Schweiz. mineral. petrogr. Mitt. 55, 419–429, 1975

Growth Conditions of Quartz Crystals from Val d'Illiez (Valais, Switzerland)

By *Josef Mullis* (Fribourg) *)

With 9 figures and 1 table

Abstract

Quartz crystals from Val d'Illiez show a close relationship between tectonics at the outcrop scale, quartz morphology and fluid inclusions.

Four different habits (normal prismatic, prismatic with a white stripe, sceptres and skeletal habit) are found in four different generations of growth, each one showing two stages, an early and a late one.

Microthermometric methods gave temperatures and pressures of formation of the four generations.

Sceptres and skeletal forms (early stages) grew quickly in a methane-rich phase during enlargement of alpine clefts. Methane-rich phase in alpine clefts was formed by quick diffusion of methane into the cleft-cavity due to lower pressure in the cavity (70–1200 bars difference). Prismatic growth (late stages) are the product of slower growth, when crystallization was influenced by presence of water.

INTRODUCTION

Quartz crystals from Val d'Illiez deserve special attention because they show a variety of habits at their different stages of growth. Morphological and fluid inclusion studies have already been made on them at a regional scale, mainly by Poty and Stalder (1970) and Stalder and Touray (1970).

This paper is a brief review of a more extensive study, the aim of which was to relate the tectonics of cavity formation to the morphology of quartz crystals and their fluid inclusion content (Mullis, 1976, PH. D. thesis).

---

*) Institut de Minéralogie et Pétrographie, Université, 1700 Fribourg-Pérolles.

MORPHOLOGY OF QUARTZ CRYSTALS AND THEIR ORIGIN

The quartz crystals are found in alpine clefts of Parautochthonous "Flysch" of Rupelian age (SCHROEDER and DUCLOZ, 1955). A close relationship has been found between tectonics at the outcrop scale, quartz morphology and fluid inclusions. Four different habits have been recognized:

— Normal prismatic habit.
— Prismatic habit with a white stripe of fluid inclusions (LEMMLEIN 1946) (Fig. 1). (This stripe corresponds to the "Syntaxial or 'Stretched' crystal growth fibers" of DURNEY and RAMSAY 1973.)
— Sceptre habit (Fig. 2).
— Skeletal habit (Fig. 3).

These habits – excepting quartz with a white stripe – are found in four different generations of quartz, each one of which shows two stages:

a) An early stage, influenced by tectonics, subdivided into:
   — A slow and rhythmic growth of prismatic quartz with a white stripe (gen. Ia).
   — Or a more rapid growth of sceptres and skeletal quartz (gen. IIa, IIIa, IVa).

b) A late stage of slow growth, not disturbed by tectonics, giving a prismatic quartz which envelops the earlier generations (gen. Ib, IIb, IIIb, IVb).

The prismatic late-stages show strong concentrations of colour-centers after irradiation with gamma-rays. In general sceptres and skeletal quartzes remain uncoloured, but they display thin dark zones separating rhythms of growth belonging to one generation (Fig. 4). Another difference between early and late stages is shown by the composition of fluid inclusions. The sceptre and skeletal quartz have fluid inclusions containing >95–99 Vol.-% methane (Fig. 5), but prismatic late quartz contain fluid inclusions mainly consisting of water with not more than 8 Vol.-% of methane (Fig. 6). Only quartz with a white stripe may contain both types of fluid inclusions, those with methane and those with water. The ideal sequence of growth can be considered as follows (Fig. 7): a white stripe quartz is overgrown by 3 following generations of sceptres or skeletal quartz each one separated by a prismatic stage. In reality the Val d'Illiez alpine clefts do not necessarily show all four generations with early and late stages: complete sequences do not often exist in one single crystal (Fig. 4).

