

# Rapid subsidence and upthrusting in the Northern Apennines, deduced by fluid inclusion studies in quartz crystals from Porretta Terme

Autor(en): **Mullis, Josef**

Objektyp: **Article**

Zeitschrift: **Schweizerische mineralogische und petrographische Mitteilungen  
= Bulletin suisse de minéralogie et pétrographie**

Band (Jahr): **68 (1988)**

Heft 2

PDF erstellt am: **21.07.2024**

Persistenter Link: <https://doi.org/10.5169/seals-52057>

## **Nutzungsbedingungen**

Die ETH-Bibliothek ist Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Inhalten der Zeitschriften. Die Rechte liegen in der Regel bei den Herausgebern.

Die auf der Plattform e-periodica veröffentlichten Dokumente stehen für nicht-kommerzielle Zwecke in Lehre und Forschung sowie für die private Nutzung frei zur Verfügung. Einzelne Dateien oder Ausdrucke aus diesem Angebot können zusammen mit diesen Nutzungsbedingungen und den korrekten Herkunftsbezeichnungen weitergegeben werden.

Das Veröffentlichen von Bildern in Print- und Online-Publikationen ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Die systematische Speicherung von Teilen des elektronischen Angebots auf anderen Servern bedarf ebenfalls des schriftlichen Einverständnisses der Rechteinhaber.

## **Haftungsausschluss**

Alle Angaben erfolgen ohne Gewähr für Vollständigkeit oder Richtigkeit. Es wird keine Haftung übernommen für Schäden durch die Verwendung von Informationen aus diesem Online-Angebot oder durch das Fehlen von Informationen. Dies gilt auch für Inhalte Dritter, die über dieses Angebot zugänglich sind.

# Rapid subsidence and upthrusting in the Northern Apennines, deduced by fluid inclusion studies in quartz crystals from Porretta Terme

by Josef Mullis<sup>1</sup>

## Abstract

Early fluid inclusions in fissure quartz from Porretta Terme in the Northern Apennines contain methane-bearing water-rich and methane-rich fluids trapped at approximately 220 to 230°C and 2.0 to 2.1 kbar. These values refer to minimum to approximate rock burial of 8 to 9 km at low grade anchimetamorphic conditions during the Apenninic orogeny.

Sedimentation, subsidence to a depth of at least 8 to 9 km, maximum heating, and upthrusting were short, lasting approximately 10 Ma. Such a scenario can be explained by rapid subduction-like subsidence beneath the north-east advancing Liguride nappes and rapid upthrusting as a consequence of compressional tectonics.

High fluid pressures approximated probably lithostatic conditions favouring nappe transport during compressional tectonics. Repeated fluid pressure drops during crystal growth of 0.5 to 1.5 kbar led to methane-water unmixing and rapid precipitation of skeletal quartz from a methane-rich emulsion-like fluid.

Fluid inclusion data do not correspond with preliminary results of illite 'crystallinity' as they only indicate diagenetic conditions. If fluid temperature is equal to rock temperature, fluids probably display, in presence of short-lived heating, greater sensitivity to metamorphism than minerals.

*Keywords:* Fissure quartz, fluid inclusions, rock burial, anchimetamorphism, Apenninic orogeny, Porretta.

## 1. Introduction

Fluid inclusions trapped in quartz crystals of syntectonic fissures represent small amounts of paleofluids present in rocks after compaction and during a specific part of the deformation and metamorphic history. Composition and volume of different well defined inclusion populations record the physico-chemical evolution of fluids during crystal growth. When methane-bearing water-rich and methane-rich fluid inclusions are present, approximate trapping temperatures and pressures can be inferred (MULLIS, 1979).

Fluid inclusions were studied by means of microthermometry, gas chromatography and Raman spectroscopy on a well known occurrence of window shaped fissure quartz from

Porretta Terme in the Northern Apennines (figure 1). Fluid inclusion studies were combined with coal rank (REUTTER et al., 1983) and illite 'crystallinity' data, contributing new insight into the thermal and pressure evolution of the local to regional tectonic history.

## 2. Geological setting

The host rock of the studied quartz crystals is the Suviana sandstone (figure 1) of Middle Miocene age (Serravalian according to the geological map of Italy, foglio 98, 1970; GUENTHER and REUTTER, 1985). It comprises well-bedded graywackes alternating with fine layers of marly-schists.

The Suviana formation crops out north of the Monte Modino and Monte Cervarola gray-

<sup>1</sup> Mineralogisch-Petrographisches Institut der Universität Basel, Bernoullistr. 30, 4056 Basel, Switzerland.

wacke units and is interpreted either as a marginal facies of the Cervarola-sandstones (HEYMANN, 1968; RENTZ, 1971) or as part of the marnoso arenacea of the Umbro-Marches (GHELARDONI et al., 1962). The Modino-Cervarola graywackes occupy, together with their intercalated olistostromes and the Suviana sandstone formation, an intermediate position between the allochthonous Tuscan unit in the south-west and the Umbra-Marches zone in the north-east and is overlain by the Liguride nappes. According to REUTTER and GROSCURTH (1978), the Modino-Cervarola unit as well as the Suviana sandstone were synkinematically deposited at the front of the advancing Liguride nappes and pushed towards the north-east where, finally, they were over-

thrust and buried beneath them. After compressional tectonics, rocks had returned more or less to the present level at the end of Miocene or beginning Pliocene (REUTTER and GROSCURTH, 1978; REUTTER et al., 1983).

### 3. Morphology of the quartz crystals and their fluid inclusions

Quartz is the main fissure mineral precipitated in shear and extension fissure veins of the Suviana sandstone from Porretta Terme. Most of these quartz crystals display a strongly distorted window shaped habit, first described by GAMBARI (1868) and BOMBICCI (1898). Quartz crystals collected from these fissures can be

