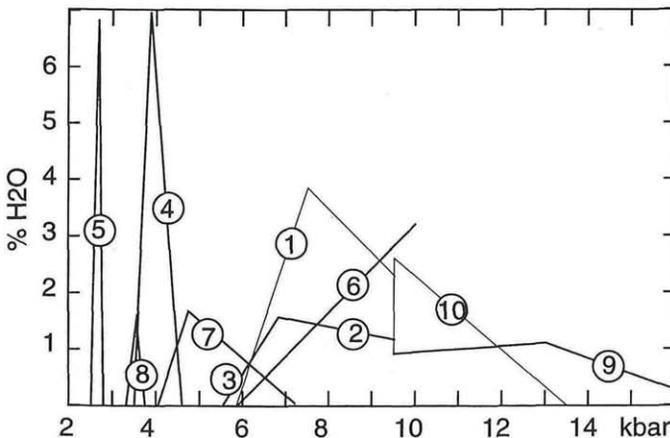


Fig. 5: Fluid production of individual univariant reactions appearing on the pseudosection for *bulk 2* (see Fig. 2). The abrupt change in slope of the fluid production curves occur at the transition from one divariant assemblage to the next. Fluid production goes to zero where the univariant terminates in a trivariant field. See text for labeling of reactions. Reaction (6) is only shown up to 10 kbar because it is likely to interfere with melting at higher P . The percentage of H_2O released is per mole and one oxide of assemblage. To convert the H_2O percentages into g H_2O per gram of assemblage, the values must be multiplied with the molar weight of H_2O (i.e. 18 g mole^{-1}) and divided by the weight of the assemblage (i.e. 58.5 g).

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 reactions, Fig. 3, confirms the result of previous authors that this is not warranted (CONNOLLY & THOMPSON, 1989). A simple calculation, based on the values calculated above, can confirm this. An enthalpy change of 51.5 kJ kg^{-1} of rock, and an average heat capacity of $1500 \text{ J kg}^{-1}\text{K}^{-1}$, increases temperature by only 34°C . It also has to be noted that this calculation assumes that there is no heat conducted away from the reaction site during the period of heat production. Any heat flow during the enthalpy production will decrease these thermal effects.

3.3 Buffering Effects on Parageneses

While it has been shown above that the effects of thermal buffering are comparatively small, we will now discuss how such effects may, nevertheless, be recorded by the rocks of the Koralm complex. For this purpose, it is clarified that "thermal buffering" refers to processes that decrease the rates of temperature change that may arise as the consequence of higher effective heat capacities in certain temperature ranges. The reader is also reminded that the considerations presented below are extremely simplified as they neglect, for example, the energetic effects of volume change and – of course – also neglect other heat production processes, for example those caused by rheology of a deforming rock. Thus the discussion below should be considered as a plausible possibility, but not be taken as the final word.

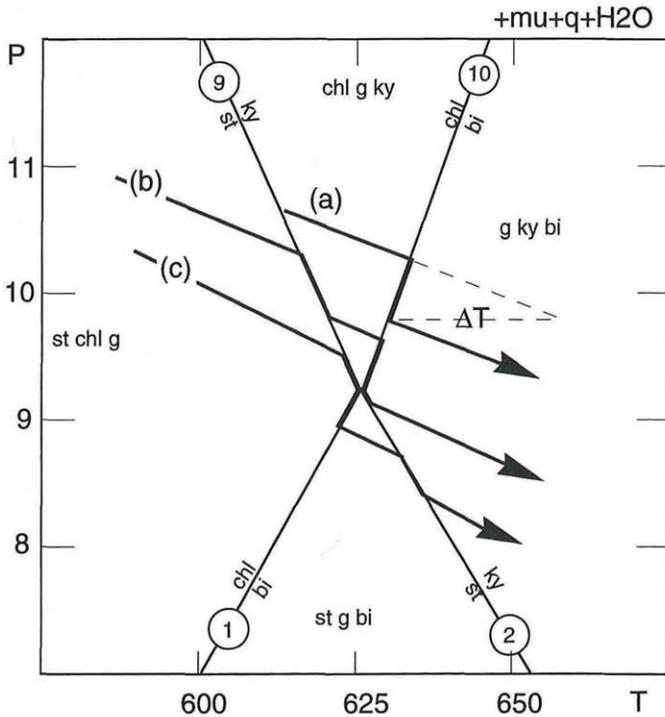


Fig. 6: *PT* diagram showing the effects of thermal buffering around the invariant point involving the reactions (1), (2), (9) and (10) (see Fig. 2). The univariant reactions are labeled by the reaction number (see text) and by the net-reaction effects across them. All 4 reactions are endothermic with increasing *T* so that the reactions *chl* → *bi* and *st* → *ky* are endothermic, while *bi* → *chl* and *ky* → *st* are exothermic.

