P-T-t path of quartz formation in extensional veins of the Central Alps

SHORT COMMUNICATION

P-T-t path of quartz formation in extensional veins of the Central Alps*

by *Josef Mullis[1]*

Abstract

The evolution of crystal growth in extensional veins from the Central Alps is visualized in space and time by combining fluid inclusion data, radiometric ages, and plate tectonics. The main precipitation of quartz crystals in extensional veins from La Fibbia (Gotthard massif) and Zinggenstock (Aar massif) occurred 21 to 13 Ma before present, caused by continent subplating, crustal thickening, exhumation, erosion and cooling of the Alpine mountain belt.

Keywords: P-T-t path, quartz growth, extensional veins, plate tectonics, fluid inclusions, Central Alps.

Introduction

Plinius 2nd, who lived 2000 years ago, thought that "a crystal solidified under severe frost" ("... crystallum facit, gelu vehementiore concreto."; Historia naturalis, liber 37, I. 29, 1a; in: MAISSEN, 1955). Today, modern investigation techniques give new insights into crystal growth in Alpine extensional veins. In the present paper, the parameters PVTX of crystal growth in two extensional veins from the Central Alps are described and combined with radiometric cooling ages of the surrounding rocks and the knowledge of plate tectonics of the Central Alps. Most of the information is derived from fluid inclusions trapped within quartz crystals of different growth stages. Because of their formation during the late neo-Alpine tectonometamorphic phase of the Central Alps, the extensional veins presented are commonly called "Alpine fissures" (alpine Zerrklüfte).

Geology and mineralogy of the investigated Alpine fissures

The two Alpine fissures described in this paper are from La Fibbia, located at the southern border of the Gotthard massif (Fibbia granite-gneiss) and from Zinggenstock, located in the Aar massif (Grimsel granodiorite). They are representative of several hundreds of investigated Alpine fissures from the Central Alps (MULLIS, 1976, 1979; MULLIS et al., 1994). The main fissure mineral is quartz, accompanied by a mineral assemblage of approximately 20 phases. Clear transparent quartz from La Fibbia crystallized with a Tessin habit. By contrast, quartz from Zinggenstock has a prismatic shape, is alternately white and brownish colored and displays several growth stages (quartz generations). In both localities, at least three populations of secondary fluid inclusions were recognized and investigated.

Analytical techniques and results

MICROTHERMOMETRY

Investigations of fluid inclusions were made with a Chaixmeca heating and freezing stage, designed to work in the range of −180 to +600 °C (POTY et al., 1976). The approximate fluid inclusion compositions in table 1 were calculated with the equations relating bulk densitiy and composi-

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Tab. 1 Approximate compositions, K+/Na+ ratios and formation temperatures and pressures of fluid inclusions in quartz crystals of the Alpine fissures from la Fibbia and Zinggenstock (n.a. = not analyzed; * = data inferred from intersection of the 30 °C/km geothermal gradient with the isochore).

Locality	Fluid populations	Number of measured fluid inclusions	Volume (%) volatiles	Mole %			K+/Na+	T (°C)	P (kbar)
				H_2O	NaCl	CO_2			
La Fibbia (Mu 209.1)	1	33	~ 20	91.8	1.3	6.9	0.156 ± 0.010	420 ±15	3.3
	2	8	~ 8	97.8	1.0	1.2	n. a.	320*	2.5*
	3	4	~ 4	≥ 97.8	1.2	≤ 1	n. a.	240*	1.8*
Zinggen-stock (Mu 320)	1	9	~ 10	96.9	1.6	1.5	0.172	450	4.4
	2a	27	~ 9	96.1	2.1	1.8	0.133 ± 0.001	385	3.3
	2b	9	~ 9	95.4	2.1	2.5	0.130 ± 0.008	375 ± 10	3.2
	3a	61	~ 12	94.8	1.2	4.0	0.103 ± 0.007	330 ± 10	2.3
	$3b_1$	55	~ 6	≥ 96.4	2.6	≤ 1	n. a.	320*	2.6*
	$3b_2$	8	~ 5	≥ 96.6	2.4	≤ 1	n. a.	300*	2.4*

tion of fluid inclusions published in MULLIS et al. (1994).