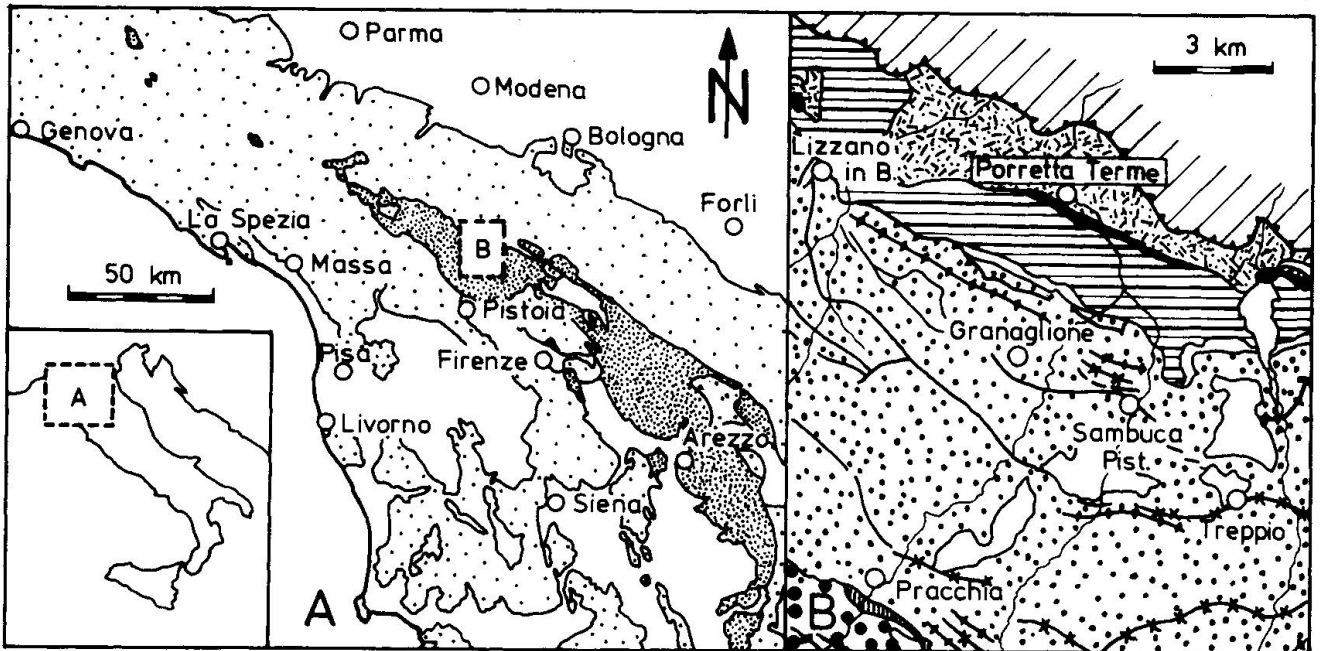
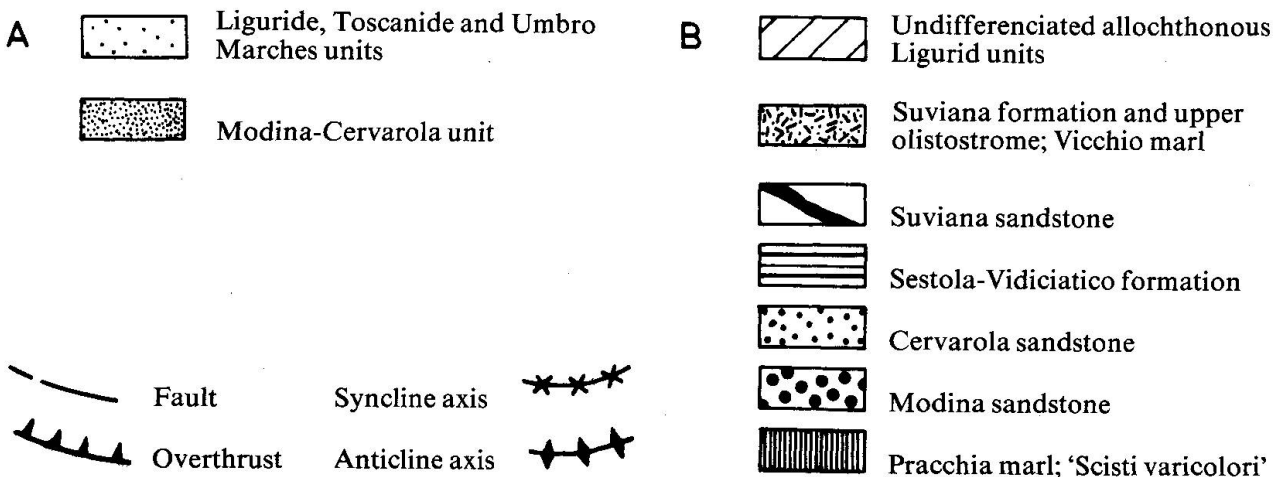
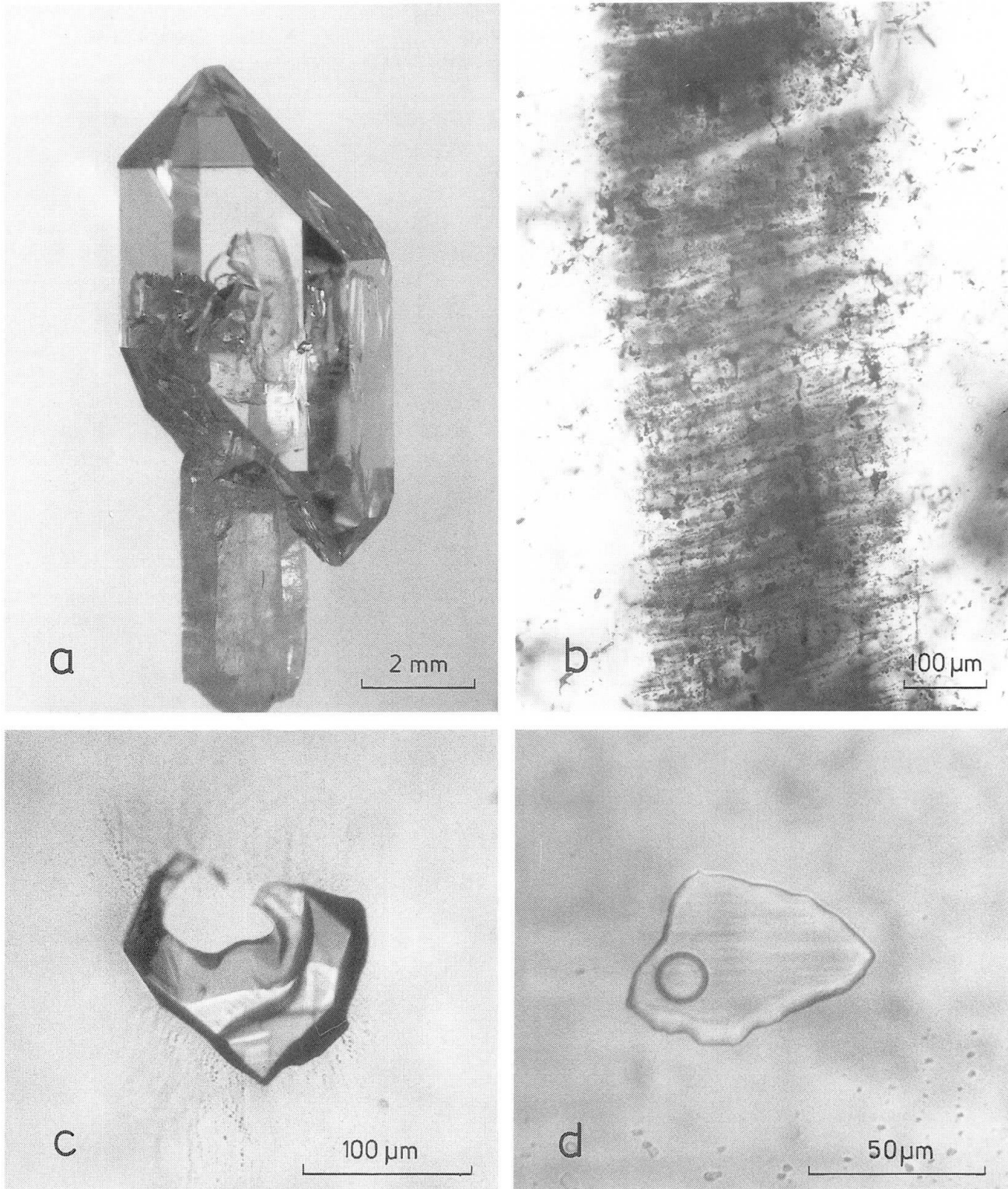


Fig. 1 Geologic situation of Porretta Terme. Mappe sections slightly modified after GUENTHER and REUTTER, (1985).





*Fig. 2* Quartz crystals and fluid inclusions from Porretta Terme.

- a) Prismatic quartz overgrown by sceptre quartz. Prismatic quartz contains methane-bearing water-rich inclusions. Sceptre quartz is characterized by methane-rich inclusions.
- b) Syncinematically crystallized fibre quartz, containing methane-bearing water-rich inclusions. Fluids were trapped during crack and seal of the growing quartz (RAMSAY, 1980).
- c) High density methane-rich inclusion of fluid population 2a, slightly stretched during pressure drops.
- d) Methane-bearing water-rich inclusion of fluid population 2b (the bubble consists of more or less pure methane).

subdivided into prismatic, fibre and skeletal habits (figure 2a and b, figure 3a-d). The juvenile form of the latter resembles a sceptre quartz (figure 2a) and the adult form displays a window shaped habit. These quartz habits are characteristic of low grade anchimetamorphic PT conditions when methane- and water-bearing fluids are present, as described in STALDER and TOURAY (1970) and MULLIS (1979, 1987).

Several quartz generations are distinguished by morphological criteria (figure 3e), particularly under X-ray irradiation. Synkinematically grown fibre quartz (generation 1a) is overgrown by prismatic quartz (generation 1b). Further quartz precipitation is documented by at least four subsequent generations. Each generation begins with a skeletal growth stage (a-generations) and ends with prismatic overgrowth (b-generations). In a given quartz sample, one or more of these generations may be poorly crystallized or may even be absent.

Different fluid inclusion populations have been distinguished during the quartz growth history. In fibre and skeletal quartz, primary and pseudosecondary fluid inclusions are characteristic; in late prismatic overgrowth, pseu-

dosecondary and secondary fluid inclusions are widespread. Primary inclusions of the skeletal quartz generation 2a often are surrounded by tension features (figure 2c), indicating stretching of high density fluid inclusions during pressure drops.

