

Metamorphism of mesozoic calcareous metasediments in the Hohe Tauern, Austria

By V. HÖCK* and G. HOSCHEK**

With 7 Figures and 2 Tables

Zusammenfassung

In der Oberen Schieferhülle der Westlichen Hohen Tauern wurde die regionale Verteilung der Mineralparagenesen in kalkigen Gesteinen kartiert. Im niedrig-gradigen Bereich begleiten Kalifeldspat, Stilpnomelan und Chloritoid die Hauptparagenese Muscovit + Chlorit + Quarz + Calcit + Dolomit. Bei zunehmendem Metamorphosegrad wurde die Bildung von Biotit, Zoisit, Plagioklas, selten auch von Talk und Tremolit festgestellt. Die Isograden für das Auftreten von Biotit und Calcit (auf Kosten des Abbaus von Kalifeldspat und Dolomit) und von Biotit + Zoisit + Calcit (auf Kosten von Muscovit + Chlorit + Calcit + Dolomit) sind in Übereinstimmung mit den Isothermen aufgrund der Untersuchungen von Sauerstoffisotopen (HOERNES & FRIEDRICHSEN 1974). Von diesen Daten und den experimentell bestimmten Gleichgewichten der Kalksilikatparagenesen kann ein Mindestdruck von 5 kb bei Temperaturen von 550–570° C für den hochtemperierten Bereich der Alpenin Metamorphose in den Westlichen Hohen Tauern abgeleitet werden.

Im Gegensatz zu den Westlichen Hohen Tauern ist in den Kalkschiefern der Mittleren Hohen Tauern Kalifeldspat und Biotit selten, Granat und Margarit besonders im höher metamorphen Teil relativ häufig. Die Metamorphose kann innerhalb des Sechs-Komponentensystems $\text{CaO} - \text{Al}_2\text{O}_3 - \text{MgO} - \text{SiO}_2 - \text{CO}_2 - \text{H}_2\text{O}$ durch die Paragenesen: Calcit + Chlorit + Dolomit + Margarit + Zoisit/Klinozoisit + Quarz, den sogenannten „Margarit“ Isograd und Calcit + Chlorit + Granat + Zoisit/Klinoisit + Quarz, den sogenannten „Granat“ Isograd beschrieben werden. Für den „Margarit“ Isograd wird eine Temperatur von 500° C bei einem Gesamtdruck von 4–6 kb geschätzt. Die Unterschiede in der Mineralogie zwischen Westlichen und Mittleren Hohen Tauern werden auf unterschiedliche Temperaturen und Gehalte von CO_2 in der fluiden Phase bzw. auf unterschiedliche Gesteinszusammensetzungen zurückgeführt.

Summary

Regional distribution of mineral assemblages has been mapped in calcareous rocks of the Upper Schieferhülle in the Western Hohe Tauern. In low grade areas

Adresse der Verfasser:

* Institut für Geowissenschaften, Universität Salzburg,
Akademiestraße 26, A-5020 Salzburg.

** Institut für Mineralogie und Petrographie, Universität Innsbruck,
Universitätsstraße 4, A-6020 Innsbruck.

K-feldspar, stilpnomelane or chloritoid join the main assemblages muscovite + chlorite + quartz + calcite + dolomite. Towards higher metamorphic grade, formation of biotite, zoisite, plagioclase and rarely talc and tremolite has been observed. Isogrades for the incoming of biotite + calcite (due to breakdown of K-feldspar + dolomite) and of biotite + zoisite + calcite (due to breakdown of muscovite + chlorite + calcite + dolomite) are in accordance with isotherms based on oxygen isotope studies (HOERNES & FRIEDRICHSEN 1974). From these data and the constraints given by experimentally determined calc-silicate equilibria a minimum pressure of 5 kb at temperatures of 550–570° C is deduced for the high grade part of the Alpine metamorphism in the Western Hohe Tauern.

In contrast to the Western Hohe Tauern K-feldspar and biotite are rare in calcschists in the middle part of the Hohe Tauern, whereas garnet and margarite are relatively abundant especially at higher metamorphic grade. The metamorphism can be described within the six component system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{MgO} - \text{SiO}_2 - \text{CO}_2 - \text{H}_2\text{O}$ by the phase assemblages: calcite + chlorite + dolomite + margarite + zoisite/clinozoisite + quartz, called the "margarite" isograd and calcite + chlorite + garnet + zoisite/clinozoisite + quartz, the "garnet" isograd. Temperatures for the "margarite" isograd are estimated 500° C, the total pressure 4–6 kb.

The differences in the mineralogy between western and middle part of the Hohe Tauern are ascribed to several facts: different temperatures and mole fractions of CO_2 as well as variable rock compositions.

Introduction

The posthercynian sequences in the Hohe Tauern are grouped by FRASL (1958) into three series: the "Wustkogelserie" = Permoscythian quartzites and meta-arcoses, the mainly Triassic "Karbonatgesteinserie" composed of metamorphic limestones and dolomites intercalated with minor amounts of rauhwacke and gypsum; the uppermost Triassic part, the pelitic "Quartenschiefer" horizon leads to the "Bündnerschieferserie" comprising a sequence of metamorphosed marls, shales, breccias, sandstones and basic rocks (ophiolites) of late to post-Triassic age. Only the latter part of the sequence represents eugeosynclinal facies of the Penninic trough in the Hohe Tauern.

From the petrological point of view the Mesozoic rocks can be divided in four groups:

- 1) metapelites and metasammites without carbonate minerals
- 2) almost pure calcareous rocks and siliceous dolomites including dolomite breccias with siliceous matrix and quartzites with dolomitic impurities (carbonate-quartzites)
- 3) calcschists (marly rocks)
- 4) metabasic and ultrabasic rocks (ophiolites)

Several recent investigations have dealt with Alpine metamorphism in the Hohe Tauern, especially the isotherms based on oxygen isotope studies in the western

part (HORNES & FRIEDRICHSEN, 1974) have been a major step towards clarification of the metamorphic P-T conditions. Regional distribution of mineral assemblages are in principle in accordance with the isotherm pattern, showing the thermal maximum $\sim 600^{\circ}\text{C}$ around the main alpine chain the "Alpenhauptkamm (AHK)" in the Zillertal area and the Venediger group (HOERNES, 1973, HOERNES & HOSCHEK, 1973, MORTEANI & RAASE, 1974).

Table 1 Mineral Assemblages

Western part of the Hohe Tauern	Middle part of the Hohe Tauern
Siliceous dolomites:	
cc + do + qu	cc + do + qu + trem + chl
cc + do + qu + tc	cc + do + qu + trem + clz + chl
cc + do + qu + tc + trem	cc + do + trem + chl
cc + do + qu + trem	cc + do + trem + chl
cc + qu + trem	cc + do + trem + di + chl + ep
Marly rocks, with muscovite (phengite) + quartz always present (calcschists):	
do + cc + chl + stilp + plag	cc + chl
do + cc + kf	cc + zo
do + cc + bi + stilp	cc + stilp + plag
do + cc + bi + chl	cc + kf
do + cc + zo/ep + chl + plag	cc + kf + bi
cc + zo	cc + chl + pa
cc + bi + zo/ep	cc + chl + pa + ma
	cc + chl + pa + clz + plag
	cc + do + chl + clz/zo
	cc + do + chl + pa + ma
	cc + do + chl + pa + ctd
	cc + do + chl + pa + ma + ctd + zo
	cc + do + chl + zo + gar
	cc + do + chl + pa + zo + gar
	do + bi + plag + chl
	cc + chl + zo/clz + gar

Abbreviations:

bi	biotite	kf	K-feldspar
cc	calcite	ma	margarite
chl	chlorite	pa	paragonite
clz	clinozoisite	plag	plagioclase (acid)
ctd	chloritoid	qu	quartz
di	diopside	stilp	stilpnomelane
do	dolomite	tc	talc
ep	epidote	trem	tremolite
gar	garnet	zo	zoisite

Proceeding further along the AHK the thermal maximum decreases to about 500°C in the Großglockner-Hochtor area (HÖCK, 1974, BICKLE & POWELL, 1977).