RAMAN SPECTROSCOPY

Some fluid inclusions from La Fibbia were analysed with the Raman microprobe MOLE (DELHAYE and DHAMELINCOURT, 1975). The method is discussed by DUBESSY et al. (1989). Results were published in MULLIS et al. (1994) and confirm that the volatile phase within the first fluid inclusion population is pure CO_2. Only the second inclusion population is contaminated with a very small amount of N_2 (0.02 mole %).

SODIUM-POTASSIUM THERMOMETRY

Carefully examined thick quartz sections which contained exclusively fluid inclusions of a single population were selected for K+/Na+ analysis of fluids released by bulk extraction. The method has been described in POTY et al. (1974). Assuming equilibrium conditions between the K-feldspars of the sourrounding host rock and the fluid within the extensional veins, K+/Na+ ratios were interpreted after LAGACHE and WEISBROD (1977) to yield approximate formation temperatures of fluid inclusion populations (Tab. 1).

Pressure-temperature path

Figures 1 and 3 show sketches of quartz crystals from La Fibbia (southern Gotthard massif) and Zinggenstock (southern Aar massif), respectively. Crystals from La Fibbia are characterized by three fluid inclusion populations of different ages. Crystals from Zinggenstock display three quartz generations with well definded fluid inclusion populations. Knowing the composition (Tab. 1) and the bulk density of fluid inclusion populations, their isochores are constructed applying the equation of state of the system $H_2O–CO_2–NaCl$ from BOWERS and HELGESON (1983). Furthermore, the approximate formation temperature is deduced from the K+/Na+ ratio after LAGACHE and WEISBROD (1977), or from the intersection of an assumed geothermal gradient of 30 °C/km with the isochores. Knowing both, the isochore and the approximate formation temperature, the PT path of crystal growth can be approximately retraced by intersection of the temperatures with the isochores (Figs 1 and 3). The first fluid inclusion population from La Fibbia formed at 420 °C and 3.3 kbar, the second at 320 °C and 2.5 kbar, and finally, the third at 240 °C and 1.8 kbar. The earliest fluid inclusion population from Zinggenstock formed at 450 °C and 4.4 kbar, and the latest at around 300 °C and 2.4 kbar. If fluid pressure is assumed to be close to lithostatic pressure, then the
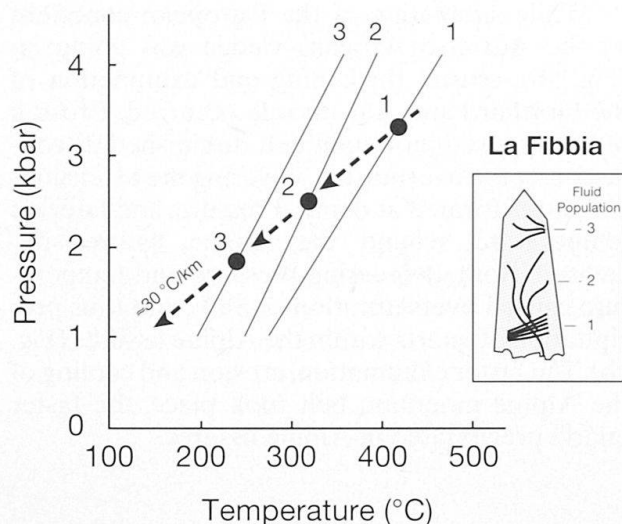
Fig. 1 Pressure-temperature path of a Tessin Habit quartz from La Fibbia. (Slightly modified, after: MULLIS, 1995.)