Consider a hypothetical prograde PT path evolving in the vicinity of the invariant point involving reactions (1), (2), (9) and (10) (Fig. 6, see also Fig. 2). A typical rate of temperature change of a PT path may be some tens of $^{\circ}\text{C my}^{-1}$ implying that energy is withdrawn from the rocks at a rate of some $10^4 \text{ J kg}^{-1} \text{ my}^{-1}$ and rates of pressure change may be 0.5 kbar my^{-1} . If such a PT path meets the endothermic reaction (9), where the effective heat capacity becomes infinite until the reaction has gone to completion, it will be buffered along this reaction until the assemblage is fully converted. The enthalpy changes and heat capacities discussed above indicate that this buffering will occur over a T interval of $4\text{--}70^{\circ}\text{C}$ which may correspond to a depth change corresponding to 3.5 kbar (at a heating rate of $10^{\circ}\text{C my}^{-1}$, decompression rate of 0.5 kbar my^{-1}). Faster or slower energy transfer rates will *not* change the magnitude of the temperature interval over which buffering may occur. However, it *will* change the time duration of this buffering. Therefore, this PT path may well be buffered into the invariant point (path (c) on Fig. 6) stabilising a four phase assemblage. Correspondingly, PT paths at greater depths (paths (a) and (b) on Fig. 6) may have crossed reaction (9) previously and reach reaction (10). Similarly to path (c), these paths will be buffered along this reaction until the assemblage is fully converted with the difference being that temperature may actually decrease. These paths too may be buffered into the invariant point. At the invariant point, reaction may be understood in terms of two net-transfer reactions occurring simultaneously. For path (c), these are the reactions $\text{st} \rightarrow \text{ky}$ and $\text{chl} \rightarrow \text{bi}$ which are both endothermic. Considering the net transfer reaction $\text{st} \rightarrow \text{ky}$ has commenced previously along the univariant reaction (9), this reaction will be completed first and the subsequent, endothermic reaction will occur by buffering along reaction (1). The situation is equivalent for path (b). Clearly, if all PT paths cross all reactions, the paths will leave the reaction space in the same T -spacing as they entered it. However, it is conceivable that a range of PT paths is buffered towards a common point in PT and produce a common four phase assemblage during this process.

As a particular example, consider the parageneses on Fig. 6. Without any buffering affects, the three PT paths will all cross from the divariant assemblage $\text{g}+\text{st}+\text{chl}$ by the net transfer reaction $\text{st} \rightarrow \text{ky}$ into $\text{g}+\text{chl}+\text{ky}$ and later by the net transfer reaction $\text{chl} \rightarrow \text{bi}$ into the divariant field $\text{g}+\text{bi}+\text{ky}$. Each PT path will encounter the different fields at different times, depending on their temperature. The coexistence of st and bi is unlikely as they are separated by the divariant field $\text{g}+\text{chl}+\text{ky}$. Including the effects of buffering, several PT paths will encounter the stability field $\text{g}+\text{st}+\text{bi}$ at the same PT as they encounter $\text{g}+\text{chl}+\text{ky}$ at the invariant point. Therefore, the five phase assemblage $\text{g}+\text{st}+\text{bi}+\text{chl}+\text{ky}$ is at least encountered by the PT paths which it would not if no buffering occurred. Clearly, all preservation of these equilibria depends on the reaction kinetics involved and therefore also on the overall rates of energy transfer into the rock. However, it is clear that the buffering effects cause a kinetically much more favourable situation for preserving apparently low variant assemblages than would be encountered otherwise.

In the Koralm, the invariant point discussed above is met by aluminous assemblages on the decompression path from high grade conditions. It is met during cooling, rather than heating as illustrated above, but the buffering processes are equivalent. It is therefore possible, that surprisingly common existence of assemblages involving up to 7 or even 8 phases in parts of the Complex, and indeed in many metamorphic terrains, may be attributed to such a process.