Up to date the estimation of metamorphic pressures has been based principally on the widespread occurrence of kyanite defining a minimum pressure of 4–6 kb depending on several experimental determinations (ALTHAUS, 1967, NEWTON, 1969, RICHARDSON et al. 1969, HOLDAWAY, 1971). Contrary to the petrographic work on the pre-Hercynian rock series, including the Hercynian "Zentralgneis" and basic rocks of the Bündnerschiefer series, no systematic studies of mineral assemblages and corresponding PTX conditions have been carried out so far for the widespread Mesozoic calcareous rocks in the Western Hohe Tauern (Brennerpaß – Felbertauernstraße), and only few papers are concerned with these problems in the middle and eastern part of the Tauern window (CLIFF et al. 1971, HÖCK 1974, 1977). The present paper is a further step towards this aim.

Mineral assemblages

Specimens have been collected from relatively pure calcareous rocks and siliceous dolomites (Triassic-Jurassic age) and from marly rocks (Jurassic-Cretaceous age). A detailed study of the lithology and stratigraphic development is given by FRISCH (1975) for the western part and by FRASL (1958), FRASL & FRANK (1966) for the middle part. The assemblages for the western and middle part of the Hohe Tauern are listed in tab. 1.

Western Hohe Tauern (G. HOSCHEK)

From the regional distribution of mineral assemblages (fig. 1) follows, that K-feldspar + dolomite is predominantly restricted to the northern part of the area and to relative pure calcareous rocks (Hochstegenkalk, Kaserer Serie, Triassic dolomitic marbles). Towards the AHK this mineral pair is replaced by biotite + calcite. The reaction isograde approximates a line from the Brennerpaß – Tuxer Joch – Mayerhofen S Gerlos Paß – Krimml. Due to different bulk composition no equivalent reaction isograde could be established in the southern part of the AHK. The lack of K-feldspar and occurrence of talc and tremolite S of the AHK points to rather low K-contents of these rocks. Sporadic distribution of clinzoisite-epidote is known from low grade metamorphic areas, however, Fe-poor zoisite is restricted to a higher grade zone around and S of the AHK. A similar distribution is shown by coexisting biotite + zoisite assemblages. This isograde is situated around the Brennerpaß in the North and around Sterzing – Ahrntal in the South. Compared with this zone, biotite + clinzoisite/epidote assemblages occupy a larger area. Rare calcareous assemblages with stilpnomelane or with chloritoid are confined to low grade rocks. Garnet in calcareous rocks is restricted to higher grade rocks in the East Tyrol. In adjacent pelitic-psammitic or tuffitic metasediments, however, these minerals are more common than in calcareous rocks.

Fig. 1: Regional distribution of mineral assemblages in Mesozoic calcareous rocks of the Western Hohe Tauern.

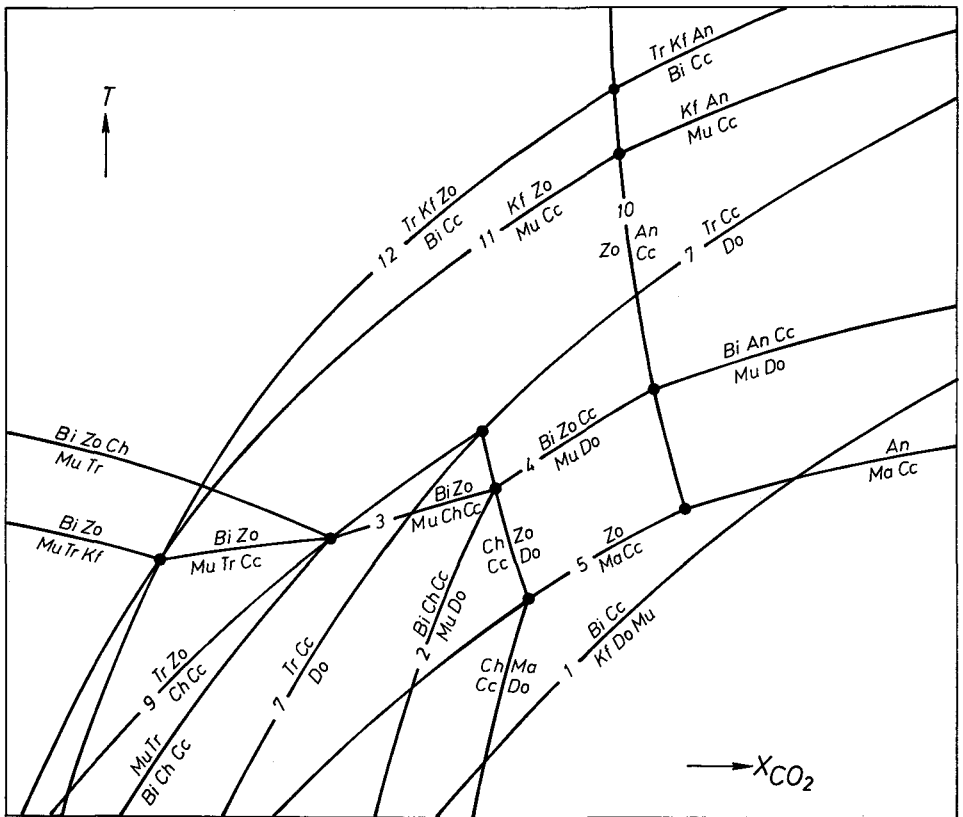
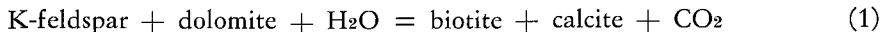


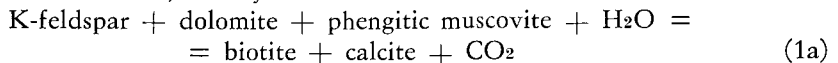
Fig. 2: Schematic isobaric TXCO₂ diagram based on petrographic data from Fe poor calcareous rocks of the Western Hohe Tauern. Due to clarity several phase equilibria have been omitted. XCO₂ is restricted to low values.

As can be deduced from the regional distribution of assemblages and partly by thin section observation, several mineral reactions have taken place in these rocks. Some of them are discussed briefly with regard to the schematic TXCO₂-diagram in fig. 2.

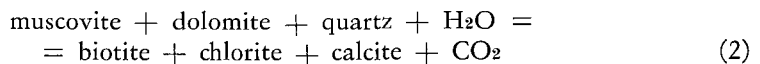
Reaction



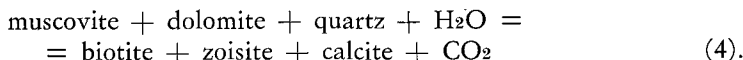
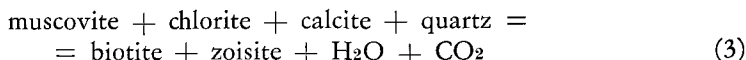
has gone to completion in high grade rocks. Only in rare cases all four minerals are present in hand specimen, but apparently due to alternating layers, K-feldspar is not in contact with dolomite. In some thin sections a zonal growth of biotite + calcite around dolomite can be observed. Additional microprobe data suggest a slightly modified reaction, namely



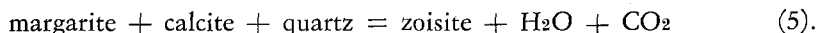
Reaction



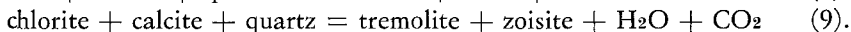
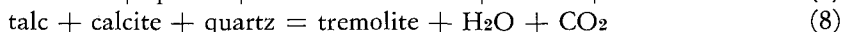
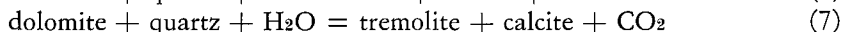
is suggested by parallel intergrown lamellae of stable coexisting biotite + chlorite. Encountering the zone of coexisting biotite + zoisite additional reactions must have been reached, namely