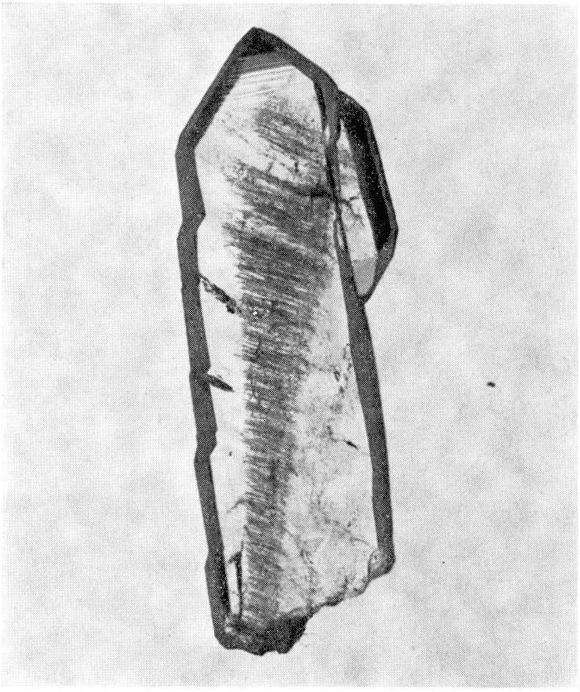

Fig. 1. Quartz crystal with a white stripe of inclusions (Generations I a and I b). Size: 7 mm.

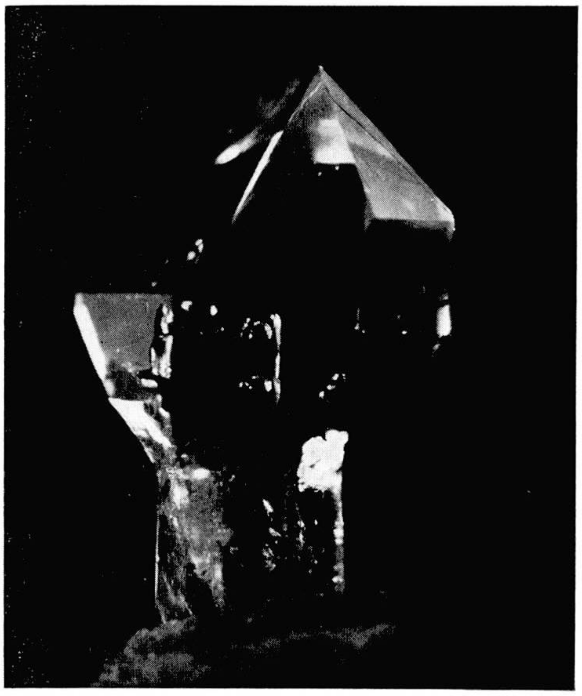

Fig. 2. Sceptre-like quartz crystal. Early stage of skeletal growth, with short prisms and well developed rhombohedral faces. Size: 7 mm.

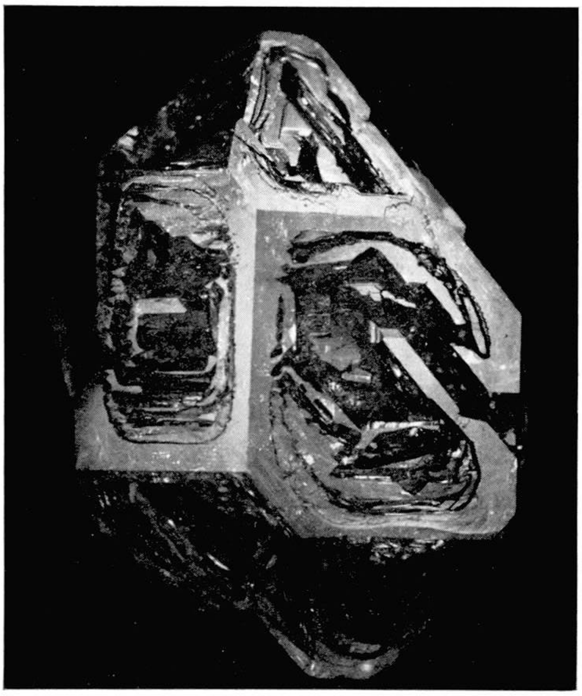

Fig. 3. Skeletal stage of growth, window shaped holes on prism and rhombohedra. Size: 32 mm.

