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**ON MODIFICATIONS OF FLUID
INCLUSIONS IN QUARTZ**

**RE-EQUILIBRATION EXPERIMENTS AND
THERMODYNAMICAL CALCULATIONS ON FLUIDS IN
NATURAL QUARTZ**

RONALD J. BAKKER

ON MODIFICATIONS OF FLUID INCLUSIONS IN QUARTZ

RE-EQUILIBRATION EXPERIMENTS AND THERMODYNAMICAL CALCULATIONS ON FLUIDS IN NATURAL QUARTZ

**OVER VERANDERINGEN VAN VLOEISTOF
INSLUITSELS IN KWARTS**

**REËKWILIBRATIE EXPERIMENTEN EN THERMODYNAMISCHE
BEREKENINGEN AAN VLOEISTOFFEN IN NATUURLIJKE KWARTS**

(Met een samenvatting in het nederlands)

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aan mevrouw W.ToeLaer (1911-1988)

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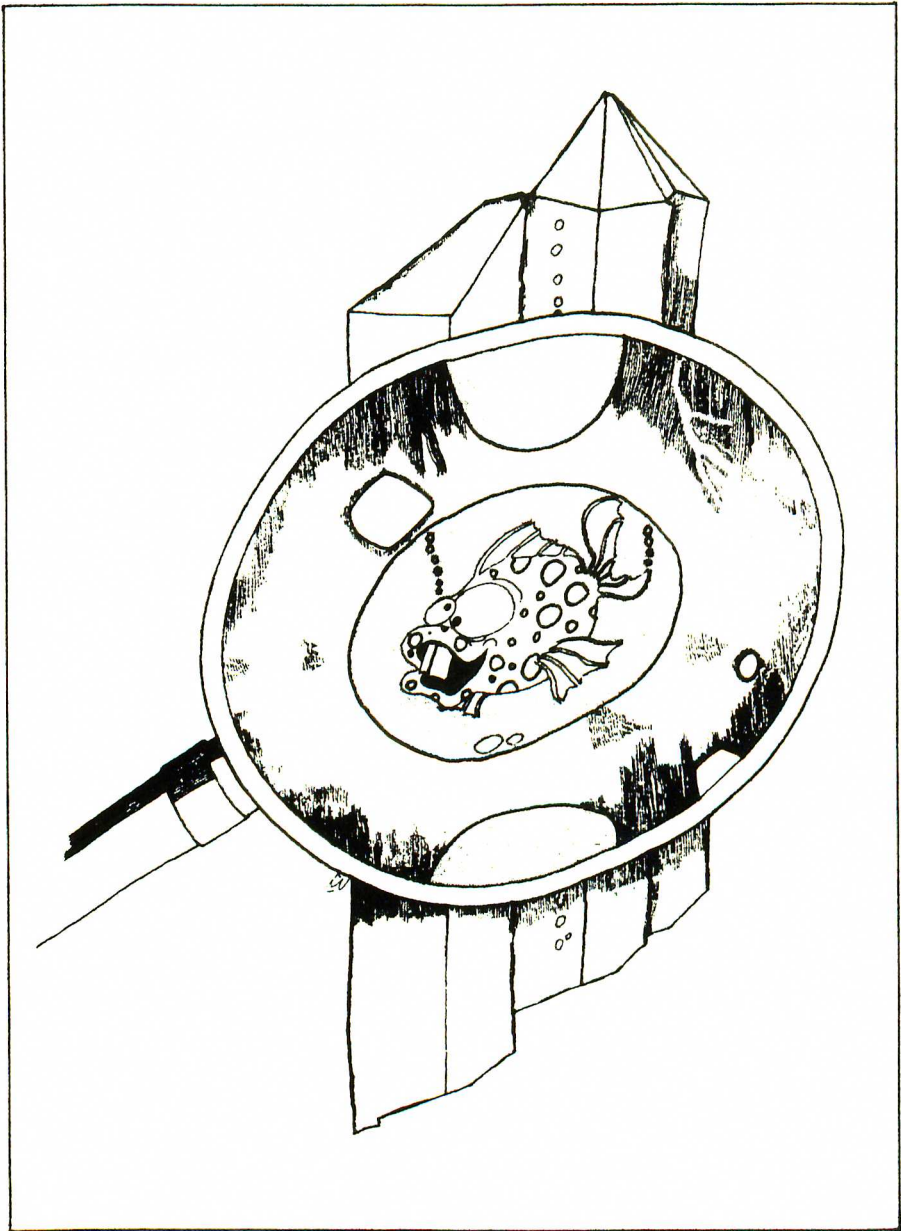
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3.4.4 Re-equilibration for isothermal decompression in E463	40
3.4.5 Re-equilibration for isothermal compression in E490	43
3.5 DISCUSSION	47
3.5.1 Type 1 fluid inclusions	48
3.5.2 Type 2 fluid inclusions	48
3.5.3 Point defects	51
3.5.4 Dislocations	53
3.5.5 Channels	54
3.5.6 Cracks	55
3.6 GEOLOGICAL APPLICATIONS OF OUR EXPERIMENTS	56
3.6.1 Natural fi.s in metamorphic quartz	56
3.6.2 Isothermal decompression, as exemplified by the rocks on Naxos (Greece)	56
3.6.3 Isobaric cooling, as exemplified by the rocks on Rogaland (SW Norway)	57
3.7 CONCLUSIONS	58