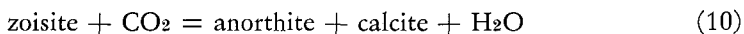
Intergrowth of biotite + zoisite + calcite supports this interpretation. In many cases coexisting phases indicate that mineral equilibria were buffered along the schematic univariant reaction lines of fig. 2. Regional distribution suggests only slightly higher temperatures for (2) compared with (1a), but distinctly higher T-conditions for (3) and (4). Following FREY & ORVILLE (1974) the lower stability of zoisite should be defined by reaction



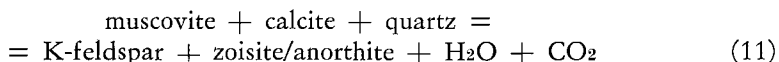
Margarite or other potential precursors of zoisite, such as pyrophyllite, paragonite or lawsonite (+ calcite) have not yet been identified from optical and microprobe data. In greenschists of the Pfitschtal however, rectangular aggregates consisting of zoisite + epidote + chlorite are probably products of a breakdown reaction of lawsonite + actinolite = zoisite/epidote + chlorite. No pseudomorphs of lawsonite have yet been found in calcareous rocks. Additional reactions have been recognized from siliceous dolomites of the South and East Tyrol:



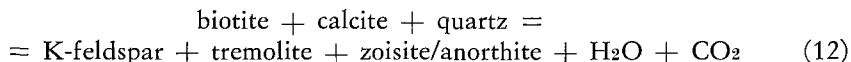
Reaction



is indicated by replacement of zoisite/epidote by plagioclase in some specimens of the higher grade area (Pfitschtal, Pfunderer Tal). According to present observations the reactions



and



have not been reached during the high grade metamorphic event in calcareous rocks of the Schieferhülle.

As a first step towards determination of metamorphic PTXCO₂ conditions, several experimentally determined equilibria are shown in the TXCO₂-diagram, fig. 3, for a total pressure of 6 kb. Experimental data have been used for reaction (1) PUHAN & JOHANNES 1974, PUHAN 1978; (11) HEWITT 1973; (12) HOSCHEK 1973, HEWITT 1975. Phase boundaries in fig. 3 have been calculated from these experimental data using log K vs. 1/T plots and corresponding ΔH and ΔS values corrected to 1 bar. The modified Redlich Kwong equation

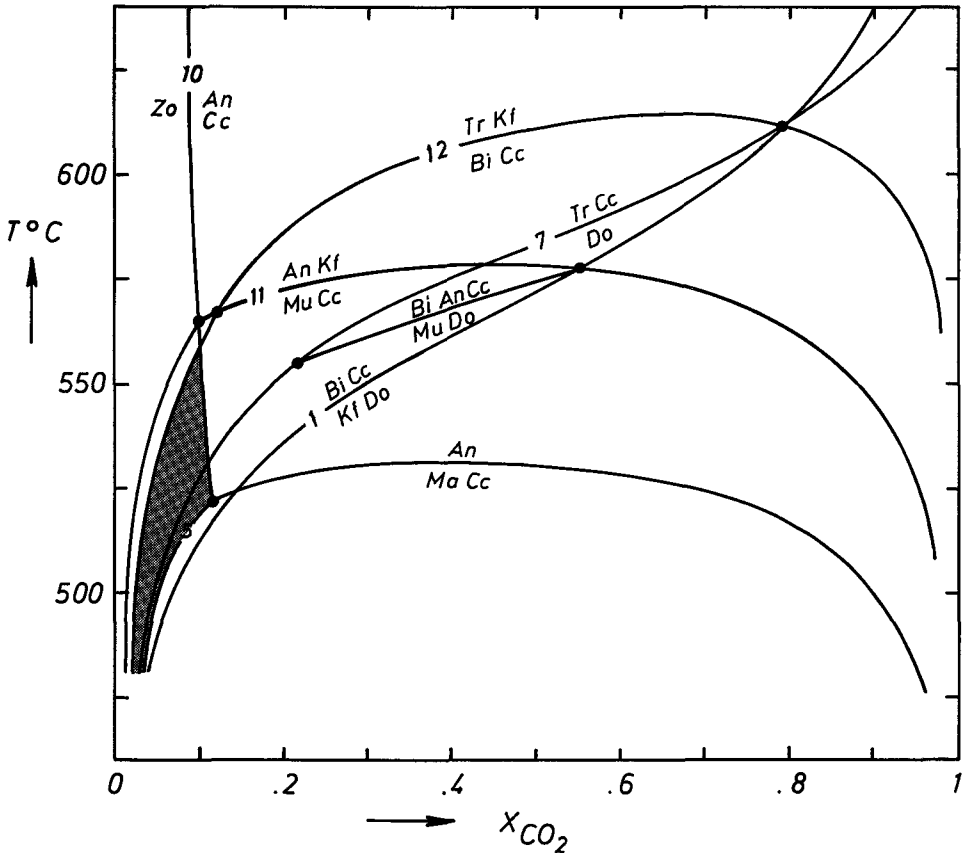


Fig. 3: TXCO₂ diagram for a total pressure of 6 kb, based on experimental and thermodynamic data from the system K₂O - CaO - MgO - Al₂O₃ - SiO₂ - H₂O - CO₂. The shaded area approximates the inferred TXCO₂ conditions for biotite + zoisite bearing Fe poor calcareous rocks of the Western Hohe Tauern.

(HOLLOWAY 1976) was used for computation of fugacity coefficients in non ideal H₂O-CO₂ mixtures. For reaction (7) a linear combination of (1) and (12) was evaluated. The result is consistent with experimental determinations of (7) at high X_{CO₂} values (METZ 1976, SLAUGHTER et al. 1975). For all reactions independent calculations were performed using thermodynamic data of HELGESON et al. (1978) and taking into account the activities of calcite and dolomite (GORDON & GREENWOOD 1970). Results of both calculations are in good agreement. With regard to reaction (10) however, considerable uncertainty arises due to very small values for ΔH and ΔS . The position in fig. 3 lies intermediate to experimental data (STORRE & NITSCH 1972, JOHANNES & ORVILLE 1972), but the extrapolated low temperature part reaches a higher maximal X_{CO₂} value ($\sim 0,25$), according to the thermodynamic data of HELGESON et al. (1978). The reaction margarite + calcite = anorthite is based on

thermodynamic data of HELGESON et al. (1978). Other reactions have been calculated by the linear combination method. Due to the uncertainties of experimental and derived thermodynamic data on chlorite, relevant equilibria are not shown in fig. 3.

Comparison of the TXCO₂-model (fig. 2) and the experimental and calculated TXCO₂-diagram (fig. 3) reveals a general accordance. However, several differences in the topology of the two diagrams can be noticed, due to several factors, namely different total pressure, deviations from a pure H₂O-CO₂ gas phase, additional components to the experimentally determined equilibria in the system K₂O - CaO - MgO - Al₂O₃ - SiO₂ - H₂O - CO₂, and experimental and thermodynamic data uncertainties. For example, increase in total pressure results in a shift of (10) to higher XCO₂ values and accordingly the position of the isobaric invariant point generated by the intersection of (11) and (12) changes to the low XCO₂ side of (10), as shown in fig. 2. According to present microprobe data from these rocks and published compositions of coexisting mineral phases from other areas, the same shift will result by the incorporation of additional components Fe and F. As a consequence of this shift a stability field of biotite + zoisite is generated and the stability field of muscovite + tremolite is reduced. Only in case of very Al-rich amphibolites this trend is reversed (CARMICHAEL, 1970), but such compositions are not represented in this study. Similarly the incorporation of the additional component Na counteracts the trend mentioned above. Due to these variable parameters a set of PTXCO₂ models have been developed, one of them (fig. 2) showing the best fit to petrographic data from the Western Hohe Tauern. All different models can be continuously transformed into each other and into the experimentally based topology of fig. 3 by changing the positions of a few independent base reactions due to variation of pressure and solid solution.

For the common assemblage biotite + zoisite + calcite of the high grade zone rocks around the AHK the TXCO₂ conditions must have been between the lower and upper stability of biotite + calcite, (1) and (12). Furthermore for Fe-poor zoisite, maximum values are given by (10) and (5). The position of this shaded area is dependent on total pressures, gas phase composition and mineral composition. At present the effect of solid solution can only be estimated on the basis of preliminary microprobe and optical determination of mineral composition and calculation via ideal solution models. For reaction (1) the shift towards lower temperatures is $\leq 25^\circ\text{C}$.