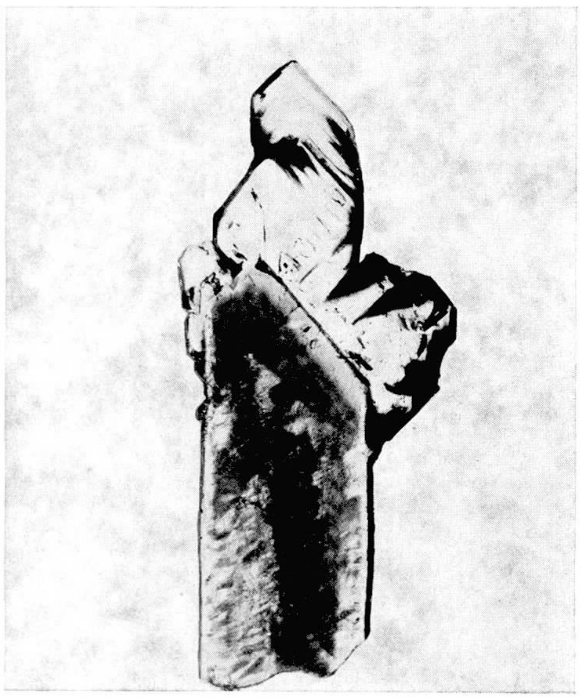

Fig. 4. Polished cross-section of a quartz crystal showing several stages of growth, after irradiation by gamma-rays. Dark zones are generations I a and II b. Thin dark zones in gen. IV a see text, p. 420. Generations I b, II a, III a, III b and IV b are not developed. Size: 36 mm.

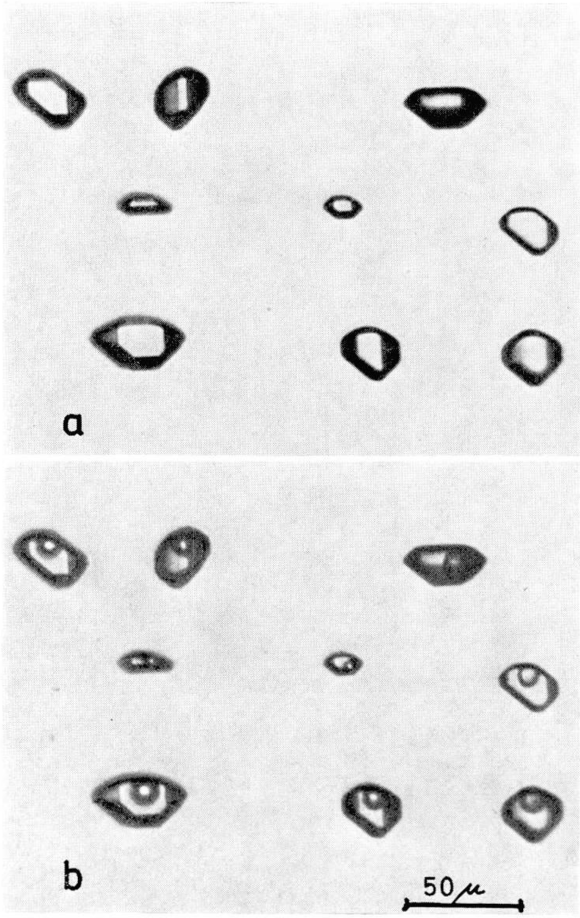

Fig. 5. Fluid inclusions of methane, primary inclusions: a) $+25°C$, supercritical state, b) $-100°C$, CH_4-gas (bubbles) in liquid CH_4. (Homogenization temperature of CH_4 $-95°C$.)

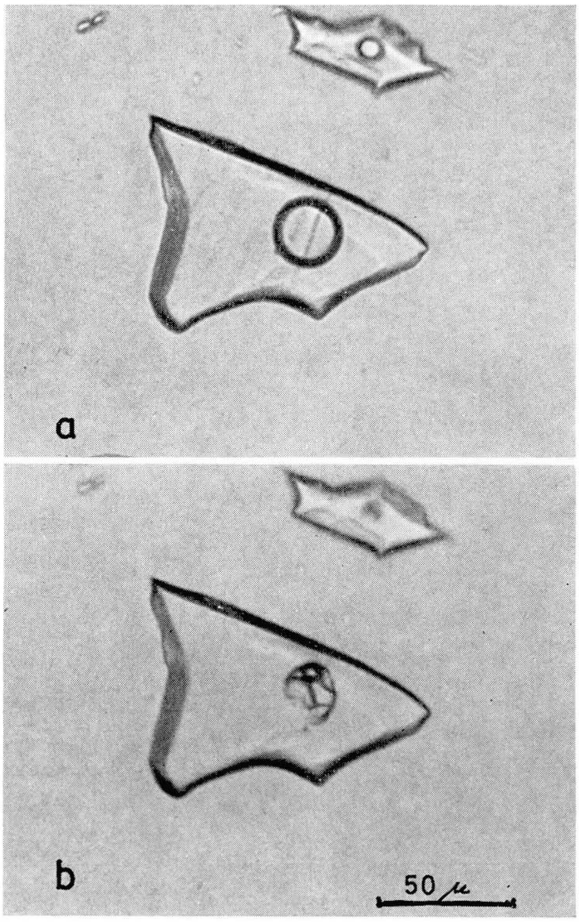

Fig. 6. Fluid inclusions with H_2O-NaCl-CH_4, secondary inclusions: a) $+25°C$, bubble of supercritical CH_4 in water, b) $-100°C$, bubble of CH_4-gas in liquid CH_4 surrounded by ice. (Homogenization temperature of CH_4 $-93°C$; Melting point of ice $-1{,}5°C$.)

