



## Abstract

Reactions in fluid inclusions in plagioclase: thermodynamic modelling, constrains on *PT* paths and a natural example

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Thermodynamic modelling illustrates that reactions in inclusions between the entrapped fluid and a plagioclase host do take place at retrograde metamorphic conditions. The general form of the reactions is *Plagioclase + Fluid = Products*. The composition of both the plagioclase and fluid put important constrains on the occurrence of those reactions. Valuable petrogenetic information can be derived from the identification of these processes in fluid inclusions, and more precise estimation of *PT* conditions during earlier metamorphic stages or fluid entrapment can be obtained.

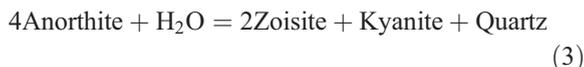
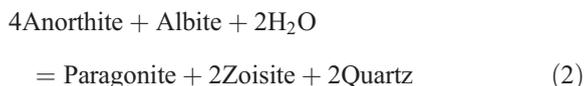
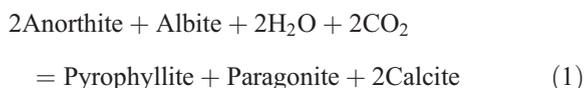
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**1. Introduction**

Post-entrapment changes in fluid inclusions are likely to occur in metamorphic rocks. A chemical reaction between host and entrapped fluid is one possible mechanism for those changes (see also Kleinfeld and Bakker, 2002, and reference therein). During the formation of fluid inclusions, both primary and secondary, the enclosed fluid and its host crystal are not chemically reactive. The inclusions are formed during precipitation processes of the mineral host out of an oversaturated solution. However, at temperatures and pressures different from the formation conditions, the micro-system may become unstable and therefore react. Quartz, the most studied host mineral, is not chemically reactive with most of the enclosed fluids over a wide range of *P–T* conditions.

For feldspars, the following reactions have been taken into account:



These reactions are thermodynamically modelled in this study to predict their occurrence at specific temperature, pressure, plagioclase composition and

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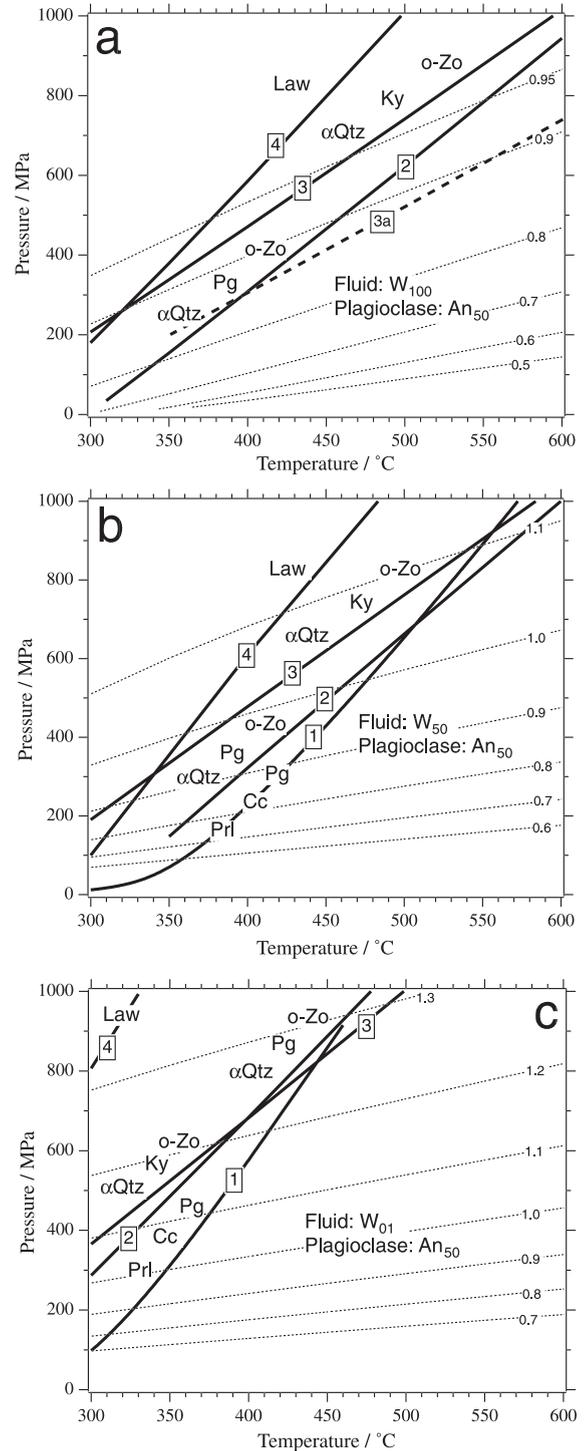
fluid composition. Natural fluid inclusion in plagioclases from the O.-v.-Gruber Anorthosite complex, central Dronning Maud Land (east Antarctica) has been characterised by microthermometry and micro-Raman spectroscopy to identify the presence of reaction products as occur in reactions (1)–(4) (see also Kleinfeld and Bakker, 2002).