Chapter 4

A MECHANISM FOR PREFERENTIAL H₂O LEAKAGE FROM FLUID INCLUSIONS IN QUARTZ, BASED ON TEM OBSERVATIONS	61
4.1 INTRODUCTION	61
4.1.1 Naxos, a case study	61
4.1.2 Experiments	63
4.1.3 Review and intentions	64
4.2 SAMPLE PREPARATION	65
4.3 EXPERIMENTAL RESULTS	66
4.4 INTERPRETATION OF MICROSTRUCTURES	75
4.5 DISCUSSION	77
4.6 VEIN QUARTZ FROM NAXOS	87
4.7 CONCLUSIONS	91
Appendix	
Orientation electron micrographs	93

Chapter 5

THE PROGRAMS COHN: THEORETICAL BACKGROUND AND PROGRAM-STRUCTURE	97
5.1 INTRODUCTION	97
5.2 THEORETICAL BASIS FOR THE PROGRAM	98
5.2.1 Statistical Thermodynamics	98
5.2.2 Pressure of gases	100
5.2.3 Heat capacity	105
5.2.4 Mineral volumes	108
5.2.5 Fundamental equations	109
5.2.6 Phases	111
5.2.7 Equilibria	114
5.3 THE COHN PROGRAMS	115
5.3.1 Units	118
5.3.2 Programs	122
APPENDIX	132

Chapter 6

CALCULATED FLUID EVOLUTION PATH VERSUS FLUID INCLUSION DATA IN THE COHN SYSTEM AS EXEMPLIFIED BY METAMORPHIC ROCKS, ROGALAND SW NORWAY.	133
6.1 ABSTRACT	133
6.2 INTRODUCTION	134
6.3 OXIDATION AND NITRODATION TRENDS IN ROCKS	136
6.4 ROGALAND (SW NORWAY)	139
6.5 FLUID EVOLUTION CALCULATION	146
6.5.1 COH-system	146
6.5.2 COHN-system	150
6.6 DISCUSSION	155
6.7 CONCLUSIONS	164

Chapter 7

CONCLUDING REMARKS	165
7.1 EXPERIMENTS	165
7.2 LEAKAGE MODEL	166
7.3 IMPLICATIONS FOR NATURAL FLUID INCLUSIONS IN METAMORPHIC ROCK	167
REFERENCES	169
CURRICULUM VITAE	189

ABSTRACT

Fluids in rocks can be traced to great depths, and are found in crustal rocks as well as in mantle rocks. Information about the deep fluid which is obtained from fluid inclusions must be handled with care, for the way up after entrapment in a crystal is long and full of interferences at different pressures and temperatures. The fluid system may be a very complex mixture (H_2O , CO_2 , CH_4 , N_2 , CO , NH_3 , and H_2) with distinct physical and chemical properties.

Chapter 1 indicates that many types of fluids have been recognized in rocks, and that each type may be related to a distinct grade of metamorphism (eg. Sorby 1858). For example, the type of fluid recognized in inclusions from very deep rocks, like granulites and upper mantle rocks is pure CO_2 . Many interpretations of fluid inclusions are based on the assumption that fluid inclusions do not change in density and composition after entrapment. In recent years it was recognized that fluid densities may change during the long way up, and some voices were heard arguing compositional changes. In this study (**Chapter 2** and **Chapter 3**) it is experimentally proven that CO_2 - H_2O fluid inclusions, which are synthesized in Brazilian quartz at 835 K and 200 MPa, leak preferentially H_2O during re-equilibration at different conditions. The inclusions are submitted to an internal overpressure and underpressure. The remaining inclusions become relatively enriched in CO_2 , and the H_2O must have diffused through the crystal, for there are no traces of cracks. Several underpressurized inclusions have "implosion halos" after re-equilibration, which consist of many small secondary inclusions.

