Stockholm University

Bachelor Thesis

Degree Project in
Geology15 hp

Interpretation of the P-T-X_{CO2} environment during metamorphism of carbonates, central Utö, Stockholm archipelago.

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Stockholm 2013

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Abstract

This thesis attempts to interpret the metamorphic condition and fluid composition experienced by metacarbonates on Utö, located in the south-eastern parts of the Stockholm archipelago. Utö is a part of the Svecofennian domain, and the area Bergslagen, that has hosted several mines over the last millennia. The bedrock in this area has been dated by the U-Pb technique to 1.90-1.87 Ga, placing it in the Paleoproterozoic era (Allen et al. 1996, Lundström et al. 1998). The rocks, of the studied area on the island of Utö, are mainly metacarbonates with a varying purity and thin layers of volcanic ash. These rocks become more felsic towards the north-western coast as the layers of felsic ash become more dominant.

To determine the P-T-X_{CO2} of metamorphism, metacarbonates were examined, in the field, in thin sections and mineral chemistry was determined by SEM analysis. Three samples were collected along a 1km transect, along which the assemblage calcite + dolomite + quartz + tremolite + diopside was observed. Petrographic and SEM analysis were performed to gather chemical data from co-existing calcite and dolomite in order to calculate temperature using the calcite-dolomite geothermometer. Chemical data from the SEM analysis were also run with AX and THERMOCALC together with pressure data received from a study by Engström (2011) of the adjacent island, Persholmen to generate a T- X_{CO2} diagram. Pressure was estimated to 3.1 $\pm$ 1.3 kbars, temperature calculated to 442°C$\pm$30°C and X_{CO2} to range from 0,00067-0,0038 with the standard deviation taken in to account. These results record equilibration with a CO_2-bearing hydrous fluid at greenschist facies conditions.

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Aim

The Metamorphic map of Sweden is a nationwide project which intends to widen the understanding of our country's metamorphic history. It will build from existing metamorphic data that have been compiled as part of the IGME 5000 Geological Map of Europe (Asch, 2005). The project was initiated and is now led by Professor Alasdair Skelton at Stockholm University. It is funded by SGU (Geological Survey of Sweden) and performed by students at geology departments around Sweden. This thesis is a part of that project and focuses on an area at the island Utö with the aim to determine the P- T- X_{CO2} environment during metamorphism. To attain the information needed to achieve this goal, I performed a petrographic study of metacarbonates from Utö. I then used SEM (scanning electron microscope) analysis to determine mineral compositions and finally the computer programs AX and THERMOCALC (www.metamorph.geo.uni-mainz.de) to determine P-T- X_{CO2}.

Method

Field work

The project began with two weeks of mapping and field studies with the purpose of becoming familiar with the rocks and surroundings. A 1km^2 area was mapped and samples, representative for the site, were collected for further analysis. Classifications made in the field were mostly done through visual mineral identification with the help of a hand-lens and differences in hardness obtained by use of a hammer and a knife. The hardness differences were mainly used to separate marble and skarn from each other as the weathered surface of both rock types are very similar.

Preparation for analyses

Five samples were chosen from those gathered during the fieldwork to represent the various types of metacarbonates found within this area. The samples were chosen to be useful for P-T- X_{CO2} studies. These contained calcite, dolomite, pyroxenes and amphiboles. The samples were cut, polished and then sent to Vancouver Petrographics Ltd, Canada for thin section making (30 Microns, 26x46mm, microprobe quality). The thin sections were visually analysed by using a petrographic microscope (further description in section: *Petrographic analysis*) to determine mineralogy, equilibrium/disequilibrium between minerals and to choose measurement spots for SEM analysis. From the initial five thin sections three were chosen for SEM analysis.

SEM analysis

Further analyses of the thin sections were performed, first with a brief SEM session at the department of Geological Sciences, Stockholm University to find the most interesting and representative spots to analyse at the Department of Earth Sciences at Gothenburg University. Minerals of interest were dolomite and calcite for calcite-dolomite geothermometry which is used to calculate the solvus between them based on their magnesium and calcium contents. Before the analyses in Gothenburg began, the thin sections were carbon coated in a vacuum to increase the electrical conductivity; thus minimising the error from electrostatic charge. The samples were then mounted on a movable stage in the SEM for analyses of the chemical composition of the minerals of interest. The equipment used was a Hitachi S-3400N scanning electron microscope with an Oxford Instruments EDS system which was calibrated to a simple oxide and metal standard. The standard were linked to a cobalt reference standard and verified with Smithsonian Microbeam standards.

The Microbeam standards come from analyses of 58 naturally occurring and synthetic samples since the beginning of 1960s (Jarosewich 2002). Settings during the analysis at Gothenburg University were: 20 kV, a working distance at 10 mm and a 3.5 nA current for the electron beam. During the analysis an electron beam, shot from an electron gun mounted on the SEM, were focused on the spot meant to analyse. Through this the electrons in the sample atoms are excited, promoted to a higher energy orbit, and the spectra that appears when this happens are specific for each element and can thus be used for identification of the composition (Reed 2005). The data sets from the SEM analyse can be found in the appendix.

Data processing in AX and Thermocalc

The data obtained by SEM analysis where processed in the computer programs AX - Windows version, and THERMOCALC - 3.25 Windows version, by Holland and Powel. The output data from the SEM was first used in AX to calculate the activity for mineral end-members which AX does by an input of the oxide wt% data gained during the analysis. Due to some errors during the analyses and data transfer at Gothenburg University, the wt % oxide data was not registered for all carbonate analyses. To obtain the required data, wt% atom had to be recalculated to wt% oxides for it to be run with AX. This was done by multiplying the data in the column weight% with the molar weight of the oxide and then dividing it with the molar weight of the atom. AX generated an output file with calculated activity and that could be used in THERMOCALC to calculate the P-T-X_{CO2} conditions during metamorphism. THERMOCALC used the AX output file and an embedded thermodynamic dataset to calculate the location of the reaction curves. THERMOCALC was developed by R. Powell and T.J.B Holland in 1988 and the software was released together with the paper, Powell & Holland 1988 (Powell & Holland 2008).Data spread sheets and calculations can be found in the appendix.

Geothermobarometry

Geothermobarometry, which combines geothermometry and geobarometry, is used to estimate the peak pressure and temperature of formation or metamorphism. Determination of elemental distribution between coexisting minerals over a variation of temperature and pressure will provide a way to accurately determine metamorphic pressures and temperature (Winter 2001). Data to process is obtained through electron microprobe or SEM analysis that measures the chemical composition of the mineral. Thermodynamic data sets and activity models will then be used to determine the reaction location in P-T space by comparing with experimental data. Reactions that prove to be valuable for temperature estimations are called geothemometers while the ones used for pressure determination are geobarometers (Philpotts & Ague 2009).