FLUID INCLUSIONS

Microthermometry, which is the temperature measurement of phase transitions, has been extensively used.

The best results, with good reproductibility, were obtained from primary and secondary fluid inclusions of the early stages. On the contrary, for the late stages, only secondary inclusions could be measured.

The technique used has been described in Poty and Stalder (1970). Some improvements in calibrations published by Mullis et al. (1973) and Jehl (1975) have been used. Accuracy of measurements is considered to be $\pm 0.2°C$ for the range $-40/+40°C$, and $\pm 0.5°C$ for the range $-120/+300°C$. As many as 2718 measurements on fluid inclusions from 101 quartz crystals coming from 8 cavities have been made. The fluids are mainly composed of H_2O,

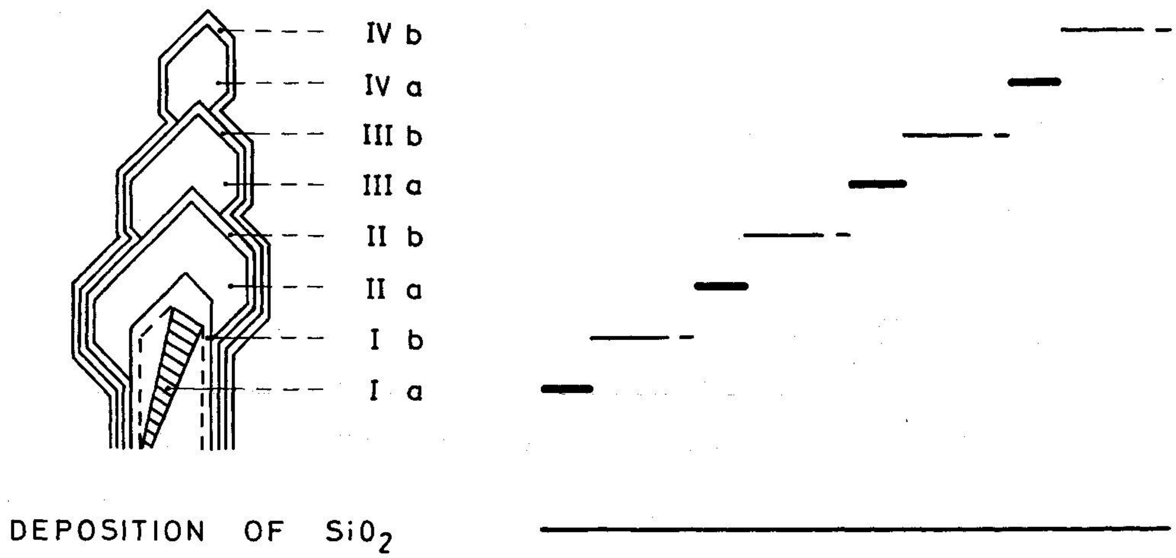

Fig. 7. Idealized sequence of quartz-growth generations. Gen. I a: Quartz with a white stripe; gen. II a, III a, IV a: Sceptres and skeletal quartz; gen. I b, II b, III b, IV b: Late stages of prismatic growth.

CH_4 and salts. Methane purity has been found around 99% by gas chromatography (Touret, J., Univ. Paris VII, Martin, R. and Masson, N., Univ. Nancy I).

DATA

Inclusions were studied on a temperature range from −150 to +300°C. During progressive lowering of temperature the following phenomena were observed: formation of hydrate, formation of ice, unmixing of methane into a gas bubble and a liquid, formation of a solid inside the liquid methane. During progressive heating from −150°C to 300°C the following phenomena were observed (Fig. 8): melting of the solid inside the liquid methane, homogenization of the methane phases, melting of ice, dissociation of hydrate and, at last, homogenization of the methane-rich phase and the aqueous solution. Measurements of these transitions give the following data illustrated by Fig. 9 and table I.

a) Homogenization of CH_4 gas and liquid

This homogenization is achieved between −110 to −82°C, for both CH_4- and H_2O-rich inclusions, as quoted in Mullis et al. (1973). On table I we see that there are significant differences between the different generations of quartz. Crystals from different cavities show variations mainly in the prismatic habit, but sceptres and skeletal quartz contain very similar fluids.