#### 4. Methods, results and interpretation of results

##### 4.1. FLUID INCLUSIONS

###### 4.1.1. Methodology

Fluid inclusions were studied mainly by means of microthermometry and verified by Raman spectroscopy and gas chromatography. Microthermometric measurements were performed on the Chaix-Meca freezing-heating stage, designed to work in the -180 to +600°C by POTY et al. (1976). The precision of the measurements is on the order of  $\pm 0.1^\circ\text{C}$  in the -60 to +40°C range and  $\pm 1^\circ\text{C}$  outside this range.

During slow heating, the melting of solid  $\text{CO}_2$  ( $T_{m\text{CO}_2}$ ) was observed between -116 and -103°C, indicating the presence of small

## PORRETTA TERME

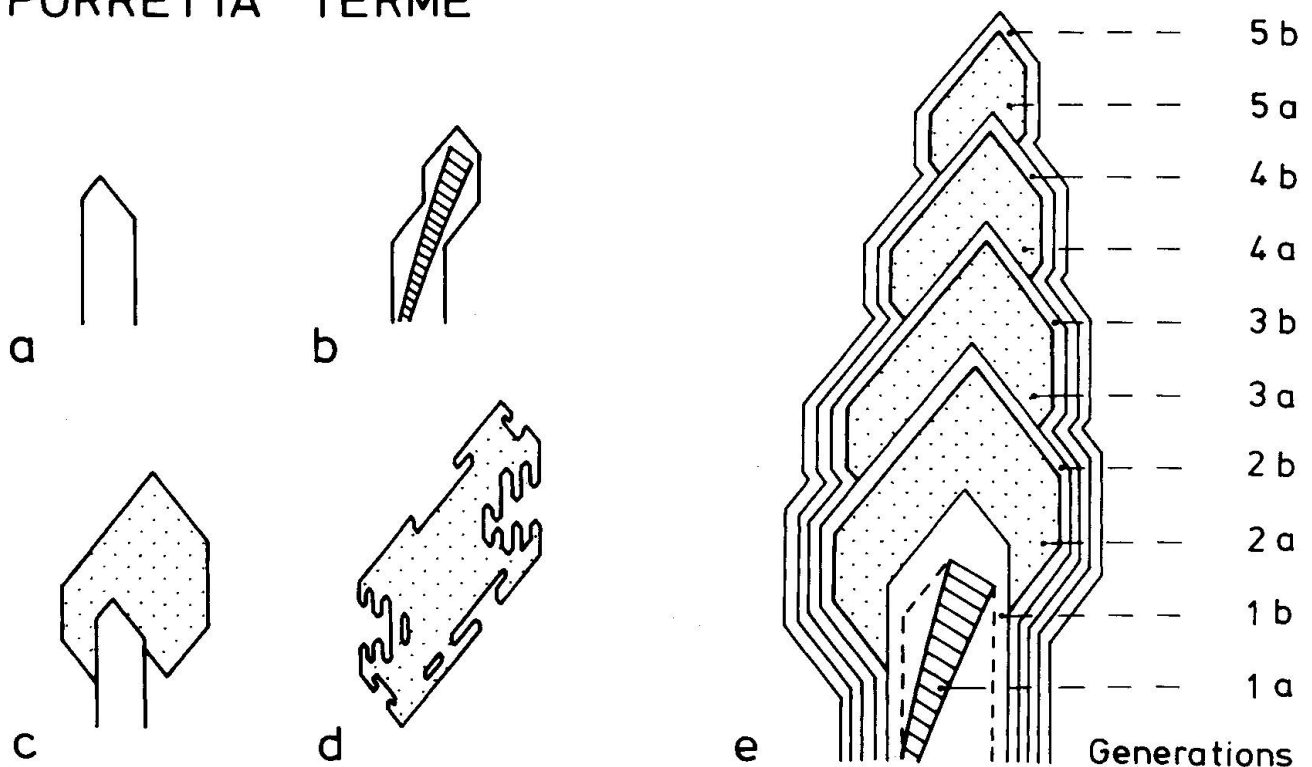


Fig. 3 Quartz morphology from Porretta Terme.

a) Prismatic quartz; b) fibre quartz; c) sceptre quartz; d) window shaped skeletal quartz; e) succession of quartz generations - a model.

amounts of CO<sub>2</sub> in the volatile phase. As the volume of solid CO<sub>2</sub> never exceeds 1% with respect to the inclusion volume, the amount of CO<sub>2</sub> remains  $\leq 3$  mole % of the trapped volatiles.

Between -119 and -80°C liquid-vapour equilibria of the methane phase (Th<sub>CH<sub>4</sub></sub>) have been measured. If methane is the only component, then the density can be deduced from the homogenization temperature (ZAGORUCHENKO and ZHURAVLEV, 1970; ANGUS et al., 1976). For a given molar volume, the presence of CO<sub>2</sub> and H<sub>2</sub>S (DONELLY and KATZ, 1954) and higher hydrocarbons (HHC) increase Th<sub>CH<sub>4</sub></sub>, whereas N<sub>2</sub> lowers it (SWANENBERG, 1980).

Eutectic melting of the water-rich inclusions lies between -29 and -21°C, and therefore, ice melting is referred to the NaCl-H<sub>2</sub>O system (POTTER et al., 1978) with the salt content expressed in terms of NaCl equivalents (ROEDDER, 1963). Salinity is slightly overestimated when melting of ice occurs in presence of the methane-clathrate (MULLIS, 1976a).

Dissociation of the clathrate was measured between 15 and 28°C, confirming the presence of methane in the inclusions at different internal pressures (DEATON and FROST, 1948; MULLIS, 1979).

Bulk homogenization temperatures (Th<sub>I</sub>) were only measurable in methane-bearing water-rich inclusions, as the aqueous phase in methane-rich inclusions was practically invisible. Th<sub>I</sub> are equivalent to approximative trapping temperatures (see section 4.1.3).

#### 4.1.2 Results (table 1)

Fluid inclusions can be divided into two groups: Methane-rich inclusions (figure 2c) typical in skeletal quartz and methane-bearing water-rich inclusions (figure 2d) widespread in prismatic quartz.

Methane decreases in *methane-rich fluid inclusion populations* from  $\geq 95.8$  mole % in population 2a to  $\geq 87.1$  mole % in population 5a. Raman spectra<sup>1</sup> at room temperature show traces of CO<sub>2</sub> (XCO<sub>2</sub>  $\leq 0.03$ ). The presence of CO<sub>2</sub> was confirmed by the spectrum of solid

CO<sub>2</sub> at -150°C (DUBESSY et al., 1984). Neither N<sub>2</sub> nor H<sub>2</sub>S could be detected by gas chromatography<sup>2</sup> although small amounts of higher hydrocarbons (HHC) from C1 to C5 were present ( $\leq 0.7$  mole %). Even though methane density is slightly underestimated in presence of small amounts of CO<sub>2</sub> and HHC, methane density of population 2a is very high and decreases during further crystal growth. The water content is small in fluid population 2a (2.6 mole %; traces detected by gas chromatography) and increases up to 10 mole % in population 5a.

*Water-rich fluid inclusion populations* contain  $\leq 1.7$  mole % CH<sub>4</sub>. Liquid-vapour equilibria of CH<sub>4</sub> could not be observed in all inclusion populations because of the small size of the methane bubble within the fluid inclusions. Therefore, the amount of methane could not be determined in populations 1a and 1b. The salinity decreases during crystal growth from 0.8 mole % equivalent NaCl in population 1a to 0.4 mole % in population 5b, but in population 3b it rises to 2.4 mole %. The mean values of Th<sub>I</sub> decrease from the first to the fifth inclusion population from 227 to 220°C.

#### 4.1.3 Interpretation of fluid inclusion data in terms of approximate trapping temperature and pressure (figure 4)

##### *Approximate trapping temperature*

*Estimation of the approximate trapping temperature can be derived from Th<sub>I</sub> by the following observation: Methane-bearing water-rich inclusion populations are immediately preceded or followed by methane-rich inclusion populations. Therefore water-rich inclusions can be inferred to be virtually saturated with methane during trapping. As water-methane homogenization occurs at saturation conditions, Th<sub>I</sub>, thus, is interpreted as approximate trapping temperature (MULLIS, 1976a, 1979, 1987). Furthermore, heterogenous filling of some inclusions along the boundary from skeletal to prismatic quartz confirms fluid trapping in the two phase region. As Th<sub>I</sub> is virtually not visible in methane-rich inclusions, approximate trap-*

<sup>1</sup> Analyses by Raman spectroscopy were made at the Centre de Recherches sur la Géologie de l'Uranium (CREGU), Nancy. For details of the technique see DHAMELINCORT et al. (1979).