For this study on metacarbonates has the calcite-dolomite geothermometer been used and run with data generated by AX and THERMOCALC to calculate temperature of metamorphism. The data that was used show the elemental distribution between coexisting phases, calcite and dolomite in this case. Pressure data used in the THERMOCALC calculations was received from Engström 2011 who conducted a study of metapelitic rocks on Persholmen, an island located nearby.

The calcite-dolomite geothermometry has been widely used since its introduction by Harker and Tuttle (1955) and Graf and Goldsmith (1955) (Letargo et.al 1995). This technique is based on a solvus geothermometer and uses the magnesium content in calcite, coexisting in equilibrium with dolomite, to calculate the exchange between calcium and magnesium .This thermometer is a good tool to use for analysis of low grade metamorphic rocks as magnesium is sensitive to high temperatures and substitutes easily with iron or manganese (R. Powell, D. M. Condliffe & E. Condliffe 1984; Philpotts & Ague 2009).

Geological background

The area of this study, Utö, is located in the south eastern parts of the Stockholm archipelago and in the geological area known as the Bergslagen region. Utö is well studied by geologists as the island is very well preserved and can be seen as representative of Bergslagen. By the time of formation, Utö experienced a different environment and was located south of the equator (Lundström & Koyi 2003) and formed during the Svecofennian orogen (Stålhös 1982).The rocks in the area are dated by the U-Pb technique to the Paleoproterozoic era - 1.90-1.87 Ga (Allen et al. 1996, Lundström et al. 1998). Suits related to the Svecofennian orogen are mainly metamorphic sedimentary and volcanic rocks (Berg och Jord, 2002). This part of the Baltic shield displays a metamorphic grade that is medium to high (Allen et al. 1996), i.e. upper amphibolite-facies (Stephens et al. 2009) and is heavily mineralised with exploitable minerals and ores. The island hosted a mining industry for nearly a thousand years and is believed to have had Sweden's first mine for iron extraction. The entire Bergslagen region has long been one of the dominating mining areas in the world with a big export of iron and copper (Allen et al. 1996) and there are still at least two active mines left, Garpenberg and Zinkgruvan.

Utö can simply be described as an overturned sedimentation unit; the oldest parts are found on the south-east side of the island and can then easily be followed across the island and end up in the youngest section on the north-west side (Lundström & Koyi 2003). Formation of the island began with sedimentation of turbidity currents as greywackes in a calm environment on top of an unknown Pre-Svecofennian basement (Lundström et.al. 1998; Stålhös 1982). This initial stage can be found as exposed graded beds along the southeast coast and are interpreted to have been accreted as a prism above a subduction zone (Talbot 2008).

The next sequence indicates a less calm, shelf-like, environment as the layers consists of sandstone and conglomerates cross-bedded and with a lack of clay. This may be the result of increased thermal activity and magmatism which resulted in uplift (Talbot 2008). Volcanism originated in the area at 1904$\pm$4 Ma (age determination, Lundström et al. 1998) and the rhyolitic magma intruded as porphyritic sills within the sedimentary units. Layers of rhyolitic and dacitic volcanic ash and pyroclastic mass flows (Allen et al. 1996) are also remnants from this violent stage during the formation and can be found interbedded in the sandstones and metamorphosed mudstones (Stephens et al. 2009). The depositional setting during the volcanic stage has been interpreted by Stephens et al. (2009) to have been shallow water to subaerial. Structures in the sediment and volcanic units bear marks that earthquakes occurred during the volcanic phase; syn-sedimentary faults and sand filled cracks i.e. sandstone dykes are the major structures found that support this conclusion (Lundström & Koyi 2003, Talbot 2008).

Carbonate layers, with varying purity from high calcite content to more dolomite rich, have settled on top of the sedimentary and volcanic units, possibly in a fore-arc (Talbot 2008). These thick carbonate layers host the iron and sulphide ores found as SAS (stratiform ash-siltstone-hosted), SVALS (strata-bound volcanic associated limestone-skarn) and BIF (banded iron formation) (Allen et al. 1996). The same carbonate layers also show the most distinct deformation structures - big folds and refolded folds, from the several deformation events the island have experienced.

Study area

The area for this study is located on the northern parts of Utö, a section from the north-west coast to middle of the island which displays a variety of rock types, mainly varying carbonates but also felsic ash layers. This is the part of the island which shows the most notable deformation features as the carbonates are highly incompetent and have been heavily folded and refolded. The carbonates also host the iron and sulphide ores, but only traces of sulphide and oxide minerals have been found in the studied area.