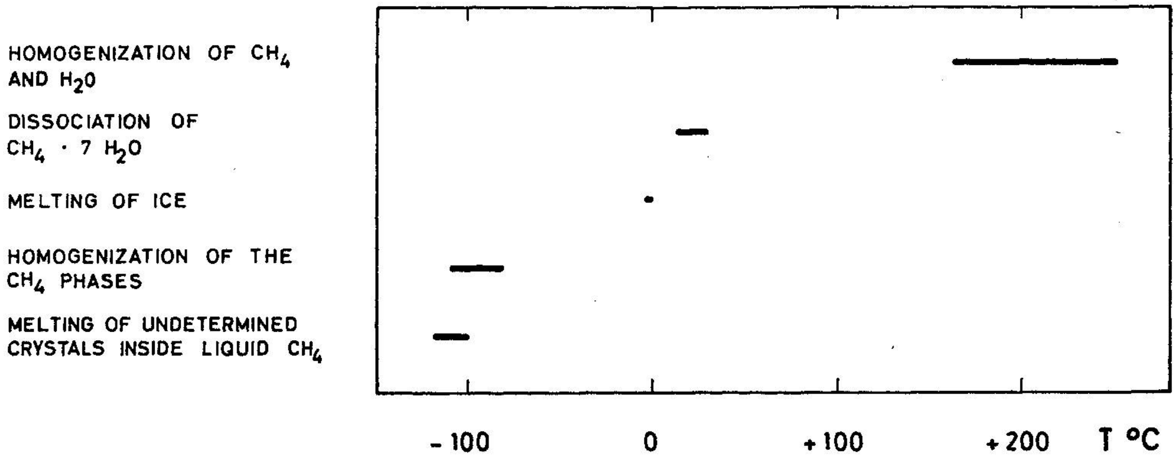

Fig. 8. Phase transitions measured by microthermometry with indicated ranges of temperature.

