The petrological importance of accessory Ti-phases: experimental constraints on an activity model for titanite in the system $CaTiSiO_4O$ – $CaAlSiO_4F$

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Experimental studies were carried out to evaluate phase relations involving titanite ($CaTiSiO_4O$) – F-Al titanite ($CaAlSiO_4F$) solid solution in the system $CaSiO_3$ – Al_2SiO_5 – TiO_2 – CaF_2. Piston-cylinder experiments at 900 – 1000˚C and 1.1 – 4.0 GPa characterized the effect of excess fluorite on titanite composition for the equilibrium titanite + kyanite = anorthite + rutile (TARK). The reaction displacement experiments show that at high pressures the assemblage (Al + F) titanite + kyanite + rutile + fluorite is stable and at low pressures the assemblage (Al + F) titanite + anorthite + rutile + fluorite is stable.

The reduction in titanite activity resulted in shifts from the stoichiometric equilibrium of 1.60 GPa to 1.15 ± 0.05 GPa at 900°C, 1.79 GPa to 1.375 ± 0.025 GPa at 1000°C and from 1.98 GPa to 1.575 ± 0.025 GPa at 1100°C. The activity of $CaTiSiO_4O$ is closely approximated by an ideal molecular activity model (X_{Ti}) at 1100°C, but shows a negative deviation at 1000°C and 900°C from ideality. Since the chemical data at 900°C and 1000°C show large uncertainties, due to chemical heterogeneities in the experiments, the molecular activity model as an approximation is recommended for use in calculations for titanites with X_{Al} = 0.1 – 0.4, until more data are available. Although our data were obtained at high temperatures (900–1100˚C), they provide important constraints on the use of a possible activity model for petrological calculations. The current data do *not* allow the extraction of meaningful values of the interaction parameter, *W*, of a regular solid solution model, due to the chemical variations of the (Al + F) titanite compositions and the experimental uncertainties. For calculations involving natural (Al + F)-rich titanites in the compositional range of X_{Al} = 0.1 – 0.3, the molecular model seems to be the better approach to predict the activity of $CaTiSiO_4O$ in titanite than the ionic models at high temperatures.

Troitzsch and Ellis (2002) recently published a study on the thermodynamic properties of F-Al titanite. In contrast to this study by Tropper et al. (2002), the two studies differ in the choice of the activity model and the estimated values of the interaction parameter *W* for the solid solution. In our calculations we used a simple symmetrical model, which resulted in a negative deviation from ideality, in contrast to the slight positive deviation in their local balance and multi-site mixing models. The data for *W* obtained in our study are directly based on experiments and have definitive negative deviations. Recalculation of the *P-T* conditions of three eclogites illustrates the difference in pressure estimates resulting from the choice of different activity models (molecular vs. ionic) ranging from 0.05 to 2.1 GPa, depending on the $CaAlSiO_4F$ substitution in the natural titanites and the sensitivity of reactions to changes in the activity of $CaTiSiO_4O$ in titanite.

Troitzsch, U & Ellis, D.J., 2002: Contrib. Mineral. Petrol., 142, 543-563.
Tropper, P., Manning, C.E., Essene, E.J., 2002: J. Petrol. (in press).

Some Insights on the geotectonic evolution of the central Southern Alps (Dolomites) along the Transalp-Traverse: Thermal maturity data and basin modelling

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The Permo-Mesozoic sedimentary succession along the TRANSALP-Traverse in the central Dolomites is very well suited for combining thermal maturity investigations and basin modelling in order to unravel the thermal and geodynamic evolution of the area. A new and detailed regional coalification pattern (i.e. thermal maturity) was established based on the microscopical analyses of about 80 samples, including the measurements of the reflectance of vitrinite. Rock-Eval pyrolysis was used for characterising the organic material. The results presented here are based on outcrop samples taken from areas along the TRANSALP Traverse. These include sedimentary rocks from the middle Permian *Gardena-Formation* up to the Cretaceous *Antruilles-Formation.*

The regional vitrinite reflectance pattern indicates an obvious increase of thermal maturity with stratigraphic age. For example a maturity of about 0.5 % VR_r was found for the late Triassic *Heiligkreuz/Raibl* Formation, whereas values of around 0.9 % VR_r measured for the middle Permian *Gardena* formation. This indicates a pre-orogenic coalification pattern as well as an overall low level of thermal maturity of the Permo-Mesozoic sedimentary successions. The measured maturities for the *Heiligkreuz/Raibl Formation* indicate a maximum burial depth of 1850 meters, based on the method described by YAMAJI (1986). Furthermore, the vitrinite reflectance values are very well in accordance with the maturity data derived from Rock-Eval pyrolysis.