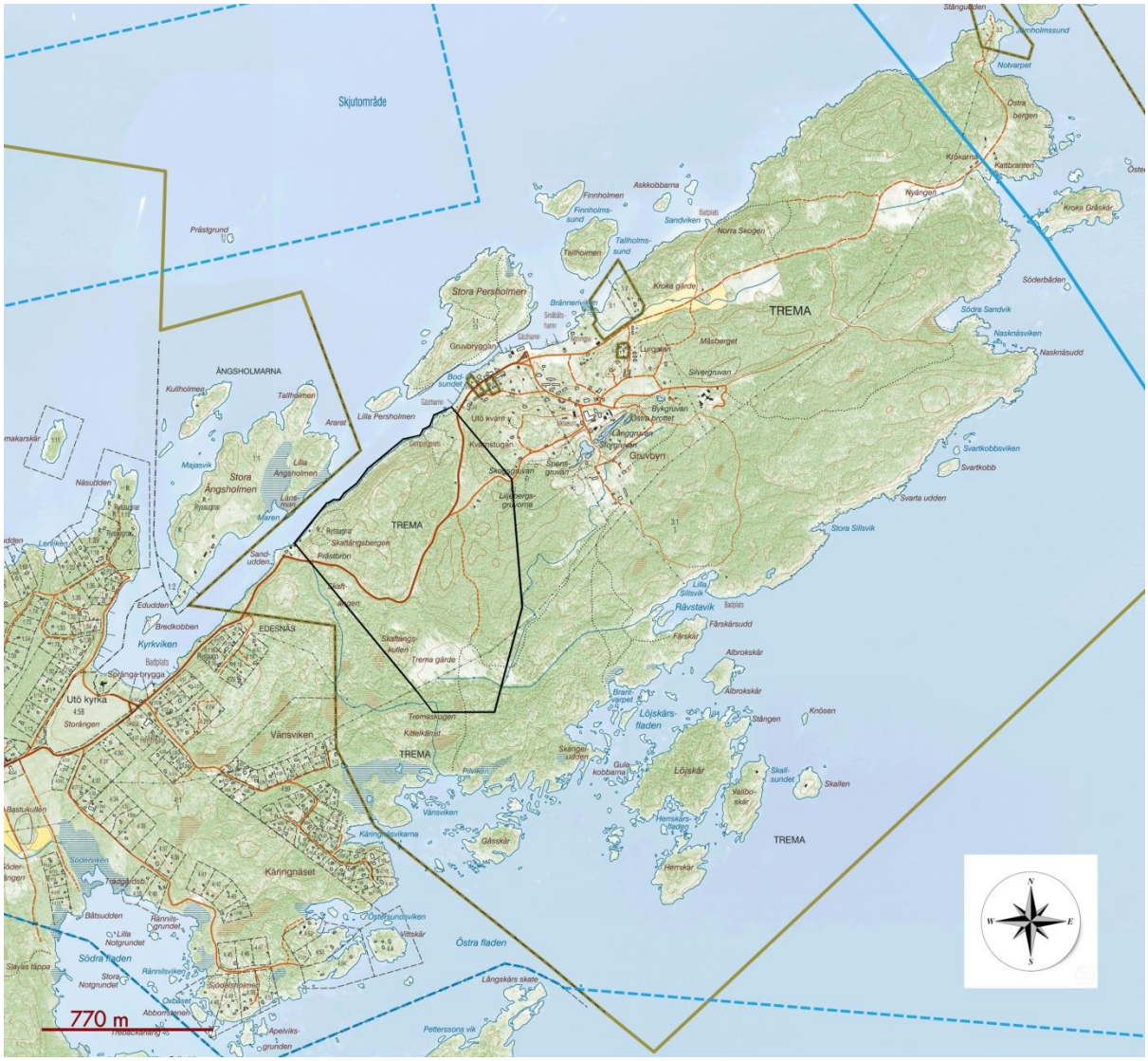


Figure 1: *Full scale map of the north cape of Utö. Black line shows the outer border of the studied area.*

The area can roughly be divided by a road (Figs. 1 and 2); on the north-western part are the felsic ash layers common while on the south-eastern side these are very uncommon and only occur as thin layers at mm-cm scale in the carbonate sequence. The same goes for the different types of deformation features; strain/sheer marks are mainly found along the north-west coast and folding increase towards the islands inner parts. The folding culminates on Skaftängskullen which is located at the hinge of the major synform that follows the centreline of the island (Talbot 2008).

As this part of the island is heavily vegetated, and the few outcrops found have experienced heavily weathering, many of my conclusions for the map are based on extrapolations.

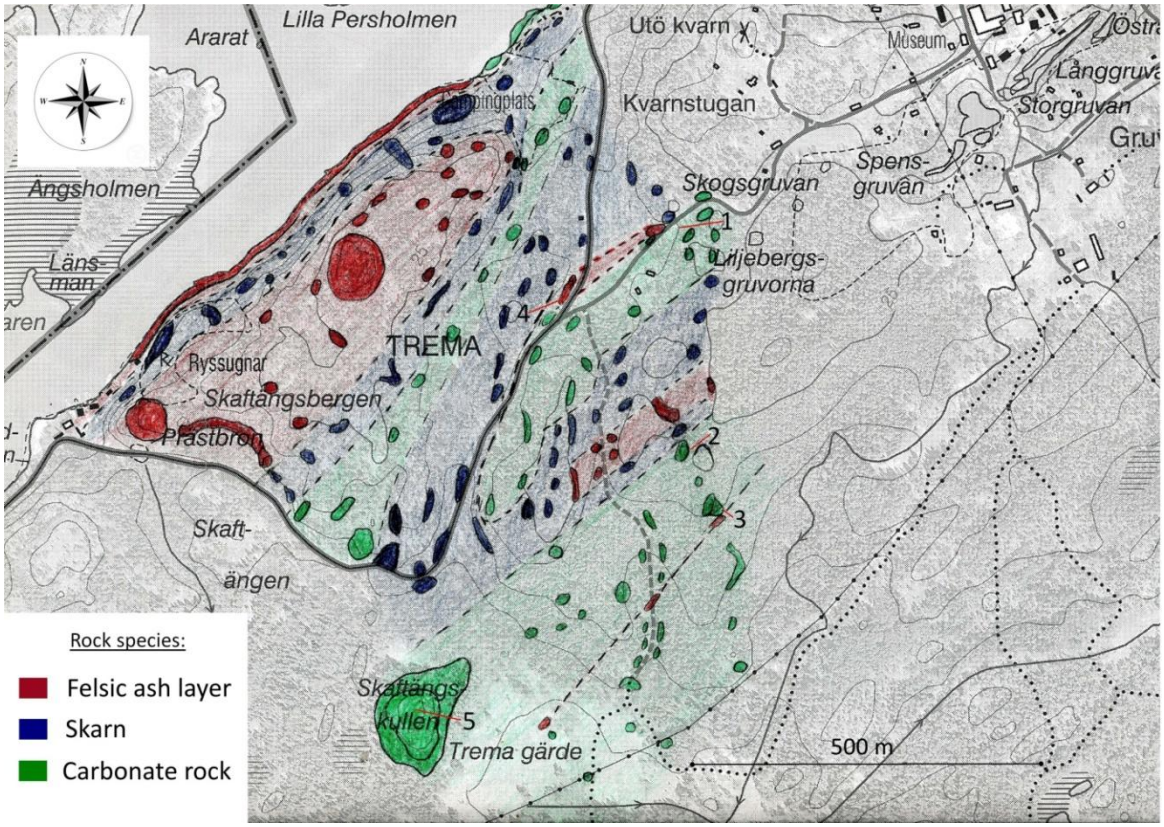


Figure 2: *Mapped area and sample sites*

Results

Petrographic analysis

Here I present petrographic descriptions of samples that were used for SEM analysis. My analysed samples have been collected along a fairly straight line that stretches ~500m with variation in calcite, dolomite and amphibole represented.