Transmission electron microscopy (TEM) observations of the re-equilibrated Brazilian quartz and of quartz lenses from Naxos, Greece, (**Chapter 4**) indicate that dislocations adjacent to fluid inclusions account for the non-decrepitative preferential H_2O leakage. Ductile strain of the quartz neighbouring inclusions, which are overpressurized and underpressurized, is

expressed in the localized occurrence of many dislocations. Selective diffusion of H_2O along dislocations, which are assumed to be inaccessible for CO_2 , results in the observed preferential H_2O leakage. Additionally, a solubility gradient of quartz in water between an underpressurized fluid inclusion and a dislocation cause the growth of small secondary bubbles at dislocations to optically visible "implosion halos" at the expense of the fluid inclusion.

The fluid which should occur at great depths can be indirectly obtained through thermodynamical calculations. The theoretical background of these calculations is described in **Chapter 5**. The well documented metamorphism from Rogaland (SW Norway) provides enough information to proceed these fluid calculations (**Chapter 6**). The calculated gaseous fluid inclusions are similar to the observed natural fluid inclusions. However, the calculated aqueous fluids are not recognized or registered by natural fluid inclusions. The absence of H_2O in low density metastable CO_2 - CH_4 -rich inclusions with graphite, and the occurrence of CH_4 - N_2 -rich inclusions are both proposed to result from preferential H_2O leakage.

The occurrence of CO_2 rich inclusions in granulites and mantle rocks may partly be caused by the fact that before exposure, these deep rocks have usually suffered more intensive recrystallization during uplift than shallow rocks. In future studies on fluid inclusions the effect of deformation on aqueous inclusions can not be ignored.

SAMENVATTING

Tot op grote diepte in de aardkorst en mantel komt een fluïde fase in gesteenten voor. Informatie over deze fase wordt verkregen uit insluitels van deze vloeistof in mineralen. Echter, vanwege de extensieve opheffing en de vele mogelijke interacties met de omgeving, moet deze informatie kritisch worden verwerkt. Het fluïde systeem kan een complex mengsel zijn van H_2O , CO_2 , CH_4 , N_2 , CO , NH_3 en H_2 met uitgesproken fysische en chemische eigenschappen.

In **Hoofdstuk 1** worden bekende typen fluïde fasen beschreven, die aan specifieke metamorfe omstandigheden gerelateerd kunnen worden (Sorby 1858). Bijvoorbeeld, in diepe gesteenten zoals granulieten en boven-mantelgesteenten bestaat de fluïde fase uit pure CO_2 . De huidige interpretatie van vloeistofinsluitels is gebaseerd op de veronderstelling dat de dichtheid en samenstelling na insluiting niet veranderen. Echter, dichtheidsveranderingen zijn onlangs aangetoond en samenstellingsveranderingen worden ter discussie gesteld. In dit proefschrift (**Hoofdstuk 2** en **Hoofdstuk 3**) wordt experimenteel bewezen dat CO_2 - H_2O vloeistofinsluitels, die gemaakt zijn in Braziliaans kwarts bij 835 K en 200 MPa, preferent H_2O lekken tijdens reëkwilibratie onder andere omstandigheden. Het insluitel wordt relatief verrijkt in CO_2 . De H_2O moet door het kristal gediffundeerd zijn, daar er geen breukjes gevormd zijn. Vele onderdrukte insluitels (dat zijn insluitels met een interne druk die lager is dan de externe druk) hebben na reëkwilibratie "implosie-halo's", die bestaan uit vele kleine secundaire insluitels.

Transmissie elektronen microscopische (TEM) waarnemingen van gereëkwilibreerd Braziliaans kwarts en van kwarts lenzen uit Naxos, Griekenland, (**Hoofdstuk 4**) laten zien dat dislocaties rondom vloeistofinsluitels verantwoordelijk zijn voor de non-decrepitatieve preferente H_2O -lekkage. Ductiele vervorming van de kwarts naast insluitels, die onderdrukt en overdrukt (dat zijn insluitels met een interne druk die hoger is dan de externe druk) zijn, komt tot uiting in de vorming van vele dislocaties.