<sup>2</sup> Analyses by gas chromatography were made at the Institut de Géologie de l'Université de Nancy. For more details of the methodology see CUNNEY et al. (1976).

Tab. 1 Microthermometric results

1 FPop	1a	1b	2a	2b	3a	3b	4a	4b	5a	5b
2 n <sub>I</sub>	50	17	27	15	13	30	10	13	68	13
3 V% <sub>Vol</sub>	5	5	99	5	99	5	98.5	5	98	5
4 Sol	?	A				A		A		
5 Th <sub>I</sub>	a	227	223		223		222		220	220
	b	221	215		230		216		217	215
	c	232	230		227		228		222	226
6 Td <sub>Cl</sub>	a	15	15	?	16	28	16	23	17	20
7 Tm <sub>Ice</sub>	a	-1.5	-1.5		-1.3		-4.7		-1.2	-0.7
	b	-1.8	-1.9		-1.5		-4.9		-1.3	-0.8
	c	-1.2	-1.0		-1.3		-4.6		-1.1	-0.6
8 Th <sub>CH<sub>4</sub></sub>	a	?	?	-114	-99	-99	-100	-91	-88	-81
	b			-119		-101		-92		-84
	c			-111		-98		-90		-80
9 Tm <sub>CO<sub>2</sub></sub>	a			-115		-111		-111		-108
	b			-116				-113		-115
	c			-114				-111		-103
10 ρ <sub>CH<sub>4</sub></sub>			0.338	0.297	0.297	0.300	0.266	0.251	0.162	
11 ρ <sub>CO<sub>2</sub>sol</sub>			1.56		1.56		1.56		1.56	
12 ρ <sub>H<sub>2</sub>O</sub>	1.015	1.015		1.013		1.049		1.012		1.006
13 x (CH <sub>4</sub> )	?	?	≥95.8	1.7	≥95.3	1.7	≥93.2	1.5	≥87.1	?
14 x (CO <sub>2</sub> )	?	?	≤1.6		≤1.8		≤2.0	?	≤3.1	?
15 x (H <sub>2</sub> O)	99.2	99.2	2.6	97.6	2.9	95.9	4.8	97.9	9.8	99.9
16 x (NaCl)	0.8	0.8	~0	0.7	~0	2.4	~0	0.6	~0	0.4
17 P <sub>trap</sub>	2.02	2.01	2.10	1.98	1.55	1.92	1.20	1.90	0.55	1.87

- |                                 |  |  |
|---------------------------------|--|--|
| 1. FPop                         | Fluid inclusion population.  | (°C). Homogenization to the liquid phase.  |
| 2. n <sub>I</sub>               | Number of studied fluid inclusions.  |  |
| 3. V% <sub>Vol</sub>            | Volume % of the volatile part at room temperature.   |  |
| 4. Sol                          | Solid phases in fluid inclusions.<br>A: anisotropic solid.   |  |
| 5. Th <sub>I</sub>              | Homogenization temperature of fluid inclusion (°C). Homogenization to the liquid phase.<br>(a: mean value; b and c: extreme values). |  |
| 6. Td <sub>Cl</sub>             | Dissociation temperature of CH <sub>4</sub> -clathrate (°C).   |  |
| 7. Tm <sub>Ice</sub>            | Melting temperature of ice (°C).   |  |
| 8. Th <sub>CH<sub>4</sub></sub> | Homogenization temperature of CH <sub>4</sub>  |  |
|                                 |  | 9. Tm <sub>CO<sub>2</sub></sub> Melting temperature of CO <sub>2</sub> (°C).   |
|                                 |  | 10. ρ <sub>CH<sub>4</sub></sub> Density of methane (g·cm <sup>-3</sup> ), derived from Th <sub>CH<sub>4</sub></sub> after ANGUS et al. (1976). |
|                                 |  | 11. ρ <sub>CO<sub>2</sub>sol</sub> Density of solid CO <sub>2</sub> (g·cm <sup>-3</sup> ), derived from Tm <sub>CO<sub>2</sub></sub> .         |
|                                 |  | 12. ρ <sub>H<sub>2</sub>O</sub> Density of aqueous chloride solution, derived from fluid salinity after POTTER and BROWN (1977).               |
|                                 |  | 13.-16. Approximate fluid composition in mole % of CH <sub>4</sub> , CO <sub>2</sub> , H <sub>2</sub> O and NaCl (in NaCl equivalents).        |
|                                 |  | 17. P <sub>trap</sub> Approximate trapping temperature of fluid inclusion population.  |

ping temperature of the *methane-rich inclusion populations* is thus derived by the interpolation of  $T_H$  of the preceding and following water-rich fluid inclusion populations.

Several further water-rich inclusion populations were detected by microthermometry, but no relationship with methane-rich inclusion populations could be found. Thus, such fluid populations are not expected to have been saturated with methane. They can not be used for PT estimation and are therefore not included in table 1.

#### Approximate trapping pressure

The approximate trapping pressure of *methane-rich inclusion* populations is evaluated along the methane-rich isochores at the value of the interpolated homogenization temperatures of preceding and succeeding water-rich inclusion populations. Taking into account all detected fluid species, isochores are constructed using the equation of state from the  $H_2O-CH_4-CO_2$  system after JACOBS and KERRICK (1981). The presence of very small amounts of HHC and dissolved salts in methane-rich fluid inclusions are ignored. The mean value of the earliest methane-rich fluid population (2a) is 2.1 kbar. From there, pressure in methane-rich inclusion populations decreases during further crystal growth down to 0.55 kbar in population 5a. Considering fluid inclusions filled only by methane, pressure values tend to be slightly overestimated (ZAGO-

RUCHENKO and ZHURAVLEV, 1970) or slightly undersaturated (ANGUS et al., 1976), but do not exceed 0.1 to 0.2 kbar.

For *water-rich inclusions*, trapping pressure has been estimated by addition of partial pressures of aqueous chloride solution (HILBERT, 1979) and methane (ANGUS et al., 1976), because PVT data of the  $H_2O-CH_4-NaCl$  system are not yet available in the PT range of interest. Fluid pressures range at the approximate trapping temperature of the water-rich inclusion populations 1a to 5b between 1.9 and 2.0 kbar. As PVT data of the  $H_2O-NaCl$  system from POTTER and BROWN (1977) are only representative for pressures below 1.2 kbar (FRANTZ et al., 1988), they are not used in this paper.

#### 4.2. ILLITE 'CRYSTALLINITY'

The width at half height of the first illite basal reflection at 10 Å on X-ray diffractograms has been measured on four samples as representing the illite 'crystallinity' (KÜBLER, 1967a) of the Suviana series from Porretta Terme. The values of the clay fraction  $\leq 2 \mu m$  range in air dried samples from 0.82 to 0.65  $\Delta^\circ 2\theta$  and after glycol treatment from 0.61 to 0.47  $\Delta^\circ 2\theta$  (table 2). These values are indicative for diagenetic conditions.

#### 4.4. VITRINITE REFLECTANCE

Vitrinite reflectance ( $R_m$ ) was determined on two samples by microscope reflectance

Tab. 2 Illite 'crystallinity' and vitrinite reflectance measurements from different rocks of the Suviana formation 1 km south-east of Porretta Terme. -  $R_m$ : mean value; n: number of measured grains; 2s: standard deviation.

SAMPLE		ILLITE 'CRYSTALLINITY' ( $\Delta^\circ 2\theta$ )		VITRINITE REFLECTANCE		
Mu Nr.	lithology	air dried	treated by ethylen glycol	$R_m$	n	2s
487.2	marl	0.82	0.61	-	-	-
487.3	graywacke	0.73	0.53	-	-	-
487.4	graywacke	0.68	0.47	1.70	56	0.23
487.5	slate	0.65	0.51	1.65	96	0.23



measurements<sup>3</sup>. Detailed description of the technique and the microscope photometer system is given by TEICHMÜLLER (1982) and REUTTER et al. (1983).