Fig. 2 Temperature-time path of quartz crystals from La Fibbia. x: radiometric age data (for further explanation: see text). (Slightly modified, after: MULLIS, 1995.)

earliest quartz generation from La Fibbia and Zinggenstock crystallized at a crustal depth of 13 to 14 km and 17 to 18 km, respectively.

Quartz precipitation

Knowing the fluid compositions and PT conditions during mineral growth, quartz solubility can be determined from theoretical and experimental data. Quartz is dissolved mainly as $[Si(OH)_4]$ in aqueous solutions, and its solubility increases with increasing pressure and temperature. In the presence of some dissolved salts and at slightly elevated pH (pH = 7 to 9), quartz solubility further increases (FOURNIER, 1983 and 1985). If the previously evaluated temperature-pressure data of inclusion formation are projected on a quartz solubility-temperature-pressure diagram (Fig. 5), the amount of SiO_2 dissolved in water can be estimated for every growth stage. During earliest growth of the quartz crystals from La Fibbia, 3 g of quartz were dissolved per kg of water. The second growth stage occurred with 1.3 g of dissolved quartz. Finally, data of the third quartz generation require a quartz solubility of 0.5 g per kg of water. This example shows that decreasing pressure and temperature in the fissure system caused a continuous oversaturation of quartz in the aqueous phase with time. As a consequence, growth of quartz took place.

Time scale of quartz growth

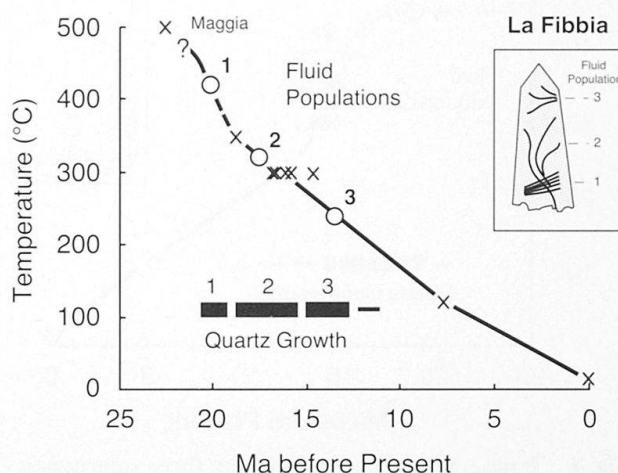Several research teams investigated the age of minerals and rocks in the vicinity of the Alpine fis-

sure from La Fibbia and Zinggenstock (for detailed literature, see HUNZIKER et al., 1992). The resulting cooling histories are shown in figures 2 and 4. The age uncertainty for the first inclusion population from La Fibbia is ± 1 Ma (compare radiometric ages from the northern Maggia valley; HURFORD, 1986), and from Zinggenstock ± 2 Ma. By projecting the approximate formation temperature of the investigated fluid inclusion populations (Figs 1 and 3) on the cooling curve from La Fibbia and Zinggenstock (Figs 2 and 4), the age of every inclusion population is approximately determined. The core of the quartz crystal from La
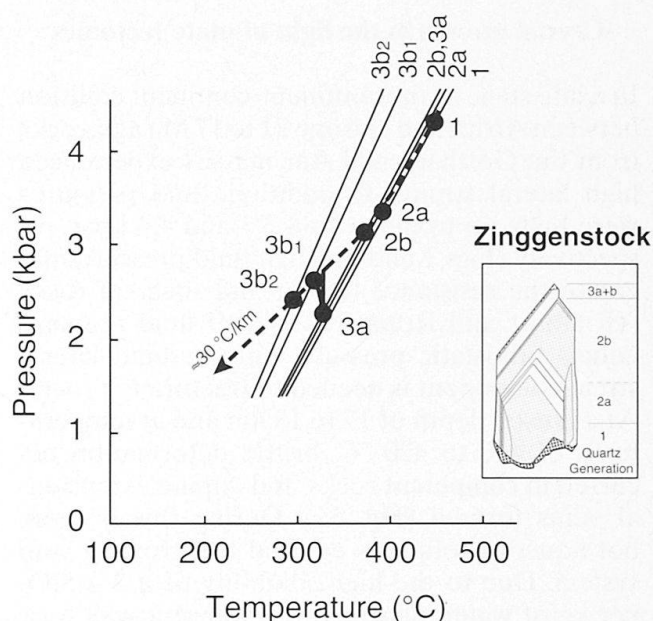