Selectieve diffusie van H_2O door dislocaties die niet toegankelijk zijn voor CO_2 , resulteren in de waargenomen preferente H_2O -lekkage. De oplosbaarheidsgradiënt van kwarts in water tussen onderdrukte insluitels en dislocaties doet kleine secundaire insluitels ontstaan op dislocaties ten koste van de grotere onderdrukte insluitels. Dit komt tot uitdrukking in de optisch zichtbare "implosie halo's".

De fluïde fase die op grote diepte voorkomt, kan thermodynamisch berekend worden. De theoretische achtergrond van deze berekeningen wordt beschreven in **Hoofdstuk 5**. De uitgebreid gedocumenteerde metamorfose van Rogaland (ZW Noorwegen) levert voldoende informatie om theoretische evolutie van de fluïde fase te berekenen (**Hoofdstuk 6**). De berekende gasrijke fasen komen overeen met waargenomen natuurlijke vloeistofinsluitels. Echter, de berekende waterrijke fasen zijn niet geregistreerd door natuurlijke vloeistofinsluitels. De afwezigheid van H_2O in metastabiele grafiet- CO_2 - CH_4 -rijke insluitels met een lage dichtheid en het voorkomen van CH_4 - N_2 -rijke insluitels zijn beiden het resultaat van preferente H_2O -lekkage.

Het voorkomen van CO_2 -rijke insluitels in granulieten en mantel gesteenten kan bijvoorbeeld gedeeltelijk verklaard worden door de intensievere rekristallisatie van deze gesteenten dan ondiepe gesteenten voordat de oppervlakte bereikt is. Het effect van deformatie op waterrijke insluitels kan in verder onderzoek naar vloeistofinsluitels niet verwaarloosd worden.

Chapter 1

INTRODUCTION

1.1 PREVIOUS STUDIES ON FLUID INCLUSIONS

Fluid inclusions in minerals are undoubtedly spotted a long time ago. Boyle (1672) mentioned several rarities in transparent crystals, which were large inclusions containing a liquid, visible with the bare eye. Motion of the liquid was easily observed when the crystal was made to change its posture. Boyle used this information to enforce his hypothesis that many gems either were once fluid bodies or in part made up of such substance as were once fluid. The role of water within the geology was emphasized by Werner (1749-1817) in his Neptunism theory, which suggests all crust materials to be initially in suspension or solution. Fluid inclusions were used as important arguments for this theory. At the end of the eighteenth century several scientists were able to distinguish different fluids in the cavities (e.g. Dolomieu, 1792, who describes petroleum). By this time, fluid inclusions were used against the Neptunism theory, mainly on the composition of fluid inclusion. A systematic analysis of fluid inclusion started a few decades later (Breislak, 1818; Deuchar, 1822; Davy, 1822; Brewster, 1823; Nicol, 1828).

The appearance of fluid inclusions in minerals raises many questions. What is in there, and what is the geological significance of their content? How and when are they formed? Can they change in shape, density and composition?

Many manuscripts have been published answering the first question, which were summarized by Smith (1953) and Roedder (1984). In the scope of this study, I wish to concentrate upon occurrence of nitrogen in fluid inclusions, which has been detected from the beginning of fluid inclusion analysis (Davy, 1822). Sorby (1858) was the first to describe a relation

between metamorphism and filling of fluid inclusions in quartz in schist samples approaching granite stocks in Cornwall. Strictly, the fluid in inclusions gives information about the fluid surrounding the crystal during entrapment. Data obtained from fluid inclusions and their applications were well summarized by Roedder (1984).

Misfits between growing sheets on a crystal face occurs, as a result of multiple nucleation on this face, which gives possibilities of fluid-entrapment. Sorby (1858) was the first to synthesize fluid inclusions in soluble salt, trapping a fluid during crystal growth on the faces. From the beginning of microscopic study of mineral inclusions (Nicol, 1828; Sorby, 1858; Van Hise, 1890) it has been recognized that cracks in crystals may heal by later crystallization, trapping some of the fluid which entered the opening. Lämmlein (1929) was the first to heal cracks artificially in saltpetre, halite and alum, producing planes of secondary type inclusions. The cracks were formed by cleaving the crystal partially with a razor blade. Lemmlein (1956) postulated that the mechanism of crack healing is based on capillary condensation and the tendency of the phase boundary to assume the form possessing the least free surface energy.