Sample 2U - Skarn/impure limestone

This sample was collected between the old Skogsgruvan and Liljebergsgruvorna on the south side of the road (Point 1 in Fig.2). The outcrop appeared as a green rock with carbonate weathering and with weathering proud green amphibole crystals, ~1 cm, growing single and in fans. The thin section shows amphibole (or amphibole and pyroxene reacting), carbonates (calcite and/or dolomite), quartz and sphene as an accessory mineral. SEM analysis showed that calcite was the only carbonate present in the sample and pyroxene was found. Amphibole appears in a retrograde phase and pyroxene as a prograde. The prograde pyroxene crystals are replaced by amphiboles and carbonates. Quartz is found as micro veins and occurs interstitially between the amphiboles and carbonates.

Amphibole/Pyroxene	Carbonates	Quartz	Accessory minerals
~60%	**~20%**	**~20%**	**~1%**

Sample 3U - Skarn/impure limestone

This sample was collected approximately half way between Liljebergsgruvorna and Trema gärde (Point 2. Fig.2) and appeared very light yellow/honey coloured. It was heavily weathered on the surface but did not show specific carbonate weathering features. Amphibole crystals had grown larger to 1-3 cm and was pale yellow/greenish with perfect developed elongated crystals showing 60˚/120˚ angles when cross cut, suggesting textural equilibrium. The thin section shows a clear dominance of carbonates and were classified as calcite and dolomite by SEM analysis. Sphene was found as an accessory mineral.

Amphibole	Carbonates	Accessory minerals
~15%	**~50%**	**~1%**

Sample 15U - Skarn/impure limestone

The last sample in the sequence, showing variation in amphibole, calcite and dolomite, was collected just a few tenths of meter away from 3U (Point 3. Fig.2). However, it appeared very different with a less weathered surface and has more similarities with 2U. The amphibole crystals had grown to ~5cm and grew as single crystals or in fan-shaped clusters. By using the petrographic microscope two generations of amphibole, or one prograde pyroxene and a retrograde amphibole, could be seen, this was later determined by SEM analysis to be amphibole and pyroxenes reacting. Two different carbonates were also visible, showing a difference in grain size, appearance and occurrence. This was lately determined by SEM analysis to be calcite and dolomite. Calcite appeared as a fine grained 'matrix' while dolomite showed well developed crystals. Sphene was found as an accessory mineral.

Amphibole/Pyroxene	Carbonates	Accessory minerals
~40%	**~60%**	**~1%**

The following descriptions are of the rocks which were not SEM analysed.

Sample 16U – Felsic volcanic ash

A sample from the ash flows was taken from an outcrop right by the roadside (Point 4. Fig.2).The rock exhibits a weather proud feature due to its high silica content and many small mm-sized veins of pure quartz. The reason for sampling was the interesting cracks, ~2 cm wide and 40 cm long, filled with biotite and amphibole growing together. Biotite was found in the centre and amphibole around the edge. The thin section showed retrograde amphibole and plagioclase, a prograde chlorite with a very pale, almost white, appearance and prograde epidote. The biotite with characteristic zircon burn marks was found to be retrograde. Chlorite and epidote was found as accessory minerals.

Amphibole	Plagioclase	Quartz	Biotite	Accessory minerals
~20%	**~5%**	**~60%**	**~15%**	**~1%**

Sample 17U – Impure limestone/marble

Sampled at the site known by geologist as 'Soptippen', located at the centre of the deformation zone at Skaftängskullen (Point 5. Fig.2). The site consists of heavy folded and refolded layers of impure limestone/marble and the sample was collected from the hinge of a fold where a carbonate mineral, probably dolomite as it had a strong red colour, had formed crystals in the low-pressure zone of the fold. Thin section analysis showed high quartz content, retrograde amphibole crystals and what was believed to be both calcite and dolomite intergrown. As this sample was not analysed by SEM, the observations will only be from visible identification in the field and microscope and the occurrence of dolomite cannot be confirmed.

Amphibole	Carbonates	Quartz
~15%	**~35%**	**~50%**

SEM acquired data

Wt% Oxides for sample 15u

Mineral ||Oxides	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
Cal.	0	0	0	0	0	0,098	0,098	0,854	29,260	0	0
Dol.	0	0	0	0	0	0,549	0,162	12,588	13,375	0	0
Cal.	0	0	0	0	0	0,084	0,140	0,826	28,210	0	0
Cal.	0	0	0	0	0	0,126	0,126	1,036	28,644	0	0
Cal.	0	0	0	0	0	0,126	0,042	1,134	28,070	0	0
Dol.	0	0	0	0	0	0,587	0,175	12,301	13,350	0	0
Dol.	0	0	0	0	0	0,487	0,150	12,289	12,913	0	0

Discussion

Data from analyses of sample 15u were used in the attempt to determine temperature and composition of the metamorphic fluid during metamorphism. Pressure data was received from Adam Engström (Engström 2011) who worked at Persholmen, an adjacent study area. Temperature was calculated with the use of calcite-dolomite geothermometry and cross-referenced to data from the Persholmen study. The composition, X_{CO2}, of the metamorphic fluid was determined with calculations in AX and THERMOCALC.

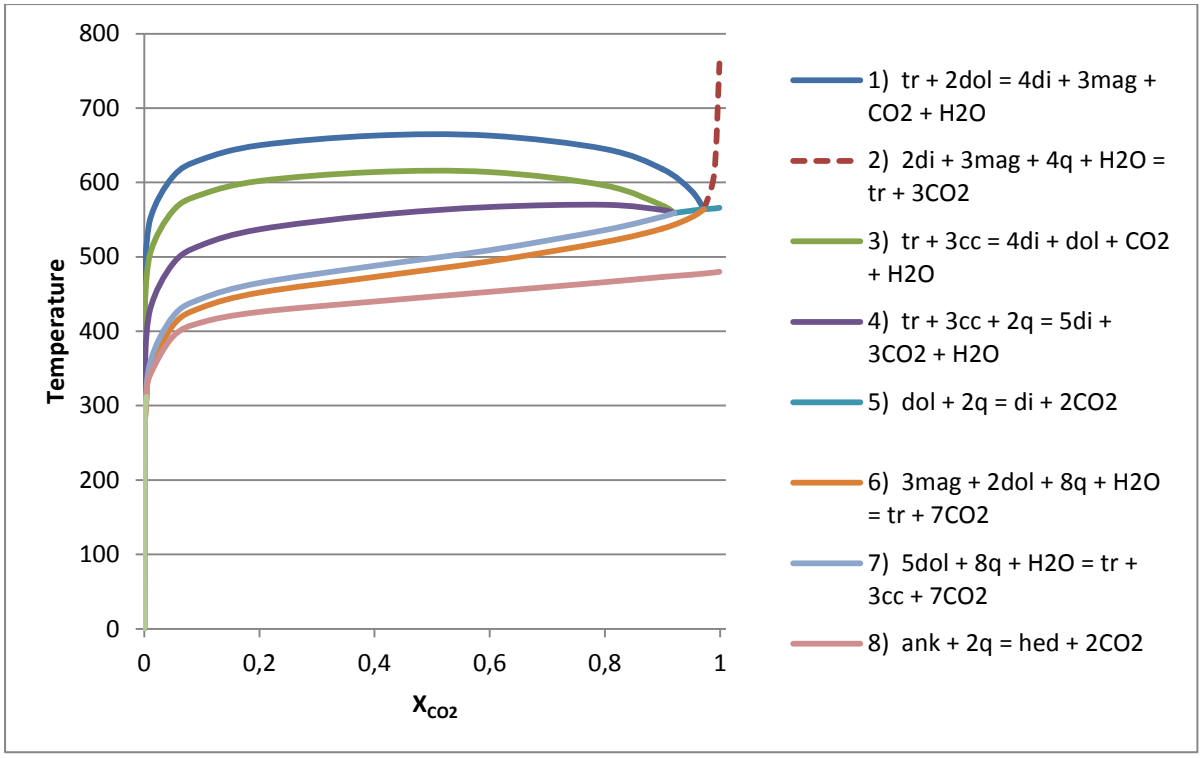
Pressure and temperature data from Adam Engströms study (Engström 2011) was acquired from chemistry data of SEM analysed muscovite and feldspar in two samples, one greywacke and one migmatite with greywacke origin. Obtained data showed a pressure of 3.1 $\pm$ 1.3 kbars and a temperature of 538 $\pm$ 36°C for the greywacke sample and 3.8 $\pm$ 3.2 kbars, 756 $\pm$ 133°C for the migmatite. Pressure data from the greywacke sample was used in this study.