Measurements were done on polished grain samples, which contained in addition to vitrinite, also some graphite, semifusinite and inertinite. Coal and pyrite were strongly oxidized in sample 487.4 (tab. 2) displaying a Rm of 1.70%, but hardly in sample 487.5, where a Rm value of 1.65% was measured. These values are slightly elevated with respect to the published Rm data from the same tectonic unit, where REUTTER et al. (1983) found Rm values of 1.43% 5 km south-east and 1.52% 11 km north-west of the investigated area. In contrast coal rank values further south-west and north-east of the Suviana sandstone are  $\leq 1.1\%$ , indicating imbricated tectonics as expected in this part of the Northern Apennines (REUTTER, 1980).

Vitrinite reflectance measurements can be interpreted in terms of maximum burial temperature. BARKER and PAVLEVICZ (1986) compiled  $T_{\max}$  and Rm data over 35 boreholes in sedimentary basins and concluded that the effect of functional heating duration (HOOD et al., 1975) is limited, and that thermal maturation of organic matter does stabilize after about  $10^6$  to  $10^7$  years. Therefore, mean random vitrinite reflectance (Rm in %) can approximately be correlated with maximum burial temperature ( $T_{\max}$  in °C). Applying the linear regression equation of BARKER and PAVLEVICZ (1986, addendum)

$$\ln(\text{Rm}) 0.0096 T_{\max} - 1.4$$

a maximum temperature of 198°C at Rm = 1.65% results.

According to BOSTICK et al. (1979) and assuming an effective heating time of 1 to 5 Ma within 15°C of maximum heating (HOOD et al., 1975), a temperature of 195 to 225°C results.

## 5. Discussion

### 5.1. HEAT REGIME

#### 5.1.1. Fluid temperature and rock temperature

The narrow temperature range between 227 and 220°C of approximate fluid inclusion

trapping from populations 1a to 5b indicates nearly constant temperature conditions during crystal growth. This consistency suggests that fluid temperature perturbations by fluid flow may be minor and that fluid temperatures may correspond to rock temperatures. Moreover, because fluid temperature in early formed fluid inclusions approximate  $T_{\max}$ , the inclusions are interpreted to have formed near peak temperature conditions (figure 4, insert). If fluid temperatures of 220 to 227°C are compared with those from regional metamorphic terrains of the external part of the Central Alps (MULLIS, 1979; FREY et al., 1980a and 1980b), fluid temperatures reflect low-grade anchimetamorphic conditions. However, it is not yet clear whether fluid trapping temperatures correspond to rock temperatures alone or if an additional constant warm fluid flow has also influenced them.

Temperatures derived from coal rank (195 to 225°C) are equal to fluid temperatures or tend to be slightly smaller. This tendency will be discussed in the following. For a rise of coal rank, temperature is generally accepted as the most important factor (TEICHMÜLLER, 1987). Rapid subsidence (LOPATIN, 1976) and great overburden (STACH et al., 1982) in contrary, would cause a lower rank at a given temperature and depth, because chemical equilibrium temperature may not yet have been reached and coalification gases are hindered to be removed. As time of subsidence, heating duration and uplift of the investigated area was short and rocks were buried at a depth of at least 8 to 9 km (see sections 5.2 and 5.5), thermal maturation of organic matter may not have been stabilized yet. Thus burial temperature of 195 to 225°C derived from a Rm value of 1.65% is possibly slightly underestimated. On the other hand, little oxidation of organic matter, as observed on sample No. 487.5, could have slightly increased vitrinite reflectance. Hence, temperature would be slightly overestimated, what counteracts temperature underestimation caused by retardation of thermal maturation.

Comparing illite 'crystallinity' data from Porretta Terme with those from regional metamorphic terrains from the external part of the Central Alps (FREY et al., 1980a and 1980b), rocks seem to have experienced only diagenetic conditions. Even though warm fluid flow could have slightly increased fluid trapping tempera-

<sup>3</sup> Vitrinite reflectance measurements were made in the laboratory of the Institut für Geologie at the Freie Universität, Berlin.

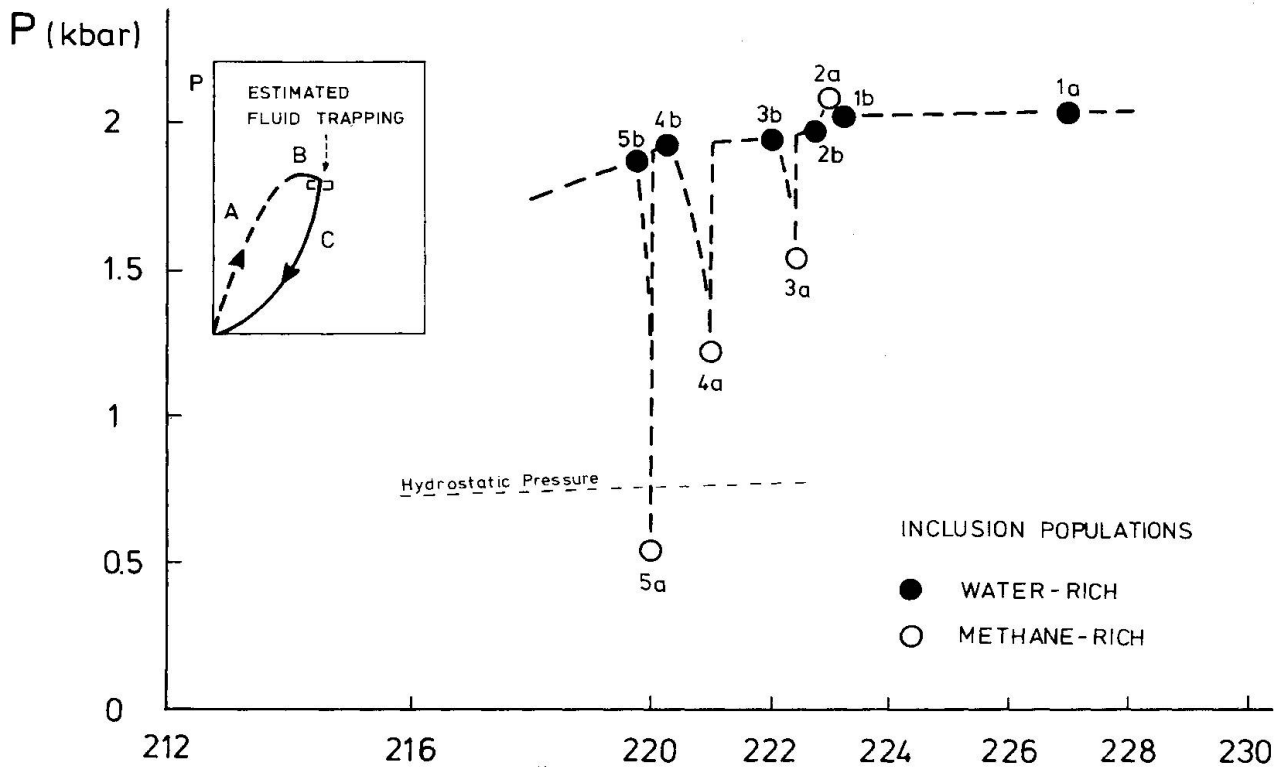


Fig. 4 Approximate pressure and temperature evolution of fluid trapping in quartz crystals from Porretta Terme. Insert: Estimated position of fluid trapping along the approximate PT path the Suviana sandstone had experienced. A: subduction-like subsidence; B: north-east thrusting and heating; C: upthrusting.

ture with respect to rock temperature, there remains a discrepancy between heating conditions derived from illite 'crystallinity' and fluid inclusion data which is object of current research. Nevertheless, temperature is generally believed to be the most important factor affecting illite 'crystallinity' (KÜBLER, 1967a and 1967b, 1968). Other parameters like high porosity and abundance of organic matter in rocks (FREY, 1987) may also have influenced illite 'crystallinity'. As time for heating was short (see section 5.5), illite 'crystallinity' may be affected by kinetic retardations in a manner similar to that presumed by ESSENE (1982) or discussed by KISCH (1987) for areas around magmatic intrusives. In consequence, if approximate fluid trapping temperature is virtually equal to rock temperature, fluids display, in presence of short-lived heating, greater sensitivity to metamorphism than minerals.