## 2. Thermodynamic modelling

The stability of reactants and products in reactions (1)–(4) has been modelled according to the thermodynamic data from Berman (1988). The activities of albite and anorthite in plagioclase are obtained from a non-ideal mixing model for ternary feldspars according to Elkins and Grove (1990). The fugacities and isochores of pure H<sub>2</sub>O fluids are calculated from the equation of state from Haar et al. (1984), whereas fugacities and isochores in mixtures of CO<sub>2</sub> and H<sub>2</sub>O are obtained from Duan et al. (1996).

With a pure H<sub>2</sub>O fluid included in plagioclase (An<sub>50</sub>), only reactions (2)–(4) may occur (Fig. 1a). Reaction (2), the formation of quartz, ortho-zoisite and paragonite, occurs at the highest temperature. The formation of lawsonite (reaction (4)) occurs at the lowest temperature. The addition of CO<sub>2</sub> to the fluid, up to 50 mol% (Fig. 1b), causes a shift of these reactions toward higher pressures. Moreover, an extra reaction (1) is introduced in the system, which occurs at higher temperatures below 700 MPa. At higher pressures, reaction (2) occurs at higher temperatures. A fluid strongly enriched in CO<sub>2</sub>, up to 99 mol% (Fig. 1c), is extending the general trend of shifting all reactions to higher pressures. Reaction (1) remains as the reaction occurring at the highest temperature below 800 MPa. At higher pressures, however, kyanite, quartz and ortho-zoisite (reaction (3)) occur at higher temperatures. The formation of lawsonite occurs at relative low temperatures. A pure CO<sub>2</sub> fluid is unable to react with its plagioclase host.

Fig. 1. Temperature–pressure diagrams with reaction curves 1, 2, 3 and 4 for fluid compositions of (a) 100 (W<sub>100</sub>), (b) 50 (W<sub>50</sub>) and (c) 1 mol% H<sub>2</sub>O (W<sub>01</sub>). The composition of the reacting plagioclase is indicated by An<sub>50</sub>. The thick long-dashed line (3a) indicates the position of reaction 3 with pure anorthite. Isochores for different densities of corresponding fluid compositions are illustrated by thin dashed lines.



### 3. Isochores and fluid *PT* path restrictions

*PT* paths of rock are defined by large-scale geological processes, whereas the *PT* path of the fluid enclosed in minerals is defined by its isochore. Several isochores have been projected in Fig. 1 to illustrate the occurrence of reactions in inclusions with different densities. In H<sub>2</sub>O-rich fluids, no reaction will take place in inclusions with a density smaller than 0.7 g cm<sup>-1</sup> (Fig. 1a). Higher density inclusions may form paragonite, ortho-zoisite and quartz. Low-density inclusions are also nonreactive in CO<sub>2</sub>-bearing fluids (Fig. 1b and c). Inclusions (50 mol% CO<sub>2</sub>) with a density lower than 1.04 g cm<sup>-1</sup> react to pyrophyllite, paragonite and calcite, whereas higher density inclusions react to paragonite, ortho-zoisite and quartz (Fig. 1b). Inclusions with 99 mol% CO<sub>2</sub> react similarly at lower pressures (<1.26 g cm<sup>-1</sup>), producing pyrophyllite, paragonite and calcite (Fig. 1c). However, higher density inclusions produce kyanite, ortho-zoisite and quartz. These examples illustrate the variety of reaction possibilities caused by difference in fluid composition and fluid density that can take place in fluid inclusions in plagioclase. Vice versa, the presence or absence of certain reaction products inside fluid inclusions puts important con-

straints on the reconstruction of the fluid originally trapped at higher *PT* conditions.