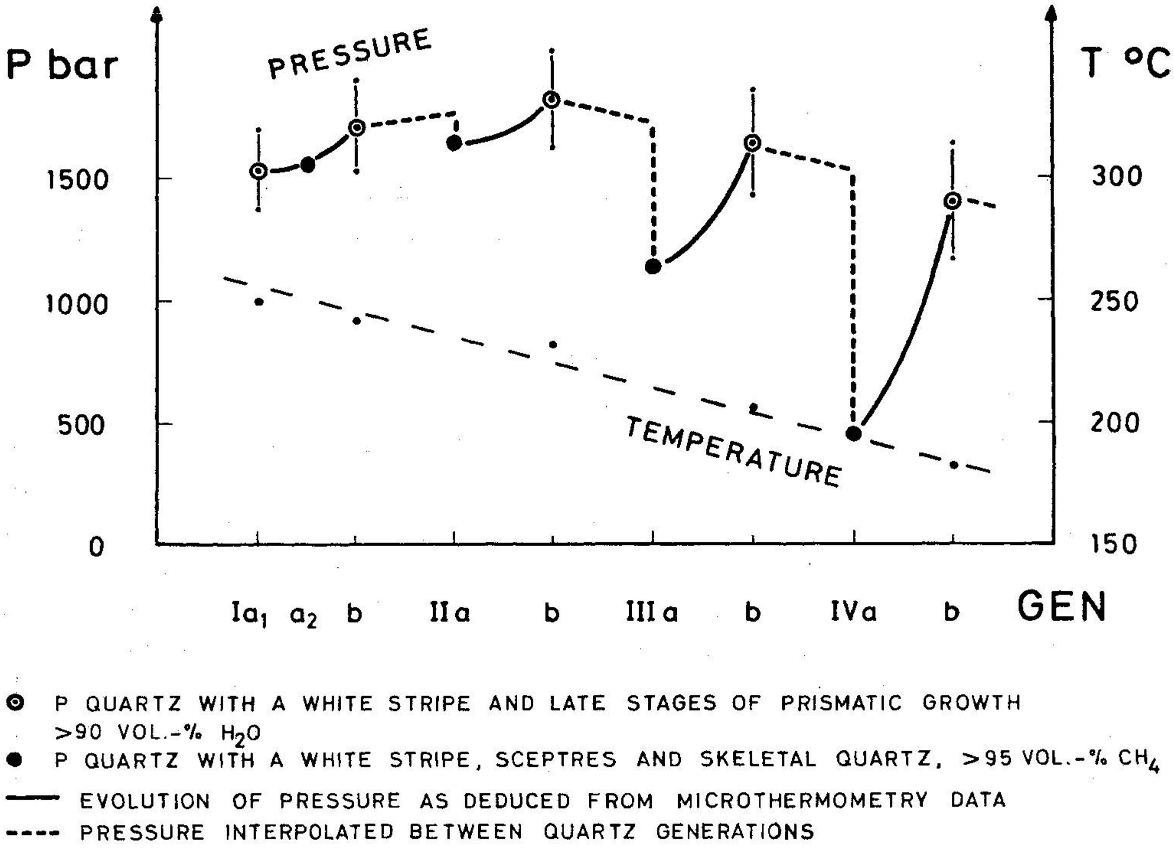

Fig. 9. Quartz crystals from Val d'Illiez: Idealized diagram showing the regime of pressures and temperatures of formation during the four generations of growth.

We can infer methane densities from homogenization temperatures using the PVT-tables in Zagoruchenko and Zhuravlev (1970). Table I shows clearly that, except for the final generation, the density of methane was lower at the beginning of growth of each generation.

Table I: *Microthermometry data for the 4 generations of growth*

	Ia_1	Ia_2	Ib	IIa	IIb	IIIa	IIIb	IVa	IVb
Vol.-% CH_4 at 25°C	7.5±1	~100	6.5±1	~100	5.5±1	~100	4.5±1	~100	4±1
Vol.-% H_2O at 25°C	92.5±1		93.5±1		94.5±1		95.5±1		96±1
CH_4 Homogenization-temperature °C	-97.3[1]	-97.0[1]	-101.8[1]	-99.2[1]	-102.1[1]	-91.4[1]	-91.8[1]	-82.5[1]	-83.0[2]
ρ CH_4	0.292	0.290	0.308	0.299	0.309	0.263	0.265	0.162	0.121
H_2O-NaCl Melting-temperature °C	-2.1		-1.7		-1.4		-1.15		-0.65
Weight % NaCl	3.55		2.85		2.35		1.90		1.10
H_2O-CH_4 Homogenization-temperature °C		[3]		[3]		[3]		[3]	
= minimum or equal temperature of formation	249	246±2	242	237±3	232	219±5	206	194±5	182
Minimum or equal pressure of formation	1530 ±165	1555 ±10	1710 ±185	1645 ±15	1820 ±195	1135 ±15	1640 ±215	455 ±5	1400 ±235

[1]) CH_4 Homogenization into liquid phase.
[2]) CH_4 Homogenization into gaseous phase.
[3]) Interpolated values.

b) Melting temperature of ice

The presence of dissolved salts lowers the melting point of ice, and by refering to the H_2O-NaCl system of LANDOLT BÖRNSTEIN (1960) we can obtain equivalent salinities. Mean values of 741 measurements show that the salinity decreases regularly from the first to the last generation. Average for generation Ia is 3.55 weight-% and for generation IVb is 1.10 weight-%. Inside one cavity salt concentration shows relatively small variation, but variations between crystals from different cavities may be high. For generation Ia, where they are the highest, the extreme values are 5.15 weight-% and 2.0 weight-%; the larger the cavity, the higher the concentration in salt.

c) Homogenization of the methane-rich phase and the aqueous solution

A slow heating homogenizes the fluid inclusion containing CH_4- and H_2O-rich phases. This homogenization temperature decreases consistently from 249° C (average for Ia_1-generation) to 182° C (average for IVb-generation). In the same cavity all quartz crystals from the same generation and especially from generation Ia_1 show a very constant homogenization temperature i.e. 250° C $\pm$ 3° C, but the range of homogenization temperatures becomes wider with the progression of growth. For generation IVb a typical cavity would give a range of 180 $\pm$ 12° C, showing the trapping of fluids during a long lapse of time.

DISCUSSION OF RESULTS

1. Evaluation of temperature

Homogenization temperatures of the methane-rich phase and the aqueous solution are quite constant for crystals of generations Ia_1, Ib, IIb, IIIb and IVb. This shows clearly that the fluid was homogeneous at the time of trapping, and therefore these homogenization temperatures are minimum temperatures of fluid trapping and growth of the host quartz. This means that generation Ia_1 grew at a temperature higher or equal to 249° C and generation IVb higher or equal to 182° C.