The subject was separated in two areas of research, involving the shape, density and composition of secondary fluid inclusions in healed cracks, and a study of the rate of crack-healing. Shelton & Orville (1980) cracked inclusion-free natural quartz by compression (Martin, 1972) and synthesized fluid inclusions at 873 K and 200 MPa water pressure. They concluded that the variation in fluid inclusion size and distribution can be directly related to former fracture-surface features. The density of supercritical water under experimental conditions was found to be in agreement with that inferred from homogenization temperature (the temperature at which liquid and vapor in an inclusion homogenize to one phase). Sterner & Bodnar (1984) evolved the applications of synthetic fluid inclusions to experimental geochemistry. They used a method described by Boyle (1672) to crack inclusion-free natural quartz, through heating the crystal and rapidly quenching it in cold water. Smith & Evans (1984) and Hickman & Evans (1987) concluded that the extent of healing was a function of time, temperature, the initial concentration of silica in the pore fluid, and

the initial crack dimension. Estimation of the rate of crack healing suggests that microcracks in quartz will have geologically short lifetimes at temperatures above 473 K (Smith & Evans, 1984).

Alterations of the shape, density and composition of fluid inclusions may occur through several mechanisms.

Lämmlein (1929) noticed the tendency of irregular shaped inclusions to recrystallize to negative crystals at constant room temperature, minimizing the amount of surface energy. Lemmlein (1956) performed the first experiments of crack healing in sodium nitrate under changing conditions (falling temperature), mimicking natural processes. He observed necking down of inclusions below the homogenization temperature, resulting in fluid inclusions with different densities. Within metallurgy and electrical material science, Nicols & Mullins (1965) explained sintering of spheres by capillary induced surface diffusion, which was also thought to cause necking down of fluid inclusions. They summarized possible diffusion routes for necking-down which were through the inclusion fluid, through the surface (interface fluid-host mineral), and through the host mineral. Gratier & Jenatton (1984) measured and modelled the rate of change of inclusion shape, which occurred in synthetic quartz and synthetic calcite. In general, the internal recrystallization through solution-deposition processes causes most fluid inclusions to have different shapes from those originally trapped, although the densities remain unchanged.

Brewster (1835, 1848 and 1861) concluded that the pressure exerted by the fluid inclusions strained the crystal when it was in a soft state at elevated temperature. Crystals which were optically isotropic (like diamond) seemed to be anisotropic around fluid inclusions. The high internal pressure caused stretching (plastic deformation) of the fluid inclusion, resulting in a larger inclusion volume. More than a century later, Larson et al. (1973), Bodnar & Bethke (1984) and Pécher (1984) noticed the change in homogenization temperature in fluorite, sphalerite and synthetic quartz, due to stretching of inclusions. The deformation mechanism associated with stretching was poorly understood and thought to be plastic flow related to movement of dislocations. Stretching of an internally overpressurized spherical fluid inclusion in olivine was investigated by Wannamakers & Evans

(1989). The dislocation microstructure around the inclusion suggested that creep mechanisms operate.

Explosive leakage of fluid inclusions (decrepitation) was described by Brewster (1823), who by accident was attracted to this phenomena during decoloring experiments of topaz. At that time, decrepitation was used to confirm the presence of water and salt in fluid inclusions. Partial decrepitation, resulting in irreversible inclusion volume increase, was described by Lemlein (1956). Pressure developed during heating in fluid inclusions caused the formation of fractures around the inclusion. A portion of the fluid was squeezed in the fractures, which began to heal and form extremely small inclusions. An aureole of minute inclusions occurred around the original inclusion with a lower density. The decrepitation clusters were also recognized in natural specimens by Swanenberg (1980) and experimentally by Gratier & Jenatton (1984).