3.4 Alternative heating mechanisms

In summary from above, the results show that the influence of reaction heat on the Cretaceous metamorphism of the Koralm complex may be reflected in low variant

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assemblages (section 3.3) , but that the overall effect on the heat budget is small (section 3.2). In conjunction with the results of EHLERS & al. (1994), STÜWE & POWELL (1994) and the predictions of STÜWE and SANDIFORD (1995) – which indicate that heat conduction alone is likely to be insufficient in causing the high grade metamorphism of the Koralm complex, – this indicates that alternative heat sources must have contributed to this metamorphism. In particular, two mechanisms are possible: 1. other heat producing mechanisms, for example shear heating and 2. advective processes, for example pervasive fluid infiltration. The influence of shear heating is speculated upon by STÜWE (1996). Further studies using relationships between timing of metamorphism, metamorphic grade and amount of deformation will be needed to test this prediction.

4. Conclusion

Quantitative calculation of the enthalpies of subsolidus equilibria in pelitic rocks confirms the estimates of earlier authors that enthalpy changes are *small* compared to the overall heat changes necessary to change a geothermal gradient. Moreover, it is shown that pelites have relatively high heat capacities compared to other rock types. Thus, in regions like the Koralm complex, where pelitic rocks dominate, it may be particularly difficult to conduct heat into complex.

In conjunction with our earlier interpretations, this result indicates that other contributions to metamorphism are likely. We speculate on the importance of shear heating. We also would like to raise the awareness to the lack of stable isotope studies in the region which may help to confirm the importance of metamorphic fluids as advective heating agents.

Despite the overall small effect of reaction enthalpy on thermal buffering of *PT* paths, it is possible that reaction enthalpy forces *PT* paths to converge locally towards the same invariant point. Such a process may allow the occurrence of low-variance assemblages. Assemblages with surprisingly many phases occur in parts of the Koralm and indeed in many metamorphic terrains. It is possible that their occurrence may be a consequence of such a process.

5. Appendix: The calculation of reaction enthalpies with THERMOCALC

All calculations presented in this study were performed in the model system, K_2O - FeO - MgO - Al_2O_3 - SiO_2 - H_2O (KFMASH) with the computer software THERMOCALC (POWELL & HOLLAND, 1988) and an updated version of the thermodynamic dataset of HOLLAND & POWELL 1990 (HOLLAND pers. comm., 1994). Calculation of reaction enthalpies is now possible on inclusion of the THERMOCALC datafile script “calch yes” (Table 1). The enthalpy of reaction across a univariant is calculated by running the corresponding divariants in the same way. Details about the method of calculation, mineral abbreviations and coding of the mineral formulas is the same as that of XU et al. 1994; STÜWE & POWELL 1995 and STÜWE 1995.

In order to see how the enthalpy of reaction for a univariant reaction involving solid solutions is calculated, it is necessary to review how such equilibria are determined. In particular, we focus on how enthalpy is determined in THERMOCALC. However, it is pointed out that other methods of calculating chemical equilibria in complex systems have been discussed (e.g. DE CAPITANI & BROWN, 1987) and that there is comprehensive reviews in the literature on the treating of chemical equilibria in rocks in general (e.g. SPEAR, 1993).

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 Table 1: THERMOCALC output for the garnet-staurilite-biotite divariant at 7kbar and a range of temperature giving the modal proportions for the given bulk composition, and the enthalpy (H in kJ) calculated from this. x and y are the $X_{Fe} = Fe/(Fe+Mg)$ and the $X_{Al} = Al/(Al+Fe+Mg)$, respectively.

THERMOCALC v2.4 PPC, Roger Powell and Tim Holland running
 at 10.29 on Tue 27 Jun,1995
 (thermodynamic dataset produced at 16.38 on Sat 5 Nov, 1994)

composition

H2O	SiO2	Al2O3	MgO	FeO	K2O
15	63.75	9.35	3.40	5.10	3.40

<=====>

phases : st, g, bi, (mu, q, fluid)

P(kbar)	T(C)	x(st)	x(g)	x(bi)	y(bi)	x(mu)	y(mu)
7.0	610	0.920	0.859	0.531	0.434	0.727	0.864

mode	st	g	bi	mu	q	H2O	bulk	H
	0.021	0.024	0.193	0.261	0.422	0.080	-1.00	-794.1578