#### 5.1.2. Heat sources

It can be assumed that heat production by radioactive decay or mineral reactions during

rapid crustal subsidence and uplift was low (THOMPSON and ENGLAND, 1984).

Large fluid pressure fluctuations during syntectonic opening and enlargement of fissure systems might have favoured fluid migration. This could have occurred along interconnected fractures or active fault zones transporting heat and mass from deeper to shallower levels. Such a mechanism may certainly have advected some heat, as it has been suggested to be significant by VROLIJK (1987) and VROLIJK et al. (in prep.), for Kodiak Island.

Frictional heating along decollement planes could also have occurred. However, as high fluid pressures approach lithostatic conditions, frictional sliding resistance to nappe transport (HUBBERT and RUBEY, 1959; FIVE et al., 1978) would be reduced and thus, frictional heating can be neglected.

Heat production may also be a result of magmatic activity. However, Pliocene to more recent volcanism has to be excluded as the rocks were buried at a depth of at least 8 to 9 km and upthrust more or less to the present level by the end of Miocene or beginning Pliocene. Nevertheless, as shown by REUTTER et al.

(1980), heat contribution from deep seated melting processes during compressional tectonics must probably be considered significant.

## 5.2. PRESSURE REGIME

### 5.2.1. Fluid pressure and lithostatic pressure

The highest recorded approximate trapping pressures of the fluids approximate the least principal stress (SECOR, 1965) and probably represent near lithostatic pressure conditions. Whilst the earliest fluid populations approximate  $T_{\max}$ , and as  $T_{\max}$  must have been achieved close to  $P_{\max}$  in such terrains of rapid uplift (THOMPSON and ENGLAND, 1984; ENGLAND and THOMPSON, 1984) fluid pressure of 2.0 to 2.1 kbar refers to a minimum to approximate overburden of around 8 to 9 km (average rock density of  $2.5 \text{ g cm}^{-3}$ ). At  $227^\circ\text{C}$ , this rock pile reflects a geothermal gradient of 23 to  $25^\circ\text{C}$  per km. These values are smaller than those derived from early fluid inclusions of the Barrovian type of regional metamorphism from the external part of the Central Alps (25 to  $45^\circ\text{C}$ ; MULLIS, 1979) and indicate burial and tectonism similar to that of an active subduction zone (REUTTER et al., 1980).

### 5.2.2. Pressure evolution

Pressure evolved in two different ways: Pressures of *water-rich inclusion populations* 1a to 5b as well as the earliest methane-rich inclusion population 2a range between 2.1 and 1.9 kbar (table 1 and figure 4). Such a pressure evolution reflects crystal growth and fluid trapping during initial uplift.

According to the pulsatory growth of skeletal quartz, *methane-rich fluid inclusion populations* 3a, 4a and 5a reveal pressure drops of several hundred bars. It seems that fluid pressure fluctuated increasingly as time proceeded, indicating fluid evacuation of the fissure systems. Such phenomena are often observed in Alpine fissures (MULLIS, 1975, 1976a, 1983) and are also detected in syntectonic extensional veins in melanges of the Kodiak accretionary complex (VROLIJK, 1987). Pressure dropped in fact below hydrostatic conditions in fluid population 5a, which can only be interpreted as a very short event.

Each pressure drop is caused either by fissure enlargement resulting from a pulse of deformation (MULLIS, 1976b) or by rising fluid pressure inducing fracture dilatation and temporary fracture permeability (SIBSON, 1981). In both cases, self-sealing of the fracture system may have occurred by sudden deposition of hydrothermal minerals, as their solubility product is lowered. During this process methane bearing fluids unmixed and migrated in direction of the smallest pressure regime, along fissure or interconnected fracture systems as well as from the surrounding rock into dilated veins (population 3a, 4a and 5a, figure 4). In consequence, evacuated and sealed fissure systems were refilled by aqueous chloride solutions, until fluid pressure within the fissures was equal to the fluid pressure within the surrounding rocks.

## 5.3. METHANE-WATER IMMISCIBILITY

Methane saturation in aqueous solutions is around 2 to 3 mole % at 2 kbar and  $230^\circ\text{C}$  (see figures 5.8 and 5.9 in MULLIS, 1987). Methane saturation decreases with decreasing P and T and with increasing salinity (salting out effect; HAAS, 1978; BLOUNT et al., 1980; KRADER, 1985). Combining methane solubility with geological evidences then raises five possible mechanisms that can be envisaged to explain unmixing phenomena:

- Unmixing caused by methane production during maturation and cracking of organic matter.
- Unmixing during isobaric decrease in temperature.
- Unmixing during isothermal pressure decrease.
- Unmixing by input of salt-enriched fluids.
- Upward and downward movement of the gas-water contact mimicking unmixing phenomena.

Isothermal pressure decrease was the dominant factor for methane-water unmixing during precipitation of quartz generation 3a, 4a and 5a. For generation 2a a small decrease in temperature operated alone or in combination with a possible up- and downward moving of the gas-water contact.

#### 5.4. QUARTZ GROWTH

Both fibre and prismatic quartz crystallized from a methane bearing water-rich fluid at approximate PT conditions of 1.9 to 2.0 kbar and 220 to 227°C. In contrast, skeletal quartz precipitated from a methane enriched fluid and under pressure conditions varying from close to lithostatic to smaller than hydrostatic pressures.

Fibre quartz crystals are repeatedly cracked and sealed, recording every increment of shear and extensional displacement of fissure walls (LEMMLEIN, 1946). Prismatic and skeletal quartz display numerous growth zones indicating also repeated pulses of rock deformation and changes in fluid composition and density. The exact growth mechanism of skeletal growth from a methane enriched and probably emulsion-like fluid is not yet known. Nevertheless, methane-water unmixing caused principally by fluid pressure drop resulted in rapid quartz precipitation of skeletal quartz.

#### 5.5. TECTONIC IMPLICATIONS OF FLUID INCLUSIONS

PT evaluation of water-rich fluid inclusions reflects neither an isothermal decrease in pressure nor an isobaric decrease in temperature. It represents just a limited part after P and T maximum along the PT path that rocks had experienced (figure 4, insert).

As rocks were buried at a depth of at least 8 to 9 km, and as time between sedimentation and upthrusting lasted hardly more than 10 Ma, sedimentation, subsidence, time duration of maximum heating and upthrusting must all of them together have been very short. Such an evolution in time can be explained by the following scenario: The Suviana sandstone was synkinematically deposited at Middle Miocene time at the front of the Liguride nappes being moved from the south-west. The just deposited sediments were overthrust by the Liguride nappes and buried at least 8 to 9 km beneath them. During the Tortonian, the paroxysmal stage of the Apenninic orogeny, rocks were involved in compressional tectonics and pushed towards north-east. At this stage, but before final thrusting, regional heating took place. Finally, rocks were upthrust again to more or less the present level at the end of Mio-

cene or beginning Pliocene (REUTTER, 1980; REUTTER and GROSSCURTH, 1978; REUTTER et al., 1980 and 1983).

As compressional tectonics are accompanied by regional heating (REUTTER et al., 1983), related fluid pressures are expected to be equal or slightly higher than those derived for crystal growth at beginning uplift (figure 4, insert). Moreover, because fluids approached most probably lithostatic conditions during compression, nappe transport must have been favoured by drastic reduction of the frictional sliding resistance to motion (HUBBERT and RUBEY, 1959; FIFE et al., 1978). Furthermore, fluid pressure repeatedly relaxed caused either by tectonic activity and fissure enlargement or by hydraulic fracturing (SIBSON, 1981). In the latter case, fluid pressures recorded by the water-rich inclusion populations 2b, 3b and 4b seem to reflect the failure margin of the sealed fractures at 2.0 to 1.9 kbar.

#### 6. Conclusions

1. Temperatures and pressures derived from the earliest fluid inclusion populations reveal approximate trapping conditions of fluids in quartz crystals from the Suviana sandstone of Porretta Terme.