2. Evaluation of pressure

For water-rich inclusious (stages Ia_1, Ib, IIb, IIIb, IVb) a lower pressure limit can be calculated by adding partial pressures of water and methane. This can be done by taking into account the volumes of methane and water in the inclusions, the density of these phases, the weight-% NaCl, the homogenization temperature of water and methane, and by using the experimental data available on the systems involved (Burnham et al. 1969, Lemmlein and Klevtsov 1961, Zagoruchenko and Zhuravlev 1970).

This lower limit increases with time from generation I a_1 (1530 bars) to generation IIb (1820 bars) and then decreases to 1400 bars for generation IVb. For methane-rich inclusions (stages I a_2, IIa, IIIa, IVa) a lower pressure limit can be calculated by using the interpolated homogenization temperature of H_2O and CH_4 and the experimental data from Zagoruchenko and Zhuravlev (1970).

A striking feature of this pulsatory growth is the repeated increase of pressure from the beginning to the end of a particular quartz generation. The probable explanation for this fact is that pressure decreases when the cavity is opened or enlarged, and then builds up again to the value attained by the fluids in the surrounding rocks. Thus quartz growth gives us a close record, through fluid inclusions, of the evolution of fluid pressure during tectonic movements.

The decrease of pressure at the beginning of generation IIa was of the order of 70 bars, at the beginning of generation IIIa around 700 bars and at the beginning of generation IVa of the order of 1200 bars. It seems that pressure regime fluctuated more and more as time proceeded.

Assuming that fluid pressure was equal to the lithostatic pressure, at least for the first generation, the lower pressure limit would give a minimum thickness of the overlying rockpile. The thickness would be approximately 6000 m for an average rock density of 2.5. If we assume that P and T were close to these lower limits the average thermal gradient would have been around 36°C/km at that time. This figure agrees well with previous estimations (Poty 1969, Clark and Jaeger 1969, Poty, Stalder and Weisbrod 1974).

CONCENTRATION OF MOTHER LIQUOR AND CRYSTAL GROWTH

Concentration of mother liquor in the Val d'Illiez alpine clefts can be estimated with good accuracy by microthermometry (table I). From the diagrams of the system methane/water (Culberson et al. 1951), ethane/water (Danneil et al. 1967) and argon/water (Lentz and Frank 1969) it can be deduced that even large pressure and temperature variations do not greatly influence an unmixing of methane/water. Since temperature could not show large variations on a local scale, the main cause of the formation of the methane-rich vapour must have been a variation in concentration of methane (X_{CH_4}) in the alpine clefts.

In general the concentration of mother liquor can vary with volume changes of the cleft and as a consequence of different velocities of diffusion of components into the cleft.

These assumptions are born out in the PT-domain of quartzcrystals from Val d'Illiez. The cleft volume is enlarged by tectonic movements, producing a lower pressure in the cleft. In consequence water/methane could unmix, but new methane will enter into the cleft by diffusion through the country rock. The greater importance of methane diffusion with regard to water diffusion may be explained by the lower viscosity of methane in the given PT-range, as well as less adsorption and ion exchange of methane than water with the country rock (shale and sandstone) (von Engelhardt 1960).

SiO_2-concentration has to be taken into account as an important factor. Conditions must be found to explain a quicker growth for sceptres and skeletal quartz, i.e. providing the necessary quantities of SiO_2. The formation of a methane rich phase is most interesting in this respect, because the quicker growth seems to depend on a lower solubility of quartz in the methane rich phase than in the water rich phase (c.f. the low quartz solubility in vapour, discussed by Nacken 1950). Perturbation of both phases will be produced by continuing tectonic movement and by diffusion of water and methane through the walls of the cavity.

The following model may explain the differences of quartz growth from Val d'Illiez:

Sceptre and skeletal habits of quartz are found during a quick, irregular enlarging-process of clefts, in a methane rich environment which results from diffusing methane into the cavity. Pressure in the cleft may be 70–1200 bars lower than in the country rock. This difference of pressure cannot be balanced by diffusing methane and will be compensated by diffusing water over a larger lapse of time giving way to a "late-stage" prismatic overgrowth.

I acknowledge encouraging and helpful discussions from Prof. J. von Raumer (Fribourg), Maître de recherche B. Poty (Nancy) and thank Dr. P. Homewood (Fribourg) for help in translation.

The author appreciated very much the financial support of a 3-years appointment from Swiss National Science Foundation, Project. Nr. 2.645–0.72.

REFERENCES

Burnham, C. W., Holloway, J. R. and Davis, N. F. (1969): Thermodynamic Properties of Water to 1,000° C and 10,000 Bars. Geol. Soc. Amer., Spec., Pap. 132.