Finally, fluid inclusions may change in density and composition by diffusion of material through the host mineral. The permeability of crystals to water was postulated and experimentally investigated by Deuchar (1822). Water passed through glass under high pressure, from observations after sinking stoppered bottles deep into the sea. Sorby (1858) stated that at very great pressure, water will not pass through solid crystal, except by cracking it. Zirkel (1873) and Ward (1875) noted that the ratio of gas to liquid may vary greatly, even in neighbouring inclusions, which was ascribed to different degrees of leakage of fluid inclusions. Kennedy (1950) mentioned experiments of J. Grunig, who noticed diffusion of liquid into fluid inclusions in fluorite at 423 K, which were exposed to confining pressures higher than the internal fluid pressure. Stephenson (1952) concluded that fluid inclusions in sphalerite and calcite leak after the liquid phase fills the space available. Diffusion of water and water-related molecules through quartz became a major subject of research after the discovery of hydrolytic weakening of rocks (Griggs, 1967; Hobbs, 1968). The role of fluid inclusions during deformation experiments were investigated by Kerrich (1976), Wilkins & Barkas (1979) and McLaren et al. (1983). Kerrich (1976) noticed a relation between mineral texture and homogenization temperature. In vein quartz, undeformed quartz grains are more abundant and have fluid inclusions with

higher density than deformed grains. Wilkins & Barkas (1979) observed that the majority of small inclusions in quartz were associated with deformation band boundaries that have been introduced during ductile deformation. Fluid inclusions were suggested to resorb during recovery, introducing structural water in the quartz, which should promote dislocation propagation. McLaren et al. (1983) modelled the formation of bubbles in synthetic quartz using transmission electron microscopy (TEM). They proposed hydrogen to be incorporated by means of $(4H)_{Si}$ defects, which diffuse to form clusters, and they proposed bubbles to increase in size through pipe-diffusion of Si and O away from the bubble into linked dislocation loop. A similar phenomenon was already observed by Wolff (1845) after annealing experiments with natural quartz, in order to measure weight loss through decrepitation. Being unaware of possible growth of small bubbles in natural quartz, he observed a rose quartz to become milky-white after annealing. Ferguson (1914) noted that the milky white color of quartz is due to a great abundance of very small fluid inclusions. Gerretsen et al. (1989) suggest that all water in quartz is mainly in the form of molecular H_2O in inclusions. Such evidence associating water with dislocations structures leads to the conclusion that, in quartz, crystal plasticity enhances fluid mobility and points to fluid inclusions as an important source of chemically active fluids necessary for fluid assisted deformation (Spiers et al., 1990), and metamorphic processes (Carter et al., 1990).

1.2 AIMS AND INTENTIONS

The aim of this study is to investigate experimentally and theoretically the re-equilibration behaviour of synthetic fluid inclusions in natural quartz within the geological relevant C-O-H-N gas system, and to relate observed and reasoned phenomena with natural fluid inclusions in metamorphic rock.

Leakage of fluid inclusion in natural quartz and its mechanisms, which are related to deformation mechanisms, is experimentally studied in

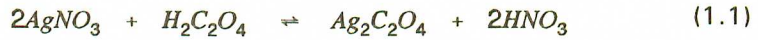
CHAPTER 2 and **CHAPTER 3**. Synthetic $\text{CO}_2\text{-H}_2\text{O}$ fluid inclusions in natural quartz are re-equilibrated under conditions different from the synthesis conditions. The inclusions are exposed to both internal underpressure (**CHAPTER 2** and **CHAPTER 3**) and internal overpressure (**CHAPTER 3**). **CHAPTER 4** includes TEM observations of quartz adjacent to both synthetic and natural fluid inclusions, in order to study possible routes for leakage. Theoretically, fluid calibrations in the C-O-H-N gas system are performed in **CHAPTER 5** and **CHAPTER 6**. **CHAPTER 5** includes the thermodynamical background of the calculations, which are executed with a computer program, written in Pascal. **CHAPTER 6** presents the application of these calculations to metamorphic rock in Rogaland (SW Norway). Finally, **CHAPTER 7** contains the main conclusions of this work.

1.3 EXPERIMENTAL METHOD

Several experiments are performed to synthesize fluid inclusions in natural quartz and to re-equilibrate these inclusions. The principles of the experimental method are described in this chapter. **CHAPTER 2** and **CHAPTER 3** describe in more detail the method for each individual experiment.

Gemstone quality natural quartz (Brazilian quartz) is used as host-mineral for synthetic fluid inclusions. The quartz is free of any primary or secondary inclusions. Orientated cores with 4 mm diameter are drilled out of single crystals. Micro-cracks are created in the cores (Fig.1.1) by sequentially heating the core to 673 K and quenching in cold distilled water. The cores are dried in a vacuum line at 383 K to remove all residual water in the cracks.