P(kbar)	T(C)	x(st)	x(g)	x(bi)	y(bi)	x(mu)	y(mu)
7.0	620	0.914	0.853	0.524	0.441	0.720	0.865

mode	st	g	bi	mu	q	H2O	bulk	H
	0.018	0.029	0.188	0.265	0.420	0.080	-1.00	-793.4186

P(kbar)	T(C)	x(st)	x(g)	x(bi)	y(bi)	x(mu)	y(mu)
7.0	630	0.906	0.846	0.518	0.448	0.714	0.867

mode	st	g	bi	mu	q	H2O	bulk	H
	0.015	0.034	0.183	0.268	0.419	0.081	-1.00	-792.6917

P(kbar)	T(C)	x(st)	x(g)	x(bi)	y(bi)	x(mu)	y(mu)
7.0	640	0.899	0.840	0.512	0.454	0.707	0.868

mode	st	g	bi	mu	q	H2O	bulk	H
	0.012	0.039	0.178	0.272	0.418	0.081	-1.00	-791.9547

P(kbar)	T(C)	x(st)	x(g)	x(bi)	y(bi)	x(mu)	y(mu)
7.0	650	0.890	0.834	0.506	0.461	0.700	0.870

mode	st	g	bi	mu	q	H2O	bulk	H
	0.009	0.045	0.174	0.276	0.416	0.081	-1.00	-791.2240

For a divariant assemblage, the equilibrium compositions of the phases at a specified PT are calculated in THERMOCALC by solving the set of non-linear simultaneous equations which are the equilibrium relationships for the independent set of reactions between the end-members of the phases. Each of the equilibrium relationships has the form:

$$0 = \Delta G^0 + RT \ln K \quad (1)$$

in which ΔG^0 is the standard Gibbs energy of reaction, R is the gas constant, T is temperature and K is the equilibrium constant. With the calculated compositions of the phases, the bulk compositions of the phases can be calculated, and it is then straightforward to determine if a specified rock composition "sees" the reaction, and, if it does, to calculate the modal proportions of the phases on each side of it (e.g. STÜWE & POWELL 1995). With the modal proportions, m_k , and the thermodynamics used in (1), the Gibbs energy of an assemblage, G , with respect to a reference state can be calculated:

$$G = \sum_k m_k G_k$$

where the sum is over the phases in the system. The Gibbs energy of phase k , G_k , is calculated from:

$$G_k = \sum_i P_{ik} \mu_{ik}$$

Table 2: THERMOCALC output for reactions between the aluminosilicate polymorphs for a range of pressures, giving the PT positions of the reactions, and the enthalpy of reaction (H in kJ).

THERMOCALC v2.4 PPC, Roger Powell and Tim Holland
 running at 15.25 on Tue 27 Jun, 1995
 (thermodynamic dataset produced at 16.38 on Sat 5 Nov, 1994)

Reactions

- 1) and = ky
- 2) sill = ky
- 3) sill = and

Temperatures in the range 200 <-> 1000C;
 uncertainties at or near 6.0 kbars

TC	3.0	5.0	7.0	9.0	sdT	sdP
1	427	592	766	949	10	0.11
H	-6.43	-7.60	-8.68	-9.72		
2	487	576	668	760	19	0.41
H	-9.72	-10.55	-11.39	-12.26		
3	642	538	448	369	56	1.3
H	-3.03	-3.01	-2.97	-2.89		

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 where the sum is over the end-members in k , with p_{ik} the proportion of end-member i in phase k , and m_{ik} the chemical potential of end-member i in phase k . The enthalpy of an assemblage, H , can be calculated from the way G changes with temperature, T :

$$H = \left[\frac{\partial \left(\frac{G}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right]_P \quad (2)$$

The only difficulty with using this equation is a consequence of the dependence of the compositions of the phases in the assemblage on T : in general all of m_i , p_{ik} and m_{ik} are a function of T . Although in principle analytical derivatives can be made, in practice, finite differences are used. Thus if the derivative at T' is required, G is evaluated at $T' - \Delta T$ and at $T' + \Delta T$, and H is evaluated as

$$H|_{T'} \approx \left[\frac{\left(\frac{G}{T} \right) |_{T'+\Delta T} - \left(\frac{G}{T} \right) |_{T'-\Delta T}}{\left(\frac{1}{T} \right) |_{T'+\Delta T} - \left(\frac{1}{T} \right) |_{T'-\Delta T}} \right]_P \quad (3)$$

the derivative calculated in this way is called a central difference. The magnitude of ΔT remains to be decided. It needs to be small enough to be capable of approximating the derivative well, but not so small that rounding errors can occur in the calculation (see below).