In the absence of breakdown products according to (11), data from such assemblages in other metamorphic areas (CARMICHAEL 1970, HEWITT 1973, THOMPSON 1975, FERRY 1976, 1976a) suggest a shift towards higher temperatures with a maximum deviation around 30°C . Compared with the position of (10), assemblages with Fe-poor zoisite + plagioclase are confined to smaller XCO₂ values. Graphite in some specimens indicates that in addition to H₂O and CO₂ other species, notably CH₄, CO and H₂ were present in the metamorphic gas phase. From the calculations of FRENCH (1966), EUGSTER & SKIPPEN (1967) and OHMOTO & KERRICK (1977) the lowering of temperatures for the shaded area in fig. 3 is estimated to be less than 25°C . According to HOERNES & FRIEDRICHSEN (1974) temperatures of $550\text{--}575^\circ\text{C}$ were arrived during the

metamorphism of the Upper Schieferhülle. The assemblage chloritoid + kyanite + staurolite in quartzites of the Pfitschtal indicates temperatures around 550°C based on experimentally determined mineral equilibria (HOSCHEK 1967, RICHARDSON 1968, GANGULY 1972). For the particular outcrop oxygen isotope measurements gave a temperature range 540–565°C (quartz-magnetite; quartz-biotite).

The position of the shaded area in fig. 3 was calculated at various pressures. A minimum pressure of 5 kb is compatible with the temperatures stated above. Taking into account the combined effects of solid solution and a gas phase deviating from pure H₂O-CO₂ mixtures this conclusion is still valid. Independently the occurrence of kyanite indicates minimum pressures around 4–6 kb. Based on study of fluid inclusions in vein minerals LUCKSCHEITER & MORTEANI (1979) have found partly rather low pressure values around 3 kb for certain areas of the Western Hohe Tauern. The apparent discrepancy between these results, however, can be resolved when taking the considerable time and PT evolution span connected with the formation of these veins into account.

As a result of current investigations on experimental phase equilibria, mineral chemistry, fluid inclusions and refined thermodynamic calculations a more detailed pattern of mineral reactions and metamorphic PTX development will be available (HOSCHEK in print).

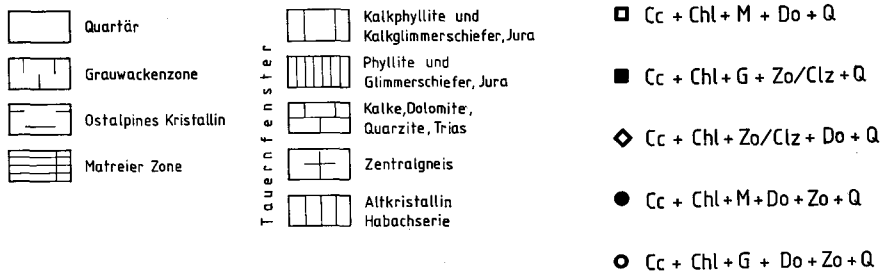
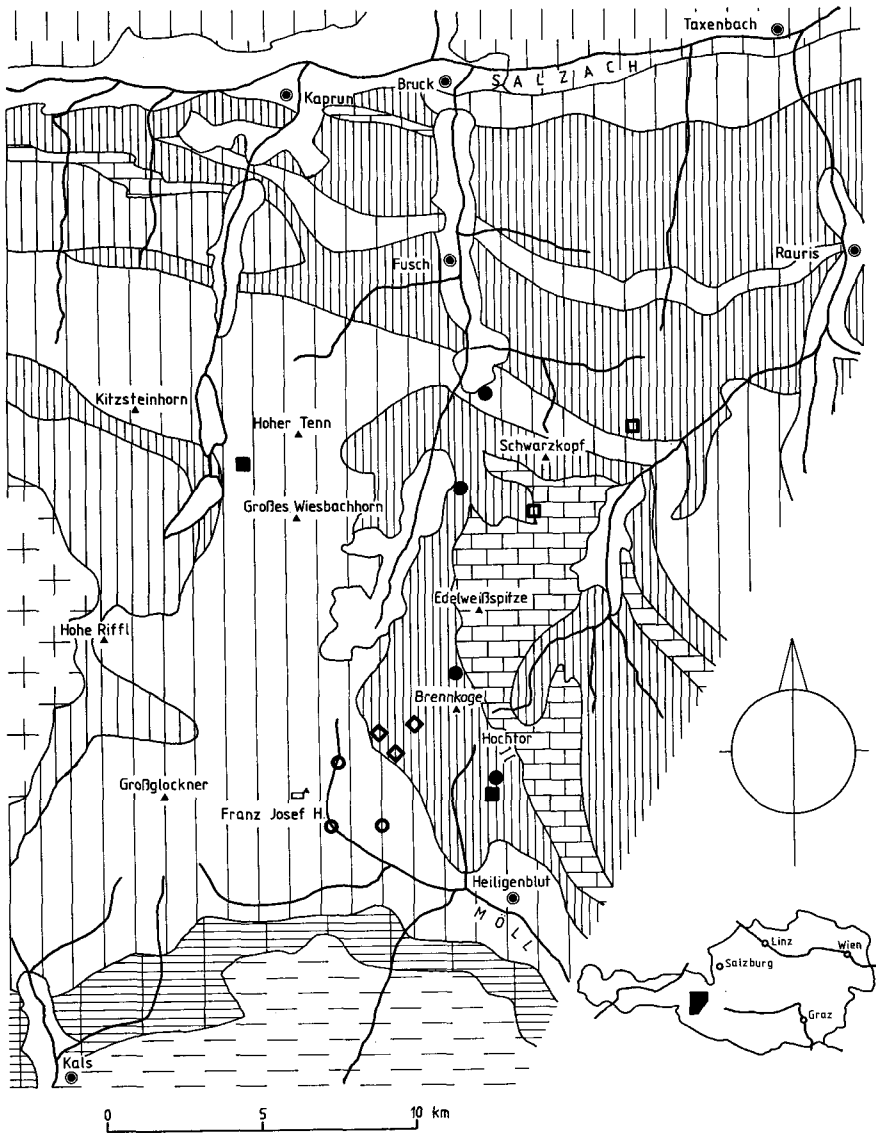
Middle part of Hohe Tauern (V. HÖCK)

According to the listed mineral assemblages in tab. 1, calc-schists in the middle part of the Hohe Tauern are characterized by the frequent occurrences of paragonite and/or margarite or garnet (fig. 4). The recorded parageneses containing K-feldspar and biotite are very rare and restricted to a small area around the Seidl-winklvalley NE of Hochtör. Stilpnomelane is restricted to some rock types in the northern part of the Tauern window near the Salzach-valley, while acid plagioclase (albite, oligoclase) is found rarely but all over the area. Margarite and garnet bearing assemblages are concentrated between the area Hochtör – Brennkogel – Großglockner (fig. 4) but extend further N to an approximate line Kitzsteinhorn – N Schwarzkopf.

Tremolite in siliceous dolomites and comparable rocks is distributed over the same area as garnet and margarite. Diopside is restricted to a small area between Hochtör – Heiligenblut – Franz Josefs Haus occurring only in some special silicia deficient rock types around the serpentinite body of Brennkogel – Heiligenblut. Preliminary data of chemistry, mineralogy and phase-relations are given by HÖCK (1977).

In order to clarify the nature of the recorded assemblages and their mutual relationships, the rocks should be treated at least in the system SiO₂ – Al₂O₃ – CaO – MgO – FeO – Fe₂O₃ – K₂O – Na₂O – CO₂ – H₂O. This ten-component

Fig. 4: Geological sketch map of the middle part of the Hohe Tauern with five- and six-phase assemblages. Muscovite is always, paragonite sometimes present. Closed circle: margarite isograde, open circle: garnet isograde. For abbreviations see table 2.