As the rocks of this study are metacarbonates with coexisting calcite and dolomite in equilibrium, temperature could be calculated with the calcite-dolomite exchange geothermometer (Anovitz & Essene 1987):

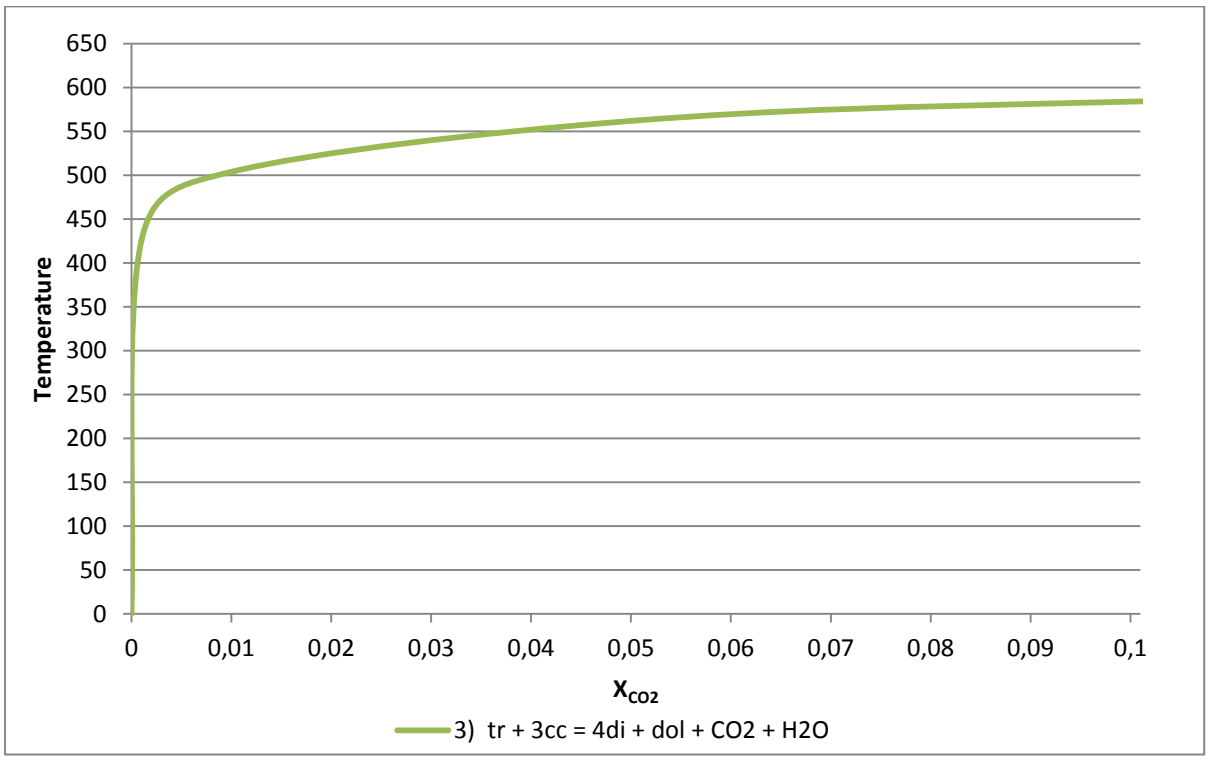
$$T = -2360X_{MgCO_3}^{Calcite} - \left(\frac{0{,}01345}{X_{MgCO_3}^{Calcite}}\right)^2 + 2620\left(X_{MgCO_3}^{Calcite}\right)^2 + 2608\left(X_{MgCO_3}^{Calcite}\right)^{0{,}5} + 334$$

The equation was run four times with $MgCO_3$ concentrations gathered from the SEM analysis of four measured calcite grains. The temperature was calculated to 442 $\pm$ 30°C, which is a bit lower than the temperature for the Persholmen samples. Difference in temperature between the two sites can be related to the deformation zone which separates them. The temperature calculated from the metacarbonates was used to determine the chemistry of the fluid released during metamorphism. $MgCO_3$concentration, from the four analysed samples, and used in this equations can be found in the appendix section: Geothermometry calculations.

Fluid composition was determined with THERMOCALC for pure end-member mineral compositions and the T- X_{CO2}diagram plotted from the THERMOCALC output file. The T- X_{CO2} diagram show the proportion between H_2O and CO_2 in the fluid related to temperature.



From the THERMOCALC output file the stability of the reactions could be determined (graph above) and metastable reactions were removed in the graph below, leaving only the stable reaction with coexisting tremolite, calcite, diopside, dolomite plotted against temperature and $X_{CO2.}$



Using the data generated by THERMOCALC, a logarithmic trend line was created using Excel. The trend line equation y = 34,513ln(x) + 664,05 was then used to calculate the X_{CO2} at the specific temperature calculated with the geothermometry. The sought X_{CO2} value, X in the equation, was obtained by replacing Y in the equation with the three temperatures, 412°C, 442°C, 472°C (442°C $\pm$ 30°C) in three different equations, generating the span in which we could expect to find the X_{CO2}.