To calculate enthalpies of divariant assemblages, (2) or (3) may be used directly. To calculate the enthalpy of reaction associated with a univariant equilibrium, the difference between the enthalpies of the divariant assemblages stable on entry into, and exit from, the reaction are sought; these can also be calculated with (2). Enthalpies of trivariant assemblages may be determined in the same way as for divariant assemblages.

The main difficulty that may arise concerns the magnitude of ΔT in (3); currently $\Delta T = 2.5$ K is used in THERMOCALC. It needs to be at least as small as this, particularly for calculations on narrow divariant fields, but for other equilibria, this value is not large enough. Amongst the divariant equilibria we have investigated in the KFMASH system, the most troublesome assemblage is chlorite+garnet+biotite. In this case, calculated enthalpies are chaotically variable as rounding errors interfere with the calculation. Such behaviour may be expected when the compositions of the phases change slowly with temperature, as they do with this equilibrium. If such behaviour is observed or suspected, the best approach is not to try and calculate H directly, but to focus on the variation of G with T . In THERMOCALC, these values can be accessed via the datafile script "calc yes" (with "calch no"). Having calculated G values over a temperature range using a small interval, a plot of G/T against $1/T$ should deliver a much better estimate of H .

The enthalpies given by THERMOCALC are with respect to a 1bar and 25°C reference state. Viewed in terms of (2), the only term involved in the Gibbs energy which involves formation from the elements is the enthalpy of formation from the elements at 1bar and 25°C (as in HOLLAND and POWELL, 1990). Gibbs energies and enthalpies are given in kJ for one mole of assemblage normalised to one oxide. Therefore, the weight of the assemblage for which the calculation is performed may be found by multiplying the proportion of each oxide in the assemblage with its molecular weight. Correspondingly, the weight for which the mode, Gibbs energy or enthalpy of each phase is given in the

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 THERMOCALC output may be found by multiplying the output value with the molar weight of the phase, and dividing by the number of oxides in this phase. For H₂O this is straight forward inasmuch as the output needs simply to be multiplied by 18, but for other phases involving solid solutions, averaged molar weights must be used and, in the case of Tschermak's substitutions, averaged numbers of oxides are also needed.

To calculate reaction enthalpies for reactions which involve phases which are not solid solutions, the procedure is straightforward. For any reaction between mineral end-members, the equilibrium relationship is given by (1). For the case where the phases are made up of pure end-members, $K=1$ (for a standard state for each end-member of the pure end-member at the PT of interest), and the equilibrium relationship reduces to $\Delta G^0=0$. For such reactions involving H₂O, the fugacity of H₂O is included in ΔG^0 . The simplest way to extract the enthalpy of reaction is to linearise ΔG^0 in a PT range of interest:

$$\Delta G^0 = a + bT + cP$$

where a , b and c are calculated from the full expression for ΔG (e.g. HOLLAND & POWELL, 1990). The values of a , b and c vary, generally slowly, with the PT around which the linearisation is done. Choosing this point to be on the reaction, (P', T'), then:

$$\Delta G^0 = b(T - T') + c(P - P')$$

because $\Delta\mu=0$ on the reaction. As:

$$\Delta H = \left(\frac{\partial \left(\frac{G^0}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right)_P$$

similarly to (2), and

$$\frac{\Delta G^0}{T} = b \left(1 - \frac{T'}{T} \right) + c \left(\frac{P - P'}{T} \right)$$

then the enthalpy of reaction of the pure end member reaction is

$$\Delta H = -bT' - cP'$$

This calculation is now performed by THERMOCALC as part of "mode 3" if the datafile script "calch yes" is included. An example run is shown in Table 2. The given value is the enthalpy change associated with reaction from the low- T to the high- T side in kJ mole⁻¹ for one oxide. For most reactions, up temperature reaction is endothermic and the given ΔH value is therefore negative. If this output is to be converted to, say, enthalpy per gram H₂O released, then the output must be divided by the number of molecules of water produced by the reaction, and by the molar weight of one mole water (i.e. 18 g).

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