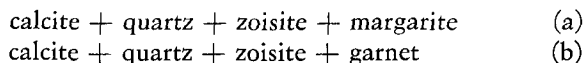


system cannot be handled by means of graphical analysis. Therefore, the simplification to the six-component system $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{CaO} - \text{MgO} - \text{H}_2\text{O} - \text{CO}_2$ is necessary for a graphical approach and justified by the following assumptions (see also FREY and ORVILLE 1974):

- 1) Assemblages containing the relatively rare minerals stilpnomelane, biotite, K-feldspar and plagioclase are omitted from the considerations, hence muscovite (phengite) and paragonite are the only K- and Na-bearing phases in the remaining parageneses. K_2O and Na_2O can be treated therefore as excess components.
- 2) Fe^{2+} and Mg^{2+} are substituting each other to a large extent in dolomite and chlorite, so FeO and MgO are taken as one component, not considering possible differences in Fe^{2+}/Mg partitioning in dolomite and chlorite. Chloritoid is neglected.
- 3) Although Fe_2O_3 is abundant to a certain extent, zoisite and clinozoisite are regarded as Fe-free endmembers.
- 4) Garnet (containing up to 30 mol-percent grossularite component) and margarite (25–30 mol-percent paragonite) are treated as pure Ca-endmembers as well as calcite, neglecting all possible solid solution series in garnet, margarite-paragonite, and calcite-dolomite-siderite.
- 5) Abundance of graphite in many rock types indicates a $\text{CO}_2 - \text{H}_2\text{O} - \text{CH}_4$ fluid. Methane may be regarded as inert component, lowering the reaction temperature, but probably not affecting the relative positions of reactions and positions of invariant points in a TXCO_2 -diagram at the interesting temperatures. The fluid pressure is assumed to be equal to the total pressure.
- 6) Observed mineral assemblages are believed to reflect mineral equilibria since all phases have mutual contact. Normally only three-phase contacts can be observed in thin-sections, four-phase contacts are very rare for geometric reasons. Five- or six-phase contacts can not be proven.

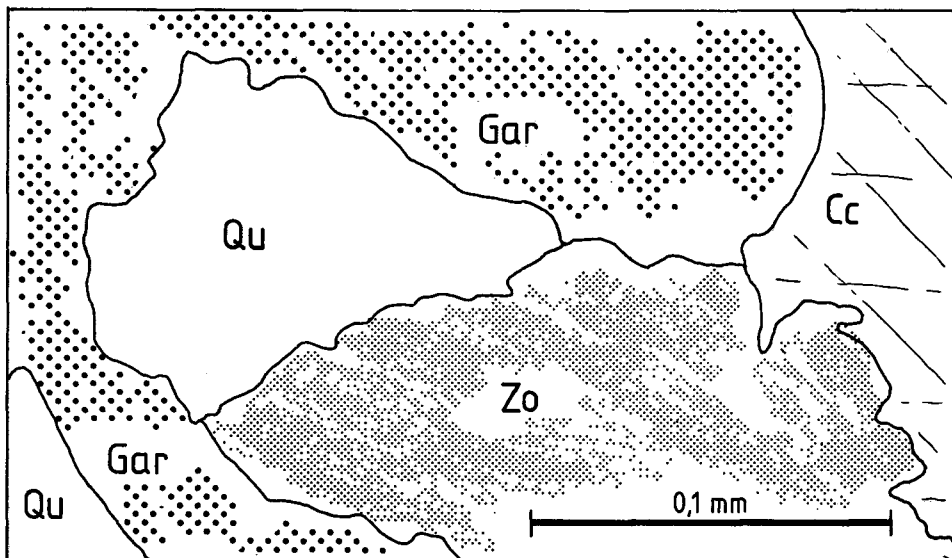
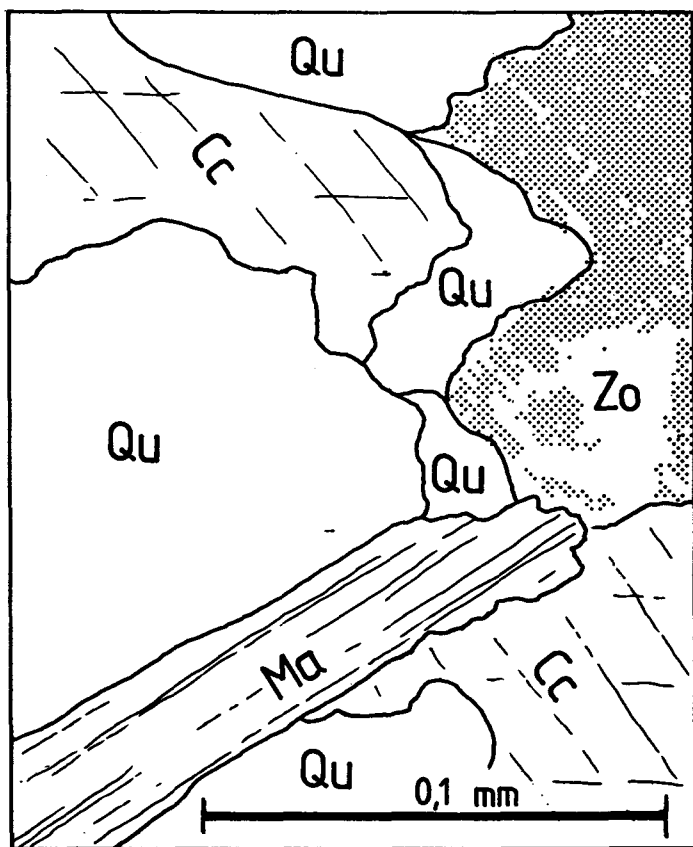
The five- and six-phase partial assemblages shown in fig. 4 involving calcite, dolomite, chlorite, zoisite/clinozoisite, margarite, quartz, (anorthite is considered for completion only) and their mutual relations may be discussed now in a part of the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{MgO} - \text{CO}_2 - \text{H}_2\text{O}$. This will be done in two steps.

First of all two frequently occurring partial assemblages (fig. 5a, b) will be discussed:



It should be noted that margarite and garnet were never found together in one single thin section.

-
- Fig. 5a: Sketch of a thin section with the four phase partial assemblage calcite + quartz + zoisite + margarite.
Location: N Brennkogel.
- 5b: Sketch of a thin section with the four phase partial assemblage calcite + quartz + zoisite + garnet.
Location: E Franz-Josephs Haus.
Abbreviations: Cc Calcite, Zo zoisite, Qu quartz, Ma margarite, Gar garnet.



The four-phase assemblages represent in the system (five components without MgO) isobaric univariant reaction equilibria according to the reactions (5) and (13) in tab. 2. They are arranged around two invariant points labelled by the missing phase I [M] and I [G], respectively, (fig. 6) since five phases define an invariant point in this system. At a third invariant point labelled I [Q] grossularite and margarite are stable together but no quartz (fig. 6). Ten equilibria reactions are emanating from these invariant points (tab. 2). The univariant reactions and invariant points are plotted in a schematically TXCO₂ section (fig. 6).

First inspection of the diagram shows, that garnet and margarite only coexist without quartz to the left of reaction (19), above (18) and (20). The assemblage margarite + quartz + zoisite + garnet would be stable only at an invariant point created by the intersection of reaction (5), (13) and (19) and a gas deficient reaction: $1M + 1G + 1Q = 2Zo$.