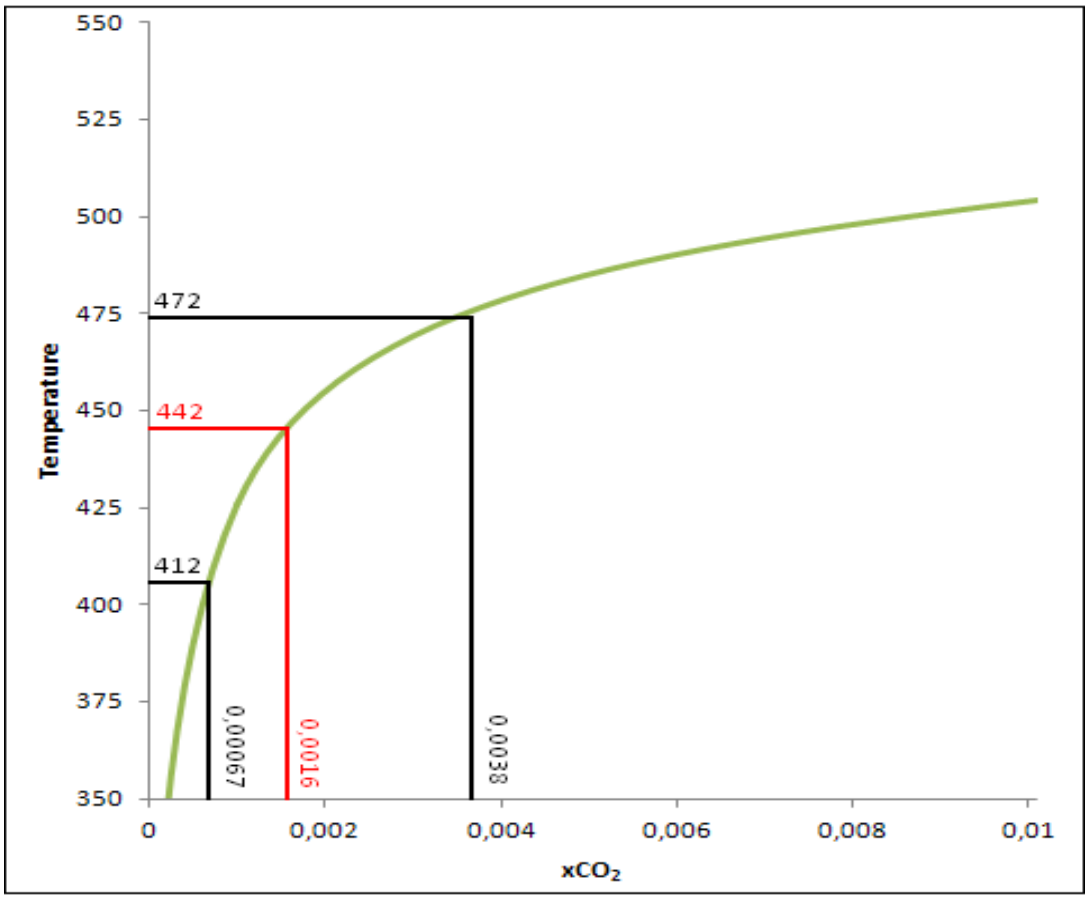
$$y = 34{,}513\, ln(x) + 664{,}05$$

$$y - 664{,}05 = 34{,}513\, ln(x)$$

$$ln(x) = \frac{y - 664{,}05}{34{,}513}$$

$$x = e^{\frac{y-664{,}05}{34{,}513}}$$

X_{CO2} was calculated, using the above equation, to range from 0,00067 at 412°C to 0,0038 at 472°C. At the calculated temperature 442°C the $X_{CO2}$was calculated to 0,0016.



This graph shows a simplified sketch over the temperature and X_{CO2} relation with markers at the calculated values and corresponding temperature.

Source of error

As all data originating from just one source, potential errors should always be accounted for to occur. This thesis is built up by several steps that can be such a source. The first stage was during the geological mapping; all interpretations made in the field were based solely on the observations and identifications made by one person. Sites, related to this thesis, that were tougher to identify were visited by a supervisor or co-workers to see if the same conclusions were drawn. The errors that could occur around mineral identification in thin sections were minimized by cross-checking made by other geologists. A crucial step in the process to gather data was the SEM analysis and as previously noted some problems with the data gathering followed. The poor results from the SEM analysis were based on the lack of experience in handling such a powerful tool and some necessary settings were changed during the analysis. Luckily this could be corrected by re-calculations but should still be noted as a source of error. Another source would be the THERMOCALC run that was made only on the calculated pressure data of 3.1 kbars and not with its standard deviation of $\pm$1.3kbars. For the data representation, all calculations made with the geothermometry equations were carried out with all the provided digits from the SEM analysis and re-calculations but have been round off when represented in the text. And lastly, the representation of the X_{CO2} may appear a bit to precise with as many digits, but have been displayed this way as the visual representation with the diagram would appear incorrect otherwise.

Conclusion

The mapped area in the central part of Utö showed a rapid variation in rock types with a composition of varying amount of silica in the metacarbonates and almost pure silica layers of felsic ash. A great variation in the appearance of the tremolite was also observed as the colour, from dark green to light yellow, and size, from ~1cm to ~5cm, changed quickly over a short distance of a few tenths of meters. This represents differences in fluid flow and fluid composition, over a short distance, and a narrow stability field for coexisting calcite and dolomite.

SEM acquired data, AX, THERMOCALC and geothermometry calculations enabled the temperature and X_{CO2} to be established. With the calculated data from the solvus thermometer and pressure data from Persholmen could the metamorphic event be placed at a pressure of 3.1$\pm$ 1.3 kbars and at a temperature of 442°C $\pm$ 30°C, this place the event in the greenschist facies. The metamorphic fluid interacting with the metacarbonate rock had a X_{CO2} composition of 0,0016 at 442°C, with the source of error for the temperature can the fluid X_{CO2} be expected to range from 0,00067 at 412°C to 0,0038 at 472°C. Thus rocks on Utö equilibrated with a CO_2 bearing hydrous fluid at greenschist facies conditions.