Basin modelling for the "Alta badia" valley indicates that the present-day surface of the *Heiligkreuz/Raibl Formation* was overlain by an approximately 1750 meter thick sedimentary sequence during maximum burial with a concurrent basal heat flow of 62 $mW{\cdot}m^{-2}$. In the study area, however, only 1000 meters of the reconstructed overburden are preserved today. These modelling results imply that Mesozoic and Cenozoic sedimentation lasted longer and was more widespread than documented by the preserved present-day sedimentary sequence. Assumptions about the exact timing of maximum burial, which was probably reached during Upper Cretaceous times are so far not fully clarified. The question whether the eroded sequence consisted of autochthonous sedimentary rocks or of allochthonous thrust sheets is not cleared either. Fission track data and cross section balancing are currently performed and will help elucidate the problem.

Yamaji, A., 1986: Analysis of vitrinite reflectance-burial depth relations in dynamical geological settings by direct integration method. Jap. Ass. Pet. Techn., 51/3: 1-8.

Eoalpine versus Tertiary deformation: Dating of heterogeneously partitioned strain (Tauern Window, Austria)

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The Salzachtal-Ennstal fault zone (SEMP) is a major crustal-scale transpressional shear zone, which developed at the northern border of the Tauern Window during Tertiary lateral extrusion and unroofing (Linzer et al. 1997; Neubauer et al., 1999). Between Zell am See and the Rauriser Ache the Salzachtal-Fault juxtaposes rocks of the Paleozoic Upper Austroalpine Greywacke Unit and the Penninic Units of the Tauern Window. Both units show distinct deformational and cooling histories, which are constrained by new kinematic data and geochronological $^{40}Ar/^{39}Ar$ age datings.

The Penninic Units of the northernmost Tauern Window are part of a transpressional shear zone accomodating sinistral ductile shear and c. NNE/SSW compression along the E-W-striking shear zone. Kinematic data are mainly obtained from mylonitic marbles. Formation ages of synkinematic minerals from 28 Ma to 35 Ma constrain the age of sinistral transpression at the northern border of the Tauern window. These ages are well defined by 9 $^{40}Ar/^{39}Ar$ data from mica of different grain size fractions (< 2 μ, 6-11 μ and 11-20 μ; Fig. 1). High temperature steps indicate Cretaceous ages of the core of micas. The rocks of the Greywacke Unit are devoid of comparable transpressional structures. The unit comprises three main Cretaceous (Eoalpine) deformation events in its current position: D_n ductile shear related to the formation of c. E-W striking, subhorizontal stretching lineations, D_{n+1} south-vergent folding and D_{n+2} normal faulting towards N indicated by SC-fabrics. 6 Createous $^{40}Ar/^{39}Ar$ -cooling ages ranging from 90 to 115 Ma from white mica (< 2 μ, 6-11 μ and 11-20 μ) indicate that the deformations D_n to D_{n+2} occurred during the Cretaceous.

Structures related to sinistral transpression provide further evidence for the kinematics of the sinistral SEMP-wrench fault, which is kinematically related to the exhumation of the Penninic Units south of the fault (Linzer et al. 1997; Neubauer et al., 1999). This wrench zone previously was interpreted as a Late Oligocene/ Early Miocene structure. However, $^{40}Ar/^{39}Ar$ data record Late Eocene/Early Oligocene (28 Ma–35 Ma) ages for the beginning of transpressional deformation at the northern border of the Tauern window. The data presented in this study are in line with previously published age data constraining the onset of decompression of the Penninic Units of the Tauern Window with 35 Ma (Selverstone 1993).