### 4. Natural example

Dense, CO<sub>2</sub>-rich fluid inclusions hosted by plagioclase, An<sub>45</sub> to An<sub>54</sub> of the O.-v.-Gruber Anorthosite body, central Dronning Maud Land (East Antarctica) (Kleinefeld and Bakker, 2002) have shown to contain varying amounts of small calcite, paragonite and pyrophyllite crystals, as detected by micro-Raman spectroscopy (Fig. 2). These crystals are reaction products (reaction (1)) that have formed during cooling of the host and the original CO<sub>2</sub>-rich H<sub>2</sub>O-bearing enclosed fluid. Variable amounts and locally absence of these reaction products illustrate, that the reaction did not take place uniformly in all fluid inclusions, possibly due to differences in kinetics as caused by differences in shape and size. Although free H<sub>2</sub>O is not detectable in plagioclase-hosted inclusions, the occurrence of OH-bearing sheet silicates indicates that the original fluid was not pure CO<sub>2</sub>, but contained significant amounts of H<sub>2</sub>O. This fluid reacted with its plagioclase host, leading to a complete consumption of the subordinate aqueous fluid component, the

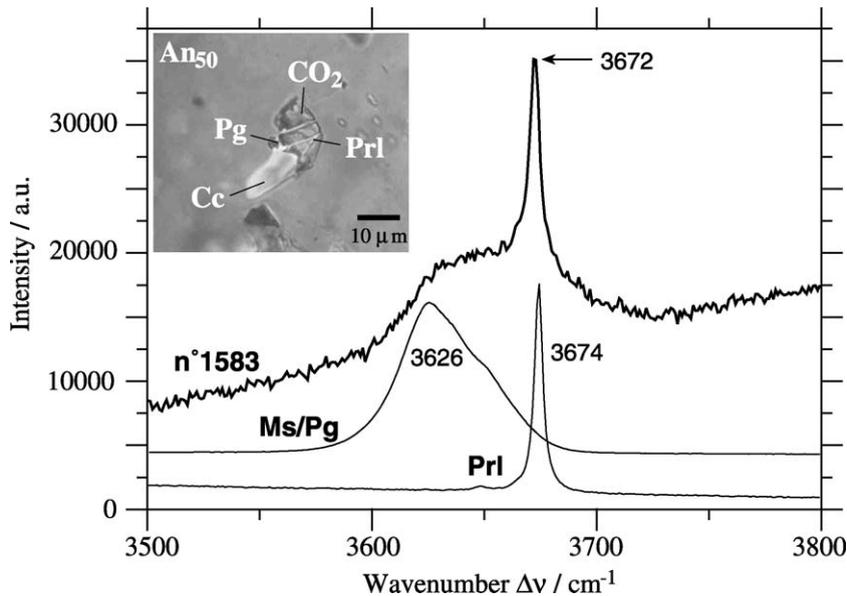


Fig. 2. Photomicrograph and Raman spectra of sheet silicates from sample no. 1583. Standard spectra of muscovite/paragonite (Ms/Pg) and pyrophyllite (PrI) are indicated as reference (after Kleinefeld and Bakker, 2002).

formation of a residual carbonic liquid and the crystallisation of carbonates and sheet silicates. The inclusion isochores can be reconstructed after recognition of the amount of reaction products present. The original density could not have exceeded  $1.04 \text{ g cm}^{-3}$  as ortho-zoisite and quartz would have formed instead (Fig. 1b).

## 5. Conclusions

Thermodynamic modelling of four different reactions between a plagioclase host ( $\text{An}_{50}$ ) and a  $\text{H}_2\text{O}$ – $\text{CO}_2$ -rich entrapped fluid illustrates post-entrapment changes that can take place during retrograde metamorphic conditions. The composition of the plagioclase and the fluid composition and density put important constraints on the occurrence of those reactions. The formation of calcite, paragonite and pyrophyllite is the most probable reaction to occur at internal pressures below 800 MPa, whereas quartz, ortho-zoisite and paragonite/kyanite form at higher internal pressures. Lawsonite is unlikely to occur as the reaction takes place at much lower temperatures. Recalculation of compositional and volumetric prop-

erties of the original fluid led to the reconstruction of unmodified inclusions, and giving more realistic estimation of  $PT$  conditions during earlier metamorphic stages or fluid capturing.

## Acknowledgements

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