Acknowledgements

I would first and foremost like to thank my supervisors, Alasdair Skelton and Joakim Mansfeld, for their patience with my questions and time for recaps when I finally returned to this thesis after my ‘excursion’ out in the world of geology consultants. Secondly, Magnus Ripa and The Geological Survey of Sweden, for literature suggestions and the opportunity to be a part of this project. Marianne Ahlbom for her input during the initial SEM analysis, Mikael Hovemyr, Outi Kilkki and Gerry McCabe for proof-reading and layout in-put. And lastly, Adam Engström and Oskar Bergkvist, for providing me with data, discussions and a second pair of eyes during the field work.

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Appendix

SEM data

Pyroxene

Element	App. Conc	Intensity corrn.	Weight%	Weight% sigma	Atomic%	Compound%	Formula	# of ions
Na	0,08	0,8366	0,09	0,03	0,09	0,12	Na2O	0,01
Mg	7,96	0,7841	10,15	0,05	9,33	16,82	MgO	0,93
Al	0,05	0,764	0,07	0,03	0,06	0,13	Al2O3	0,01
Si	22,46	0,9044	24,84	0,06	19,77	53,14	SiO2	1,98
Cl	0	0,7243	0	0	0	0		0
K	0,02	1,0516	0,02	0,02	0,01	0,02	K2O	0
Ca	17,8	0,9688	18,37	0,06	10,25	25,7	CaO	1,03
Ti	0,02	0,8437	0,02	0,02	0,01	0,04	TiO2	0
Mn	0,13	0,7969	0,16	0,03	0,07	0,21	MnO	0,01
Fe	1,1	0,817	1,35	0,04	0,54	1,73	FeO	0,05
O			42,86	0,1	59,88			6
Totals			97,93					
							Cation sum	4,02

Amphibole

Element	App. Conc	Intensity corrn.	Weight%	Weight% sigma	Atomic%	Compound%	Formula	# of ions
Na	0,09	0,8633	0,11	0,03	0,1	0,14	Na2O	0,04
Mg	10,42	0,8022	12,99	0,05	11,92	21,54	MgO	4,54
Al	0,14	0,7378	0,19	0,03	0,16	0,36	Al2O3	0,06
Si	23,02	0,8772	26,24	0,06	20,84	56,14	SiO2	7,93
Cl	0	0,7015	0	0	0	0		0
K	0,05	1,0205	0,05	0,02	0,03	0,06	K2O	0,01
Ca	9,31	0,9555	9,74	0,05	5,42	13,63	CaO	2,06
Ti	0	0,8618	0	0	0	0	TiO2	0
Mn	0,14	0,8031	0,17	0,03	0,07	0,22	MnO	0,03
Fe	2,13	0,8213	2,6	0,04	1,04	3,34	FeO	0,39
O			43,35	0,1	60,43			23
Totals			95,44					
							Cation sum	15,06

Calcite

Element	App. Conc	Intensity corrn.	Weight%	Weight% sigma	Atomic%
Mg	0,44	0,631	0,7	0,03	0,61
Ca	41,03	1,0351	39,64	0,08	20,9
Mn	0,15	0,7801	0,19	0,03	0,07
Fe	0,14	0,8023	0,18	0,03	0,07
O			59,3	0,1	78,35
Totals			100		

Dolomite

Element	*App. Conc*	*Intensity corrn.*	*Weight%*	*Weight% sigma*	*Atomic%*
Mg	8,32	0,6668	12,48	0,06	10,08
Ca	22,01	1,0073	21,85	0,06	10,71
Mn	0,29	0,7903	0,37	0,03	0,13
Fe	1	0,8084	0,37	0,04	0,44
O			64,07	0,1	78,65
Totals			100		

Calcite

Element	***App. Conc***	***Intensity corrn.***	***Weight%***	***Weight% sigma***	***Atomic%***
Mg	0,43	0,6299	0,68	0,03	0,59
Ca	39,82	1,0337	38,53	0,08	20,15
Mn	0,2	0,7803	0,25	0,03	0,1
Fe	0,12	0,8023	0,15	0,03	0,06
O			60,39	0,09	79,11
Totals			100		

Calcite

Element	***App. Conc***	***Intensity corrn.***	***Weight%***	***Weight% sigma***	***Atomic%***
Mg	0,54	0,6307	0,85	0,03	0,74
Ca	40,28	1,0343	38,94	0,08	20,46
Mn	0,17	0,7804	0,22	0,03	0,09
Fe	0,19	0,8025	0,24	0,03	0,09
O			59,74	0,09	78,63
Totals			100		

Calcite

Element	***App. Conc***	***Intensity corrn.***	***Weight%***	***Weight% sigma***	***Atomic%***
Mg	0,59	0,6305	0,94	0,03	0,81
Ca	39,6	1,0334	38,32	0,08	20,05
Mn	0,18	0,7806	0,22	0,03	0,09
Fe	0,2	0,8025	0,25	0,03	0,09
O			60,26	0,09	78,97
Totals			100		

Dolomite

Element	*App. Conc*	*Intensity corrn.*	*Weight%*	*Weight% sigma*	*Atomic%*
Mg	8,11	0,6648	12,2	0,06	9,85
Ca	21,98	1,0076	21,82	0,06	10,69
Mn	0,31	0,7904	0,39	0,03	0,14
Fe	1,08	0,8085	1,33	0,04	0,47
O			64,26	0,1	78,85
Totals			100		

Dolomite

Element	*App. Conc*	*Intensity corrn.*	*Weight%*	*Weight% sigma*	*Atomic%*
Mg	8,17	0,6658	12,27	0,06	9,84
Ca	21,38	1,0063	21,24	0,06	10,34
Mn	0,26	0,7901	0,32	0,03	0,12
Fe	0,9	0,8079	1,11	0,04	0,39
O			65,05	0,1	79,31
Totals			100		

Element	*Standard for silicates*
Na	jadeite mac 20-Jan-2010 04:04 PM
Mg	MgOMAC 20-Jan-2010 04:09 PM
Al	al2o3 mac 20-Jan-2010 04:14 PM
Si	Wollastonite 13-Nov-2009 10:15 PM
K	k-feldspar mac 13-Nov-2009 06:30 PM
Ca	Wollastonite 13-Nov-2009 10:15 PM
Ti	Rutile2 13-Nov-2009 10:14 PM
Mn	Mn 13-Nov-2009 06:29 PM
Fe	Fe met nov09 13-Nov-2009 06:28 PM

Element	*Standard for carbonates*
Mg	MgOMAC 20-Jan-2010 04:09 PM
Ca	Wollastonite 13-Nov-2009 10:15 PM
Mn	Mn 13-Nov-2009 06:29 PM
Fe	Fe met nov09 13-Nov-2009 06:28 PM

Processing option: Oxygen by stoichiometry for silicates, Oxygen by difference for carbonates.