Preliminary thermodynamic calculations yielded a unstability for the assemblage margarite + grossular + quartz in respect to zoisite for reasonable temperatures

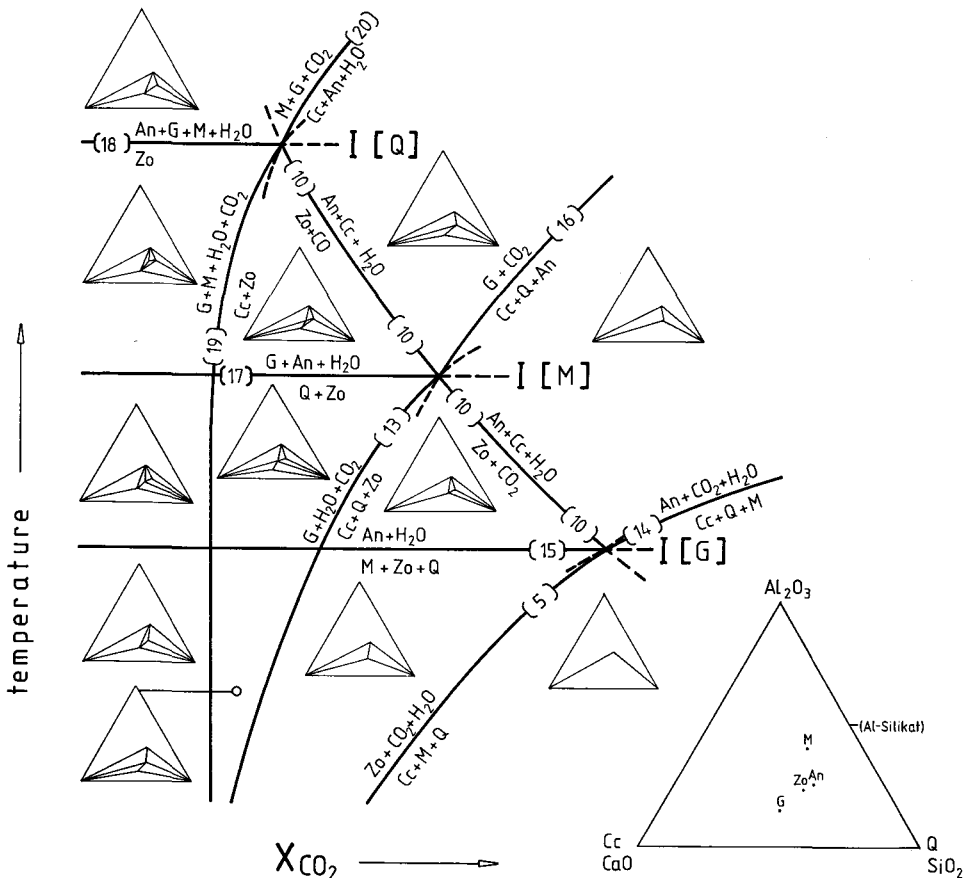
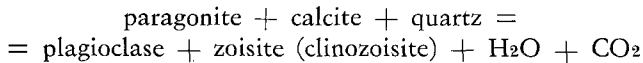


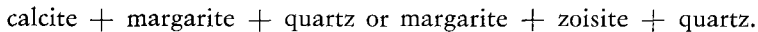
Fig. 6: Schematic TXCO₂ diagram showing the topology of a part of the margarite-grossularite-phase relations in the system CaO-Al₂O₃-SiO₂-CO₂-H₂O. For abbreviations see table 2.

and pressures. Thermochemical data were taken from CHATTERJEE (1976) for margarite and zoisite, and ROBIE and WALDBAUM (1968) for grossularite and quartz as well as refindings thermochemical data from HELGESON et al. (1978). The situation of invariant point I [G] in fig. 6 may be compared with a TXCO₂ diagram for 6 kb as in fig. 3. The position is subject to large uncertainties as discussed previously (G. HOSCHEK). Experimental work of GORDON and GREENWOOD (1971) and STORRE (1970) combined with the experimental determination of the reaction $Zo + Q = G + An + H_2O$ (17) by NEWTON (1966) and BOETTCHER (1970) indicate for I [M] temperatures around 500° C and XCO₂ < 0.1 at a total pressure of 2000 bars. Increasing total pressure would shift the isobaric invariant point to drastically higher temperatures.

The four-phase univariant assemblages (a, b) are buffering the gas phase (TROMMSDORFF 1972, GREENWOOD 1975) so that the path of composition of gas phase moves along the reaction line with rising temperature. Hence, these assemblages are stabilized over a wide range of temperature depending on different XCO₂ and are no good indicators of temperature. Unfortunately, the temperature was not high enough allowing the path of the gas phase of reaction (5) and (13) to reach the invariant point I [G] and I [M]. In this case the appearance of anorthite (plagioclase) would create a five-phase assemblage which can be taken as an isograd, because these parageneses are fixed at arbitrary total pressure to a certain temperature and XCO₂ (TROMMSDORFF 1972). Occasionally observed assemblages clinozoisite + plagioclase (tab. 1) are due to the reaction

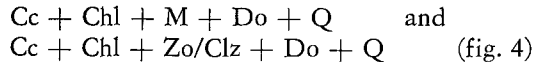


(FREY and ORVILLE 1974) and not to the breakdown of



Incorporation of MgO as additional component to the system together with dolomite and chlorite as MgO (FeO) bearing phases as a second step of the graphical approach will create several more reactions. Some of these are of specific interest as far as the calcschists are concerned (tab. 2).

Five-phase assemblages like

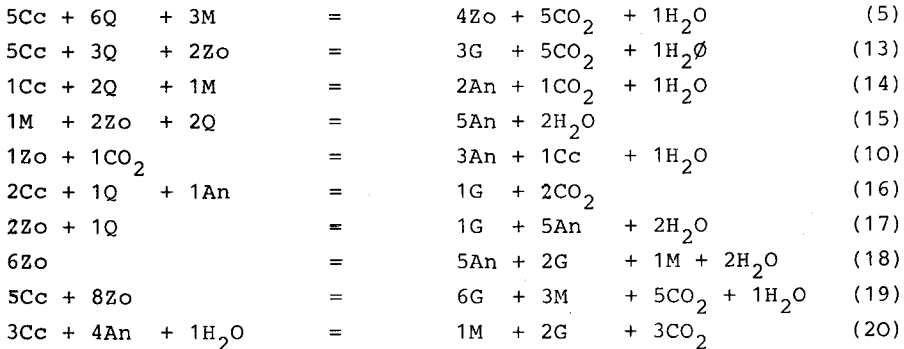


can be assigned to reaction (24) and (22) in tab. 2. Fig. 7 shows a schematically TXCO₂ section dealing with those reactions. Since anorthite (plagioclase) together with margarite was not observed so far, the diagram is restricted to a temperature range below the anorthite stability in fig. 6. From the invariant points I [M1] and I [G1] (cf. FREY, 1978, fig. 11) generated by intersection of reaction (22) with reaction (5) and (13) seven reactions are emanating.

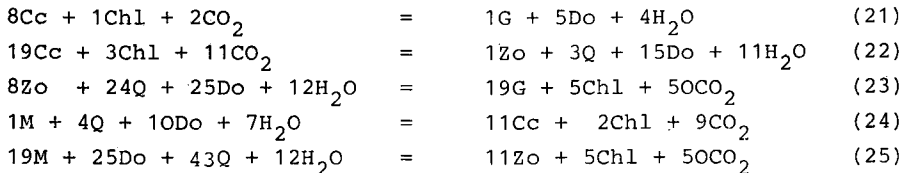
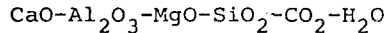
According to the schematic XCO₂ section in fig. 7 the distribution of five- and six-phase assemblages in the Glockner-area (fig. 4) can be explained as follows: The parageneses $\text{Cc} + \text{Chl} + \text{M} + \text{Do} + \text{Q}$ is found at the mountain ridge NE and SW of Schwarzkopf (fig. 4), characterized by relatively low temperatures and high XCO₂. This five-phase assemblages buffers the gas phase according to

Table 2

Isobaric unvariant reactions in the system: $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$



Isobaric univariant reactions in the system:



Stoichiometry based on chlorite composition: $5\text{MgO} \cdot 1\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$

Abbreviations: Cc calcite, Q quartz, M margarite, Zo zoisite, Clz clinozoisite, An anorthite, G grossularite, Chl chlorite, Do dolomite.

reaction (24). With increasing temperature the composition of the gas phase moves along the reaction line as indicated by the arrow, slightly increasing the mole fraction of CO_2 . As soon as the temperature reaches the invariant point I [G1] zoisite appears as additional phase according to reaction (5) and reaction (25) and (22) as well, generating a six-phase isobaric invariant assemblage subsequently called "margarite" isograd.

It is found in the Fusch valley N of Brennkogel and S of the Hochtör (fig. 4). At temperatures above I [G1] the six-phase assemblage may develop in different ways, but generally margarite, the less abundant phase, is used up first. The path of the gasphase is now changing to lower XCO_2 along reaction (22) with rising temperature (arrows in fig. 7). The pertinent five-phase paragenesis is found W of the Hochtör, distributed over an area with a limited temperature range.