2. Whilst in terrains of rapid uplift, trapping conditions of the earliest fluid inclusion populations approximate P and T of maximum loading and heating, rocks must have been buried to at least 8 to 9 km at temperature conditions of at least 220 to 230°C. When constant warm fluid flow prevailed, rock temperature is probably overestimated with respect to approximate fluid trapping temperature.

3. Because rocks were buried at a depth of at least 8 to 9 km and as time between sedimentation and uplift was approximately 10 Ma, sedimentation, subsidence, time duration of maximum heating, and uplift must have been very short.

4. High fluid pressures approaching lithostatic conditions during compressional tectonics must have favoured nappe transport in order to reduce drastically the frictional sliding resistance to motion.

5. Pulsations of fluid pressures of 0.5 to 1.5 kbar within a short temperature range of 220 to 223°C reveal tectonic activity or hydrau-

lic fracturing as well as fluid evacuation from the vein systems.

6. Isothermal pressure drops led to methane-water unmixing. Temperature decrease or up- and downward movements of the gas-water contact might have caused the same effect (population 2a).

7. Quartz precipitation was discontinuously slow for fibre and prismatic quartz, which crystallized in a methane-bearing aqueous solution, but discontinuously rapid for skeletal quartz, which precipitated from a emulsion-like methane-rich environment.

8. Illite 'crystallinity' seems to lag behind fluid homogenization temperatures. If fluid temperatures are equal to rock temperatures, fluids probably display, in presence of short-lived heating, greater sensitivity to metamorphism than minerals.

#### Acknowledgments

I owe my first thanks to R. Martin, (Nyon), who accompanied me in the field for sample collection. I am very grateful for the help in verifying microthermometric fluid inclusion data by gas chromatography (J. Touret, Amsterdam; N. Masson, Nancy), Raman spectroscopy (C. Kosztolanyi, Nancy), and for comparing them with some preliminary illite 'crystallinity' (M. Frey, Basel) and coal rank data (K.-J. Reutter, Berlin). Furthermore, I would like to thank M. Frey, K.-J. Reutter, P. Vrolijk (Cambridge), St. Burley (Sheffield), F. and B. Loher-Meier (Zürich) and M. Fischer (Basel) for helpful discussions, corrections and the reviewing of the paper.

#### References

- ANGUS, S., ARMSTRONG, B. and DE REUCK, K.M. (1976): International Thermodynamic Tables of the Fluid State - 5: Methane. International Union of Pure and Applied Chemistry, Chemical Data Series, No. 16. Pergamon Press, New York.
- BARKER, C.E. and PAWLEWICZ, M.J. (1986, addendum): The correlation of vitrinite reflectance with maximum temperature in humic organic mater. In: BUNTEBARTH, G. and STEGENA, L. (Eds.): Paleogeothermics (p. 78-93). Springer, Berlin.
- BLOUNT, CH. W., WENGER, L.M., TARULLO, M. and PRICE, L.C. (1980): Methane solubility in aqueous NaCl solutions at elevated temperatures and pressures. *Geol. Soc. Amer., Abstr.* 12/6, 276.
- BOMBICCI, L. (1898): Sulla probabilità che talune anomalie di forma nei cristalli dipendano da durevoli movimenti negli spazi naturalmente cristalligeni. *Mem. R. Accad. Sci. Ist. Bologna, Ser. V, tomo VII*, 761-780.
- BOSTICK, H.N., CASHMAN, S.M., MCCULLOH, T.H. and WADDELL, C.T. (1979): Gradients of vitrinite reflectance and present temperature in the Los Angeles and Ventura Basins, California. - In: OLTH, D.F. (Ed.): Low temperature metamorphism of kerogen and clay minerals (p. 65-96). Pacific Section, Soc. Econ. Paleont. Mineral., Los Angeles.
- CUNNEY, M., PAGEL, M. and TOURET, J. (1976): L'analyse des gaz des inclusions fluides par chromatographie en phase gazeuse. *Bull. Soc. franç. Cristallogr.* 99, 169-177.
- DEATON, W.M. and FROST, E.M. JR. (1948): Gas hydrates and their relation to the operation of natural-gas pipe lines. U.S. Bureau of Mines, Monograph 8.
- DHAMELINCOURT, P., BENY, J.-W., DUBESSY, J. and POTY, B. (1979): Analyse d'inclusions fluides à la microsonde MOLE à effet Raman. *Bull. Minéral.* 102, 600-610.
- DONNELLY, H.G. and KATZ, D.L. (1954): Phase Equilibria in the Carbon Dioxide-Methane System. *Ind. Eng. Chem. Washington*, 46, 511-517.
- DUBESSY, J., GUILHAUMOU, N., MULLIS, J. and PAGEL, M. (1984): Reconnaissance par la microspectrométrie Raman, dans les inclusions fluides, H<sub>2</sub>S et CO<sub>2</sub> solides à domaine de fusion comparable. *Bull. Minéral.* 107, 189-192.
- ENGLAND, P.C. and THOMPSON, A.B. (1984): Pressure-Temperature-Time Paths of Regional Metamorphism I. Heat Transfer during the Evolution of Regions of Thickened Continental Crust. *J. Petro.* 25, 894-928.
- ESSENE, E.J. (1982): Geologic thermometry and barometry. In: FERRY, J.M. (Ed.): Characterization of Metamorphism through Mineral Equilibria (p. 153-206). *Reviews in Mineralogy* 10. Mineral. Soc. America.
- FIFE, W.S., PRICE, N.J. and THOMPSON, A.B. (1978): Fluids in the Earth's Crust. Elsevier, Amsterdam.
- FREY, M. (1986): Very low-grade metamorphism of the Alps - an introduction. *Schweiz. mineral. petrogr. Mitt.* 66, 13-27.
- FREY, M. (1987): Very low-grade metamorphism in clastic sedimentary rocks. In: FREY, M. (Ed.): Low temperature metamorphism (p. 9-58). Blackie, Glasgow.
- FREY, M., BUCHER, K., FRANK, E. and MULLIS, J. (1980a): Alpine metamorphism along the Geotrasverso Basel-Chiasso - a review. *Eclogae geol. Helv.* 73/2, 527-546.
- FREY, M., TEICHMÜLLER, M., TEICHMÜLLER, R., MULLIS, J., KÜNZI, B., BREITSCHMID, A., GRUNER, U. and SCHWIZER, B. (1980b): Very low-grade metamorphism in external parts of the Central Alps: Illite crystallinity, coal rank and fluid inclusion data. *Eclogae geol. Helv.* 73/1, 173-203.
- GAMBARI, L. (1868): Descrizione dei quarzi di Porretta. *Ann. Soc. Nat. Modena*, III, 1-19.
- GHELARDONI, R., LUCCHETTI, L., PIERI, M. and PIRINI, C. (1962): I rapporti tra «Macigno» e «Marnoso-arenacea» tra le Valli del Dolo e dell'Idice (Appennino tosco-emiliano). *Boll. Soc. Geol. Ital.*, 81/3, 195-230.
- GUENTHER, K. and REUTTER, K.-J. (1985): Il significato delle strutture dell'unità di M. Modino-M. Cervarola tra il Passo delle Radici e il M. Fal-