Number of iterations : 3

Sample is polished.

Sample is coated with Carbon - thickness (nm): 25.0, density (g/cm3): 2.25

Thresholding has been selected : All quantitative results below 1 sigma have been set to zero

Detector efficiency : Calculation

Pulse pile up correction performed.

Recalculated data used

Element	Atomic%	X	Atomic%	X	Atomic%	X	Atomic%	X
Mg	0,81	0,0386082	0,74	0,0346118	0,59	0,0282297	0,61	0,0281755
Ca	20,05	0,9556721	20,46	0,9569691	20,15	0,9641148	20,9	0,965358
Mn	0,03	0,0014299	0,09	0,0042095	0,1	0,0047847	0,07	0,0032333
Fe	0,09	0,0042898	0,09	0,0042095	0,06	0,0028708	0,07	0,0032333
Sum:	20,98		21,38		20,9		21,65	

Geothermometry calculations

X(MgCO3)	A	B	C	D	E	K°	C°
0,038608198	-2360	-0,01345	2620	2608	334	750	477
0,034611787	-2360	-0,01345	2620	2608	334	729	456
0,028229665	-2360	-0,01345	2620	2608	334	691	418
0,02817552	-2360	-0,01345	2620	2608	334	690	417
							442
							30

THERMOCALC output files

THERMOCALC 3.21 running at 13.16 on Wed 22 Jun, 2011 with thermodynamic dataset produced at temperature-x(CO2) calculations

	di	hed	tr	parg	gl	mag	cc	dol
a	0.960	0.00390	0.880	0.219	0.000366	0.760	0.960	0.940

	ank	q
a	0.0670	1.00
sd(ln a)	0.26115	0

Excluded assemblages | mag cc | di ank |

no of reactions = 10, no of intersections = 4

1) tr + 2dol = 4di + 3mag + CO2 + H2O
2) 2di + 3mag + 4q + H2O = tr + 3CO2
3) tr + 3cc = 4di + dol + CO2 + H2O
4) tr + 3cc + 2q = 5di + 3CO2 + H2O
5) dol + 2q = di + 2CO2
6) 3mag + 2dol + 8q + H2O = tr + 7CO2
7) 5dol + 8q + H2O = tr + 3cc + 7CO2
8) ank + 2q = hed + 2CO2
9) tr + 4ank = 4hed + 3mag + 2dol + CO2 + H2O
10) tr + 3cc + 4ank = 4hed + 5dol + CO2 + H2O

Thermodynamics of reactions (0 = a + bT + cP + RT ln K)
linearised at T = 500, P = 3.1, x(CO2) = 0.500
(a, b and c includes fluid fugacities; ln K includes x(CO2), x(H2O))

	a	sd(a)	b	c	ln_K	sd(ln_K)
1	128.54	0.98	-0.12733	2.255	-2.121	0.534
2	111.32	0.53	-0.20107	8.876	-0.609	0.353
3	113.26	0.80	-0.12474	2.102	-1.361	0.504
4	233.19	0.93	-0.28893	7.667	-2.726	0.578
5	119.93	0.45	-0.16420	5.565	-1.365	0.142
6	351.18	1.12	-0.52947	20.006	-3.340	0.353
7	366.45	1.98	-0.53206	20.158	-4.100	0.580
8	127.38	1.46	-0.16850	5.570	-4.230	0.589
9	158.33	5.64	-0.14455	2.275	-13.580	2.380
10	143.06	5.60	-0.14196	2.123	-12.820	2.424

Temperatures in the range 100 <-> 900°C; for P = 3.1 kbar uncertainties at or near x(CO2) = 0.5

x(CO2)	0.001	0.01	0.05	0.1	0.2	0.4	0.6	0.8	0.9	0.95	0.99	0.999	sdT
1	470	548	606	629	648	661	661	643	616	588	524	444	30
2	206	282	339	360	376	393	414	449	480	511	584	719	9
3	422	498	554	576	594	606	605	588	562	534	471	392	27
4	340	422	482	506	526	545	557	560	553	541	511	468	13
5	291	371	433	457	478	499	517	535	544	548	552	552	6
6	257	335	396	419	438	459	479	504	522	535	562	598	4
7	268	347	409	432	452	474	496	521	539	553	579	616	7
8	265	334	385	403	417	431	444	457	463	467	469	470	18
9	291	328	352	359	363	366	366	359	349	337	309	271	56
10	253	289	311	318	321	323	323	317	307	295	268	231	56

T-x(CO2) of intersections : P = 3.1 kbar
window : T 100 <-> 900°C; x(CO2) 0.001 <-> 0.999
in excess : CO2 H2O

· stable intersection 1 involving di,tr,mag,dol,q + (CO2,H2O) or [hed,parg,gl,cc,ank]

low T high T dx/dt

1) tr + 2dol = 4di + 3mag + CO2 + H2O [q] stable-0.000780
2) 2di + 3mag + 4q + H2O = tr + 3CO2 [dol] stable 0.000645
6) 3mag + 2dol + 8q + H2O = tr + 7CO2 [di] stable 0.00192
5) dol + 2q = di + 2CO2 [tr,mag] stable stable 0.0234

T = 551 °C , x(CO2) = 0.979

· stable intersection 2 involving di,tr,cc,dol,q + (CO2,H2O) or [hed,parg,gl,mag,ank]

low T high T dx/dt

4) tr + 3cc + 2q = 5di + 3CO2 + H2O [dol] stable -0.00759
3) tr + 3cc = 4di + dol + CO2 + H2O [q] stable -0.00311
7) 5dol + 8q + H2O = tr + 3cc + 7CO2 [di] stable 0.00657
5) dol + 2q = di + 2CO2 [tr,cc] stable 0.0232

T = 547 °C , x(CO2) = 0.931

· stable intersection 3 involving hed,tr,mag,dol,ank,q + (CO2,H2O) or [di,parg,gl,cc]

low T high T dx/dt

6) 3mag + 2dol + 8q + H2O = tr + 7CO2

[hed,ank] stable stable 0.000488

8) ank + 2q = hed + 2CO2

[tr,mag,dol] stable stable 0.000566

9) tr + 4ank = 4hed + 3mag + 2dol + CO2 + H2O

[q] stable 0.00112

T = 323 °C , x(CO2) = 0.00738

Stability of reactions not involved in intersections :

metastable 10) tr + 3cc + 4ank = 4hed + 5dol + CO2 + H2O