Clark, S. P. Jr. and Jäger, E. (1969): Denudation rate in the Alps from geochronologic and heat flow data. Am. J. Sci. 267, 1143–1160.

Culberson, O. L. and McKetta, Jr., J. J. (1951): Phase Equilibria in Hydrocarbon-Water Systems. IV. Vapor-Liquid Equilibrium Constants in the Methane-Water and Ethane-Water Systems. Transactions AIME 192, 297–300 (J. Petrol. Technol., New York).

DANNEIL, A., TÖDHEIDE, K. und FRANK, E. U. (1967): Verdampfungsgleichgewichte und kritische Kurven in den Systemen Äthan/Wasser und n-Butan/Wasser bei hohen Drücken. Z. Techn. Chem. 39/13, 816–822.

DURNEY, D. W. and RAMSAY, J. G. (1973): Incremental Strains Measured by Syntectonic Crystal Growths. In: DE JONG, K. A. and SCHOLTEN, R. (Ed.): Gravity and Tectonics, 67–96. John Wiley & Sons, New York, London, Sydney, Toronto.

ENGELHARDT, VON, W. (1960): Der Porenraum der Sedimente. Springer-Verlag Berlin, Göttingen, Heidelberg.

GRIGOR'EV, D. P. (1965): Ontogeny of Minerals. Israel Progr. Scient. Transl., Jerusalem.

JEHL, V. (1975): Le métamorphisme et les fluides associés des roches océaniques de l'Atlantique nord. Thèse de spec., Université de Nancy I.

LANDOLT-BÖRNSTEIN (1960): Eigenschaften der Materie in ihren Aggregatzuständen. 2. Band, 2. Teil, Bandteil a. Springer-Verlag.

LEMMLEIN, G. G. (1946): O proiskhozhdenii kvartsev s "beloi polosoi" (The Origin of "White-Stripe" Quartz). In: Sbornik "Voprosy mineralogii, geokhimii i petrografii", 98–110, Moskva, Izdatel'stvo Akad. Nauk. SSSR.

LEMMLEIN, G. G. and KLEVTSOV, P. V. (1961): Relations among the principal thermodynamic parameters in a part of the system H_2O-NaCl. Geochemistry 1961, 2, 148–158.

LENTZ, H. und FRANK, E. U. (1969): Das System Wasser-Argon bei hohen Drucken und Temperaturen. Ber. Bunsenges. 73/1, 28–35.

MULLIS, J. (1976): Das Wachstumsmilieu der Quarzkristalle im Val d'Illiez. Ph. D. thesis in preparation.

MULLIS, J., POTY, B. et LEROY, J. (1973): Nouvelles observations sur les inclusions à méthane des quartz du Val d'Illiez, Valais (Suisse). C. R. Acad. Sci. (Paris) 277, 813–816.

NACKEN, R. (1950): Die hydrothermale Mineralsynthese als Grundlage zur Züchtung von Quarzkristallen. Chem. Ztg. 50, 745–749.

POTY, B. (1969): La croissance des cristaux de quartz dans les filons sur l'exemple du filon de La Gardette (Bourg d'Oisans) et des filons du massif du Mont Blanc. Thèse, Université de Nancy. Sciences de la Terre, Mém. 17.

POTY, B. und STALDER, H. A. (1970): Kryometrische Bestimmungen der Salz- und Gasgehalte eingeschlossener Lösungen in Quarzkristallen aus Zerrklüften der Schweizer Alpen. Schweiz. mineral. petrogr. Mitt. 50/1, 141–154.

POTY, B., STALDER, H. A. and WEISBROD, A. M. (1974): Fluid Inclusions Studies in Quartz from Fissures of Western and Central Alps. Schweiz. mineral. petrogr. Mitt. 54, 2/3, 717–752.

SCHROEDER, J. W. et DUCLOZ, CH. (1955): Géologie de la Molasse du Val d'Illiez (Bas-Valais). Matér. Carte géol. Suisse (n. s.) 100.

STALDER, H. A. und TOURAY, J. C. (1970): Fensterquarze mit Methan-Einschlüssen aus dem westlichen Teil der schweizerischen Kalkalpen. Schweiz. mineral. petrogr. Mitt. 50/1, 109–130.

ZAGORUCHENKO, V. A. and ZHURAVLEV, A. M. (1970): Thermophysical properties of gaseous and liquid methane. Israel Progr. Scient. Transl., Jerusalem.

Manuscript received October 4, 1975.