The source of the arbitrarily chosen fluid, which is meant to be included, are pure water and silver oxalate. The silver oxalate is made by a precipitation reaction (eq.1.1).



The silver oxalate is rinsed with distilled H₂O to remove the nitric acid, dried at 383 K in a vacuum line, and stored in a dry CO₂-environment. During experimentation, the silver oxalate decomposes at 413 K (eq.1.2), resulting in a pure CO₂ fluid and silver metal.

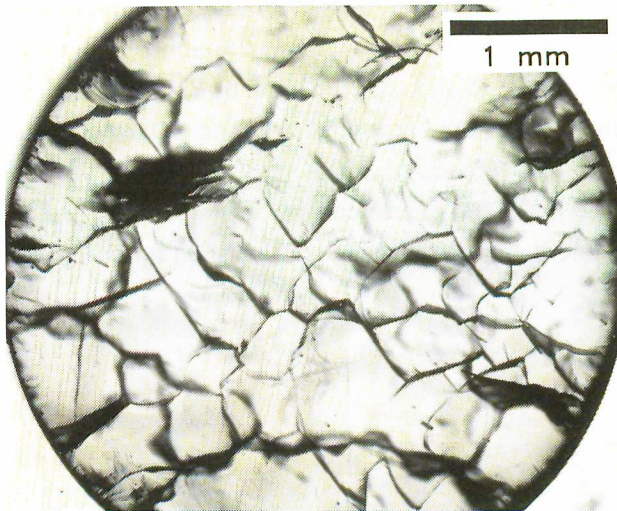
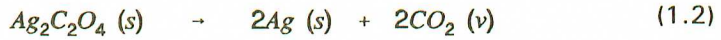


Figure 1.1

Quartz core (4 mm diameter) with various microcracks (dark parts).

A quartz core and a chosen amount of water and silver oxalate are put in a gold tube (5.8 mm and 9 mm diameter), which has been sealed at one end by arc welding. Subsequently, the gold tube is partly immersed in cold water, to prevent explosion of the silver oxalate and to prevent evaporation of the water during welding of the open side of the tube. After welding, the gold capsule is weighed and is then ready for experimentation at high temperature and pressure.

The fluid inclusion synthesis is performed in an externally heated $7\frac{1}{2}$ mm and $12\frac{1}{2}$ mm diameter Tuttle-type pressure vessels (Edgar, 1973), with an argon pressure medium (Fig.1.2). The runs are first brought to the desired pressure at room temperature, the temperature is then increased, while the pressure is adjusted in several steps, until experimental conditions are reached. After the experiments the vessels are quenched to room temperature within 30 minutes with a compressed air flow, before the pressure is released.

After the experiment, the gold capsule is weighed again to check weightloss and immersed in hot water (± 363 K) to check the welded edges for leaks, and to recognize possible diffusion through the gold. Capsules containing a mixture of H_2O and CO_2 are cooled to 255 K, punctured, and weighed again to measure the amount of released CO_2 gas. Subsequently, the capsule is dried in a furnace at 383 K, and weighed again to measure the amount of released H_2O . The quartz core with the partially healed cracks (Fig.1.3) are cut into 1 mm thick slices and polished on both sides.