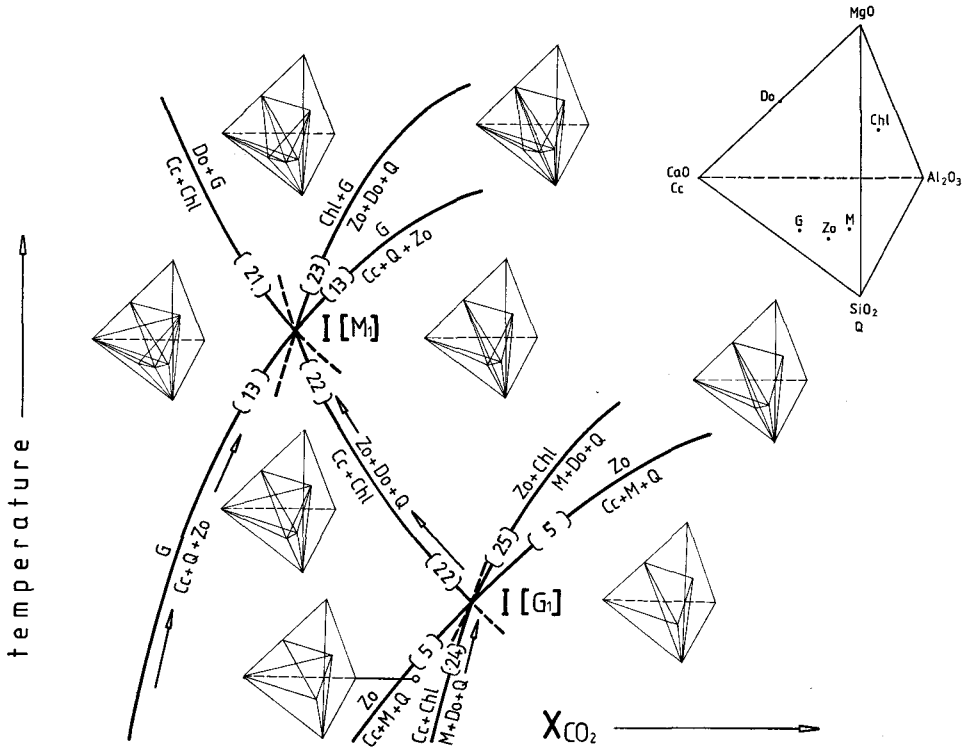


Fig. 7: Schematic TX_{CO_2} diagram showing the topology of phase relations in a small portion of the system $CaO-Al_2O_3-MgO-SiO_2-CO_2-H_2O$. The arrows indicate the path of the gasphase with rising temperature. For abbreviations see table 2.

The reaction (22) is terminated at the invariant point I [M1] where garnet appears in a second isobaric invariant six-phase assemblage $Cc + Chl + Zo + Do + Q + G$, the "garnet" isograd. It is found near Franz Josefs Haus E of the Großglockner. In carbonate poor rocks at very low X_{CO_2} an alternative way of the development of the gasphase can lead to the "garnet" isograd along the univariant reaction (13) in the presence of chlorite. These cases were seldom found in dolomite-free assemblages near Hochtort and NW of the Wiesbachhorn.

The outlined qualitative approach explaining the mineral assemblages in calcschists results in the mapping of isogrades, representing different temperatures and X_{CO_2} at a given total pressure.

The temperature is increasing from the east to the west, which is in agreement with the overall pattern of increasing metamorphism (see HÖCK, this volume). Only insufficient data are available so far to evaluate PTX conditions of formations of the calcschists. The frequent occurrence of kyanite in the area indicates a minimum pressure of 4–6 kb (HÖCK 1974). Temperature for the Hochtort region

i.e. the "margarite" isograd is estimated by HÖCK (1974) and BICKLE & POWELL (1977) using calcite-dolomite geothermometry at approximately 500°C. The mole fraction of CO₂ should be below that of invariant point I [G] in fig. 6, i.e. < 0.1 according to fig. 3.

Current microprobe investigation combined with thermodynamic calculations should yield a better understanding of phase relations and their PTX conditions.

Western and Middle part of the Hohe Tauern — A Comparison

From the record of mineral assemblages (tab. 1) of the Western and Middle Hohe Tauern (fig. 1, 4) several differences between these areas are obvious, particularly the scarcity of biotite and relative abundance of margarite, paragonite and/or grossularite bearing garnet in the latter area. These differences can be attributed to several factors: Assuming approximately the same pressure as indicated by the occurrence of kyanite across the whole area, metamorphic temperatures are lower for the middle part of the Hohe Tauern. Despite overall similarity in Mesozoic rock series, relatively higher Al and lower K contents are indicated by the presence of margarite, paragonite and the rarity of K-feldspar in calcareous rocks of the Middle Hohe Tauern and may be in part responsible for the latter assemblages.

Acknowledgements

One of the authors (G. H.) likes to thank H. Helgeson for making available thermodynamic data and J. Holloway for an extended version of his fugacity tables. Thanks also due to W. Johannes for unpublished experimental data on calc-silicate reactions. V. H. is grateful to H. P. Steyrer for drafting the diagrams and to G. Frasl for critically reading the manuscript.

This work was supported by a grant Nr. 25-2778/S of the Fonds zur Förderung der wissenschaftlichen Forschung, Wien.

References

- ALTHAUS, E., 1967: The triple point Andalusite — Sillimanite — Kyanite. — *Contrib. Miner. Petrol.*, **16**, 29—44.
- BICKLE, M. J. and POWELL, R., 1977: Calcite — Dolomite Geothermometry for Iron-bearing Carbonates. The Glockner Area of the Tauern Window, Austria. — *Contrib. Mineral. Petrol.*, **59**, 281—292.
- BOETTCHER, A. L., 1970: The system CaO - Al₂O₃ - SiO₂ - H₂O at high pressures and temperatures. — *J. Petrol.* **11**, 337—379.
- CARMICHAEL, D. M., 1970: Intersecting Isogrades in the Whetstone Lake Area, Ontario. — *J. Petrol.* **11**, 147—181.
- CHATTERJEE, N. D., 1971: Phase equilibria in the alpine metamorphic rocks of the environs of the Dora Maira-Massif, Western Italian Alps. — *N. Jb. Miner. Abh.*, **114**, 181—210.
- CHATTERJEE, N. D., 1976: Margarite stability and compatibility relations in the system CaO - Al₂O₃ - SiO₂ - H₂O as a pressure-temperature indicator. — *Am. Min.* **61**, 699—709.
- CLIFF, R. A., NORRIS, R. J., OXBURGH, E. R. and WRIGHT, R. C., 1971: Structural, Metamorphic and Geochronological Studies in the Reisseck and Southern Ankogel Group, the Eastern Alps. — *Jb. Geol. B.A.* **114**, 121—272.