- terona in relazione alla tettonica dell'Appennino settentrionale. *G. Geol.*, ser. 3a, 47/1-2, 15-34, Bologna.
- HAAS, J.L. JR. (1978): An empirical equation with tables of smoothed solubilities of methane in water and aqueous sodium chloride solutions up to 25 weight percent, 360°C, and 138 MPa. U.S. Geol. Survey Open-file Rept. 78-1004.
- HEYMANN, H.F. (1968): Zur Geologie der Toskanischen und Emilianischen Serien des Nordapennins im Bereich des oberen Panaro und oberen Lima-Tales (Prov. Modena, Bologna, Pistoia). Diss., Freie Univ., Berlin.
- HILBERT, R. (1979): PVT-Daten von Wasser und von wässrigen Natriumchloridlösungen bis 873 K, 400 Bar und 25 Gewichtsprozent NaCl. Diss., Univ. Karlsruhe. Hochschulverlag Freiburg.
- HOOD, A., GUTJAHR, C.C.M. and HEACOCK, R.L. (1975): Organic metamorphism and the generation of petroleum. *Bull. Amer. Assoc. Geol.* 59, 986-996.
- HUBBERT, M.K. and RUBEY, W.W. (1959): Role of fluid pressure in mechanics of overthrust faulting. *Geol. Soc. America Bull.* 70/2, 155-166.
- JACOBS, G.K. and KERRICK, D.M. (1981): Methane: an equation of state with application to the ternary system H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>. *Geochim. Cosmochim. Acta*, 45, 607-614.
- KISCH, H.J. (1987): Correlation between indicators of very low-grade metamorphism. In: FREY, M. (Ed.): *Low temperature metamorphism* (p. 227-300). Blackie, Glasgow.
- KRADER, T. (1985): Phasengleichgewichte und kritische Kurven des ternären Systems H<sub>2</sub>O-CH<sub>4</sub>-NaCl bis 250 MPa und 800 K. Diss., Univ. Karlsruhe.
- KÜBLER, B. (1967a): La cristallinité de l'illite et les zones tout a fait supérieure du métamorphisme. In: *Etages Tectoniques, Colloque de Neuchâtel 1966*, A la Baconnière, Neuchâtel, Suisse, 105-121.
- KÜBLER, B. (1967b): Anchimétamorphisme et schistosité. *Bull. Centre Rech. Pau-SNPA* 1, 259-278.
- KÜBLER, B. (1968): Evaluation quantitative du métamorphisme par la cristallinité de l'illite. *Bull. Centre Rech. Pau-SNPA* 2, 358-397.
- LEMMLEIN, G.G. (1946): The Origin of 'White-Band' Quartz. *O proiskhozhdenii ploskich kvartsev s «beloi polosoi»*. *Vopr. Mineral. Geokhim. Petrogr. (Izdat. Akad. Nauk SSSR, Moskva)*, 98-110. (Russian).
- LOPATIN, N.V. (1976): The influence of temperature and geologic time on the catagenic processes of coalification and petroleum and gas formation. In: *Issledovaniya organicheskogo veshchestva sovremennykh i iskopayemykh osakdov* (p. 361-366). Nauka Press, Moscow. (Russian).
- MULLIS, J. (1975): Growth conditions of Quartz Crystals from Val d'Illiez (Valais, Switzerland). *Schweiz. mineral. petrogr. Mitt.* 55/3, 419-430.
- MULLIS, J. (1976a): Das Wachstumsmilieu der Quarzkristalle im Val d'Illiez (Wallis, Schweiz). *Schweiz. mineral. petrogr. Mitt.* 56/2, 219-268.
- MULLIS, J. (1976b): Die Quarzkristalle des Val d'Illiez - Zeugen spätalpinen Bewegungen. *Eclogae geol. Helv.* 69/2, 343-357.
- MULLIS, J. (1979): The system methane-water as a geologic thermometer and barometer from the external part of the Central Alps. *Bull. Minéral.* 102, 526-536.
- MULLIS, J. (1983): Einschlüsse in Quarzkristallen der Schweizer Alpen und ihre mineralogisch-geologische Bedeutung. *Bull. Soc. Frib. Sc. Nat.* 72, 5-19.
- MULLIS, J. (1987): Fluid inclusion studies during very low-grade metamorphism. In: FREY, M. (Ed.): *Low temperature metamorphism* (p. 162-199). Blackie, Glasgow.
- POTTER, II, R.W. and BROWN, D.L. (1977): The Volumetric Properties of Aqueous Sodium Chloride Solutions from 0° to 500°C and Pressures up to 2000 Bars Based on a Regression of Available Data in the Literature. U.S. Geol. Surv. Bull. 1421-C.
- POTTER, II, R.W., CLYNNE, M.A. and BROWN, D.L. (1978): Freezing point depression of aqueous sodium solutions. *Econ. Geol.*, 73, 284-285.
- POTY, B., LEROY, J. and JACHIMOWICZ, L. (1976): Un nouvel appareil pour la mesure des températures sous le microscope: l'installation de microthermométrie Chaixmeca. *Bull. Minéral.* 99, 182-186.
- RAMSAY, J.G. (1980): The crack-seal mechanism of rock deformation. *Nature*, 284, 135-139.
- RENTZ, K. (1971): Zur Geologie der Zone zwischen der Secchia und dem Apennin-Hauptkamm. Diss., Freie Univ. Berlin.
- REUTER, K.-J. (1980): Subduktion und Orogenese im Nord-Apennin. Übereinstimmungen und Abweichungen von heutigen Inselbogenmodellen. *Festschr. M. Richter, Berliner geowiss. Abh.* A. 20, 100-115.
- REUTER, K.-J., GIESE, P. and CLOOS, H. (1980): Lithospheric split in the descending plate: observations from the Northern Apennines. *Tectonophysics*, 64, T1-T9.
- REUTER, K.-J. and GROSCURTH, J. (1978): The Pile of Nappes in the Northern Apennines, its Unravelment and Emplacement. In: CLOOS, H., ROEDDER, D. and SCHMID, K. (Eds.): *Alps, Apennines, Hellenides* (p. 234-243). Schweizerbart, Stuttgart.
- REUTER, K.-J., TEICHMÜLLER, M., TEICHMÜLLER, R. and ZANZUCCHI, G. (1983): The coalification pattern in the Northern Apennines and its paleogeothermic and tectonic significance. *Geol. Rdsch.* 72, 861-849.
- ROEDDER, E. (1963): Studies of fluid inclusions II: Freezing data and their interpretation. *Econ. Geol.* 58, 167-211.
- SECOR, D.T. (1965): Role of fluid pressure in jointing. *Amer. J. Sc.* 263, 633-646.
- SIBSON, R.H. (1981): Fluid flow accompanying faulting: Field evidence and models. In: SIMPSON, D.W. and RICHARDS, P.G. (Eds.): *Earthquake prediction: An international review: American Geophysical Union, Maurice Ewing Series*, v. 4, 593-603.
- STACH, E., MACKOWSKY, M.-TH., TEICHMÜLLER, M., TAYLOR, G.H., CHANDRA, D. and TEICHMÜLLER, R. (1982): *Stach's Textbook of Coal Petrology*, 3rd edn. Gebrüder Borntraeger, Berlin.
- STALDER, H.A. and TOURAY, J.C. (1970): Fensterquarze mit Methan-Einschlüssen aus dem westlichen Teil der schweizerischen Kalkalpen. *Schweiz. mineral. petrogr. Mitt.* 50/1, 109-130.

- SWANENBERG, H.E.C. (1980): Fluid inclusions in high-grade metamorphic rocks from S.W. Norway. *Geologica Ultraiectina*, Ph. D thesis, Univ. Utrecht. No. 25.
- TEICHMÜLLER, M. (1982): Rank determination on sedimentary rocks other than coal. In: STACH, E., MACKOWSKY, M.-TH., TEICHMÜLLER, M., TAYLOR, G.H., CHANDRA, D. and TEICHMÜLLER R. (Eds.): *Stach's Textbook of Coal Petrology*, 3rd edn. Borntraeger, Stuttgart.
- TEICHMÜLLER, M. (1987): Organic material and very low-grade metamorphism. In: FREY, M. (Ed.): *Low temperature metamorphism* (p.114-161). Blackie, Glasgow.
- THOMPSON, A.B. and ENDLAND, P.C. (1984): Pressure-Temperature-Time Paths of Regional Metamorphism II. Their Inference and Interpretation using Mineral Assemblages in Metamorphic Rocks. *J. Petrol.* 25, 925-955.
- VROLIJK, P. (1987): Tectonically driven fluid flow in the Kodiak accretionary complex, Alaska. *Geology*, 15, 466-469.
- VROLIJK, P., MYERS, G. and MOORE, J.C. (in prep.): Warm fluid migration along tectonic melanges in the Kodiak accretionary complex, Alaska.
- ZAGORUCHENKO, V.A and ZHURAVLEV, A.M. (1970): Thermophysical properties of gaseous and liquid methane. *Israel Progr. Sci. Transl.*, Jerusalem. (Russian edn., 1969).
- ZWANG, Y.-G. and FRANTZ, J.D. (1987): Determination of the homogenization temperatures and densities of supercritical fluids in the system NaCl-KCl-CaCl<sub>2</sub>-H<sub>2</sub>O using synthetic fluid inclusions. *Chem. Geol.* 64, 335-350.

Manuscript received and accepted august 8, 1988.