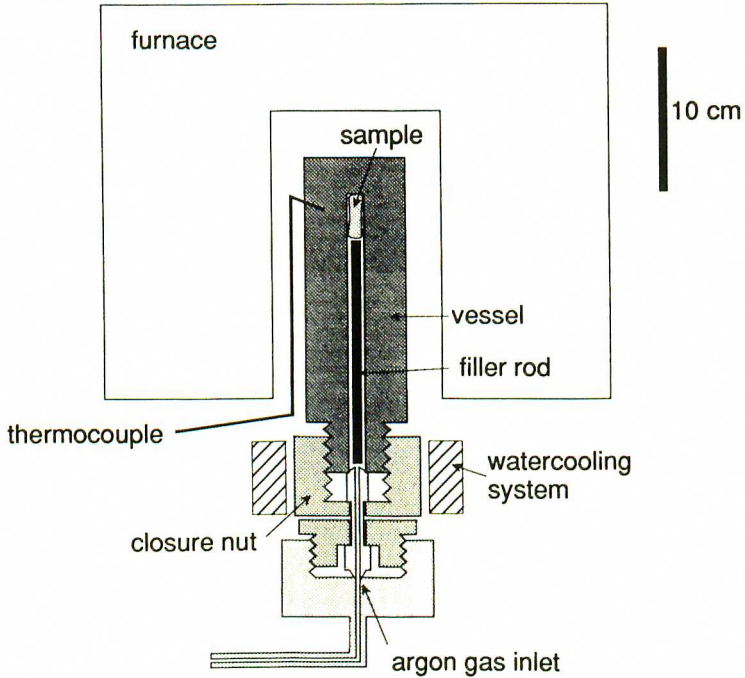


Figure 1.2

Tuttle-type pressure vessel. The hot spot of the furnace, which is shoved over the vessel in vertical position, is at the place of the sample-capsule, which is hold in position by a filler rod. The closure nut is cooled with cold water during experimentation (watercooling system). The temperature is measured with a thermocouple at the outside of the vessel.

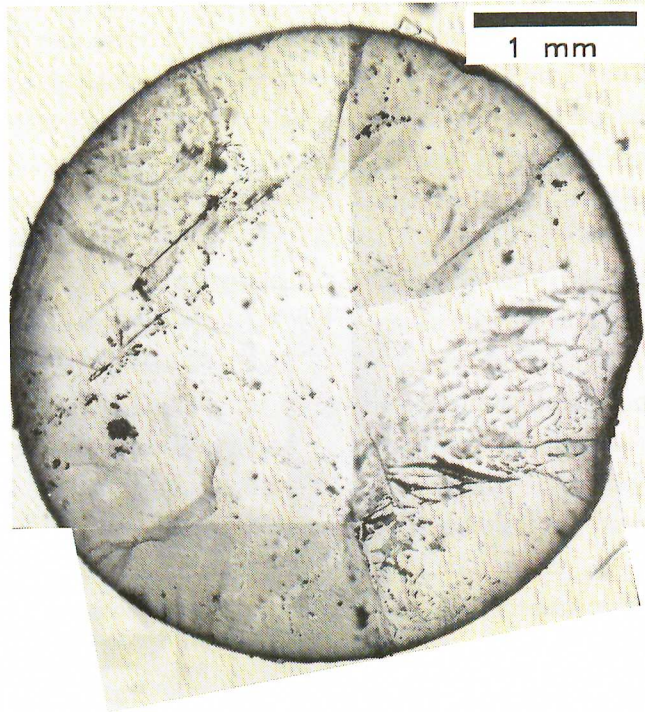


Figure 1.3
Quartz core after experimentation. Healed microcracks are marked with numerous synthetic fi.s.

1.4 ANALYTICAL METHODS

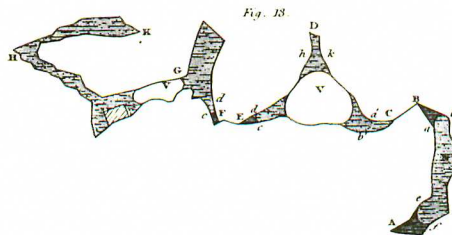
A Fluid Inc. adapted U.S.G.S. gas flow heating-freezing stage with a Doric 410A Trendicator is used to measure melting and homogenization temperatures of the phases in fluid inclusions. The stage is calibrated with pure H₂O fluid inclusions (melting temperature H₂O at 273 K), mixed CO₂-H₂O fluid inclusions (melting temperature CO₂ at 216.6 K) and NaNO₃ crystals (melting temperature at 580 K).

The fluid inclusions are photographed with a **Leica CL camera** attached to a **Leitz SM LUX Pol. Microscope** to characterize their morphology and volume percentages of individual phases at room temperature. The best volume estimates are achieved in flat fluid inclusions.

Crystal defect structures in quartz with healed cracks are examined with **Transmission Electron Microscopy (TEM)**. The specimen are prepared by ion bombardment from a 15 μm thin sections and examined in a **JEOL-200** electron microscope operating at 200 kV.

Surface morphologies of cracks, newly grown quartz in cracks, and fluid inclusion walls are photographed with **Scanning Electron Microscopy (SEM)**. The specimens are subsequently coated with carbon and gold for examination with a **CAMPSCAN** electron microscope.

A **Microdil-28 Raman microspectrometer (Dilor)** with a multichannel detector (Burke & Lustenhouwer, 1987) available at the Free University of Amsterdam, is used to check for presence of gas species other than CO_2 and H_2O .



from Brewster (1823)