- EUGSTER, H. P. and SKIPPER, G. B., 1967: Igneous and metamorphic reactions involving gas equilibria. — In ABELSON, P. H.: *Researches in Geochemistry*, Vol. 2, Wiley, New York, 492—520.
- FERRY, J. M., 1976: Metamorphism of calcareous sediments in the Waterville-Vassalboro Area, South-Central Maine: Minerals reactions and graphical analysis. — *Amer. J. Sci.* **276**, 841—882.
- FERRY, J. M., 1976a: P, T, fCO₂ and fH₂O during metamorphism of calcareous sediments in the Waterville-Vassalboro Area, South-Central Maine. — *Contrib. Miner. Petrol.* **57**, 119—143.
- FRASL, G., 1958: Zur Seriengliederung der Schieferhülle in den Mittleren Hohen Tauern. — *Jb. Geol. B.A.* **101**, 323—472.
- FRASL, G. und FRANK, W., 1966: Einführung in die Geologie und Petrographie des Penninikums im Tauernfenster mit besonderer Berücksichtigung des Mittelabschnittes. — *Der Aufschluß*, Sh. **15**, 30—58.
- FRENCH, B. M., 1966: Some geological implications of equilibrium between graphite and a C-H-O gas at high temperatures and pressures. — *Rev. Geophys.* **4**, 223—253.
- FREY, M., 1978: Progressive low-grade metamorphism of a black shale formation, Central Swiss Alps, with special reference to Pyrophyllite and Margarite bearing assemblages. — *J. Petrol.* **19**, 93—135.
- FREY, M. and ORVILLE, P. M., 1974: Plagioclase in margarite bearing rocks. — *Amer. J. Sci.*, **274**, 31—47.
- FRISCH, W., 1975: Ein Typ-Profil durch die Schieferhülle des Tauernfensters: Das Profil am Wolfendorn (westlicher Tuxer Hauptkamm, Tirol). — *Verh. Geol. B.A.* **1975**, 201—221.
- GANGULY, J., 1972: Staurolite stability and related paragenesis: Theory, experiments and applications. — *J. Petrol.*, **13**, 335—365.
- GORDON, T. M. and GREENWOOD, H. J., 1970: The reaction: Dolomite + Quartz + Water = Talc + Calcite + Carbon Dioxide. — *Amer. J. Sci.* **268**, 225—242.
- GORDON, T. M. and GREENWOOD, H. J., 1971: The stability of grossularite in H₂O-CO₂ mixtures. — *Am. Min.* **56**, 1674—1688.
- GREENWOOD, H. J., 1975: Buffering of pore fluids by metamorphic reactions. — *Am. J. Sci.* **275**, 573—593.
- HELGESON, H. C., DELANY, J. M., NESBITT, H. W. and BIRD, D. K., 1978: Summary and critique of the thermodynamic properties of rock forming minerals. — *Amer. J. Sci.* **278-A**, 1—229.
- HEWITT, D. A., 1973: The metamorphism of micaceous limestones from South-Central Connecticut. — *Amer. Miner.* **58**, 785—791.
- HEWITT, D. A., 1973a: Stability of the Assemblage Muscovite-Calcite-Quartz. — *Amer. J. Sci.* **273-A**, 444—469.
- HEWITT, D. A., 1975: Stability of the assemblage Phlogopite-Calcite-Quartz. — *Amer. Miner.* **60**, 391—397.
- HOCK, V., 1974: Zur Metamorphose mesozoischer Metasedimente in den mittleren Hohen Tauern (Österreich). — *SMPM*, **54**, 567—593.
- HOCK, V., 1977: Tremolit/Aktinolith- und Diopsid-führende Metasedimente in den mittleren Hohen Tauern. — Jahresbericht 1976 „Geologischer Tiefbau der Ostalpen“ (Hochschulschwerpunkt N 25). Publ. Zentralanst. Met. Geodyn. Wien, **221**, 32—42.
- HOCK, V., 1980: Distribution maps of minerals of the alpine Metamorphism in the Penninic Tauern Window, Austria. — *Mitt. Österr. Geol. Ges.* **71/72**, 119—127.
- HOERNES, S., 1973: Untersuchungen zur Metamorphose in den westlichen Hohen Tauern (Österreich). — *TMPM*, **20**, 81—106.
- HOERNES, S. and FRIEDRICHSEN, H., 1974: Oxygen isotope studies on metamorphic rocks of the Western Hohe Tauern Area (Austria). — *SMPM*, **54**, 769—788.
- HOERNES, S. und HOSCHEK, G., 1973: Metamorphose im Westteil des Tauernfensters. — Bericht Geotraverse IA.
- HOLDAWAY, M., 1971: Stability of andalusite and the aluminium silicate phase diagram. — *Amer. J. Sci.* **271**, 97—131.
- HOLLOWAY, J. R., 1976: Fugacity and activity coefficients of molecular species in fluids at high pressures and temperatures. — *Carnegie Inst. Wash. Yearb.*, **75**, 771—775.

- HOSCHEK, G., 1967: Untersuchungen zum Stabilitätsbereich von Chloritoid und Staurolith. — *Contrib. Miner. Petrol.*, **14**, 123—162.
- HOSCHEK, G., 1973: Die Reaktion Phlogopit + Calcit + Quartz = Tremolit + Kalifeldspat + H₂O + CO₂. — *Contr. Miner. Petrol.* **39**, 231—237.
- JOHANNES, W. und ORVILLE, P., 1972: Zur Stabilität der Mineralparagenesen Muskovit + Calcit + Quartz, Zoisit + Muskovit + Quartz, Anorthit + Kalifeldspat und Anorthit + Calcit. — *Fortschr. Miner.*, **50**, Bh. 1, 46—47.
- LUCKSCHEITER, B. and MORTEANI, J., 1979: Microthermometrical and chemical studies of fluid inclusions in minerals and the H content of quartz from Alpine veins from the penninic rocks of the central and western Tauern Window (Austria/Italy). — In press.
- METZ, P., 1976: In WINKLER, H. G. F.: *Petrogenesis of metamorphic rocks.* — Springer Verlag, Berlin, 121.
- MILLER, C., 1977: Chemismus und phasenpetrologische Untersuchungen der Gesteine aus der Eklogitzone des Tauernfensters, Österreich. — *TMPM*, **24**, 221—277.
- MORTEANI, G. and RAASE, P., 1974: Metamorphic plagioclase crystallization and zones of equal anorthite content in epidote-bearing amphibole-free rocks of the western Tauernfenster, eastern Alps. — *Lithos*, **7**, 101—111.
- NEWTON, R. C., 1966: Some Calc-Silicate equilibrium relations. — *Amer. J. Sci.* **264**, 204—222.
- NEWTON, R. C., 1969: Some high-pressure hydrothermal experiments on severely ground kyanite and sillimanite. — *Amer. J. Sci.* **267**, 278—284.
- OHMOTO, H. and KERRICK, D., 1977: Devolatilization equilibria in graphitic systems. — *Amer. J. Sci.* **277**, 1013—1044.
- PUHAN, D., 1978: Experimental study of the reaction: Dolomite + K-feldspar + H₂O = phlogopite + calcite + CO₂ at total gas pressures of 4000 and 6000 bars. — *N. Jb. Miner.* **1978**, 110—172.
- PUHAN, D. und JOHANNES, W., 1974: Experimentelle Untersuchung der Reaktion Dolomit + Kalifeldspat + H₂O = Phlogopit + Calcit + CO₂. — *Contrib. Miner. Petrol.*, **48**, 23—31.
- RICHARDSON, S., 1968: Staurolite stability in part of the system Fe-Al-Si-O-H. — *J. Petrol.* **9**, 467—488.
- RICHARDSON, S., GILBERT, M. C. and BELL, P. M., 1969: Experimental determination of kyanite-andalusite and andalusite-sillimanite equilibria. — *Amer. J. Sci.* **267**, 259—272.
- ROBIE, R. A. and WALDBAUM, D. R., 1968: Thermodynamic properties of minerals and related substances at 298.15° K (25° C) and one atmosphere (1.013 bars) and at higher temperatures. — *US Geol. Surv. Bull.* **1259**, 256 p.
- SLAUGHTER, J., KERRICK, D. and WALL, V. J., 1975: Experimental and thermodynamic study of equilibria in the system CaO-MgO-SiO₂-H₂O-CO₂. — *Amer. J. Sci.*, **275**, 143—162.
- STORRE, B., 1970: Stabilitätsbedingungen Grossular-führender Paragenesen im System CaO-Al₂O₃-SiO₂-CO₂-H₂O. — *Contr. Mineral. Petrol.* **29**, 145—162.
- STORRE, B. und NITSCH, K. H., 1972: Die Reaktion 2 Zoisit + 1 CO₂ = 3 Anorthit + 1 Calcit + 1 H₂O. — *Contrib. Mineral. Petrol.*, **35**, 1—10.
- THOMPSON, A. B., 1975: Mineral reactions in a calc-mica schist from Gassetts, Vermont, USA. — *Contrib. Mineral. Petrol.* **53**, 105—127.
- TROMMSDORFF, V., 1972: Change in T-X during Metamorphism of Siliceous Dolomitic rocks of the Central Alps. — *SMPM* **52**, 567—571.