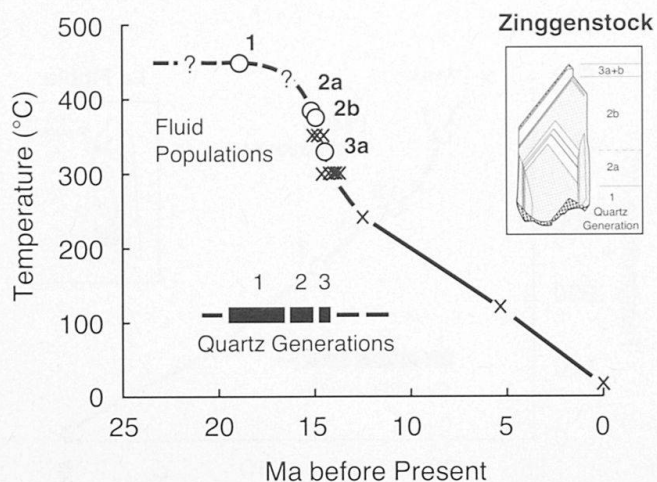*Fig. 3* Pressure-temperature path of a smoky quartz from Zinggenstock.

Fig. 4 Temperature-time path of the three quartz generations in the Alpine fissure of Zinggenstock. x: radiometric age data. (Slightly modified, after: MULLIS, 1995.)

Fibbia formed 20 ± 1 Ma ago. The middle part of the crystal grew 19 to 17 Ma ago. Finally, the third quartz generation precipitated 17 to 13 Ma ago. Applying the radiometric and fission track ages from the adjacent Grimselpasshöhe and Kessiturm (DEMPSTER, 1986; JÄGER et al., 1967, and MICHALSKI and SOOM, 1990), the approximate age for crystal growth in the Alpine fissure from Zinggenstock is also established (Fig. 4). The first quartz generation crystallized some 19 ± 2 Ma ago. The generations 2a and 2b formed 17 to 15 Ma ago, and finally, the last quartz generation crystallized 15 to 13 Ma ago.

Crystal growth in the light of plate tectonics

In a late stage of the continent-continent collision between Africa and Europe 21 to 17 Ma ago, rocks from the Gotthard and Aar massifs experienced high lateral strains. In addition, fluid pressures were high, up to more than 3.3 and 4.4 kbar, respectively (Figs 1 and 3). High fluid pressures decrease the resistance to tear and shear of rocks (HUBBERT and RUBBEY, 1959). If fluid pressure equals lithostatic pressure, only a small lateral strain component is needed to fracture the rocks. At a crustal depth of 17 to 13 km and at temperatures of 450 to 420 °C, brittle deformation occurred in competent rocks, and Alpine extensional veins formed (Fig. 5a). During this process, hot aqueous solutions entered the growing vein system. Due to the high solubility of ≥ 3 g SiO_2 per kg of water, quartz in the adjacent wall rock was dissolved and transported into the Alpine fissures.

While subplating of the European continent by the Adriatic-(African) wedge was going on (Fig. 5b), crustal thickening and exhumation of the Gotthard and Aar massifs occurred. Erosion of the exposed mountain belt diminished discontinuously the overburden covering the extensional fissures formed at depth. Pressure, and later on temperature around the Alpine fissures decreased. Both, decreasing pressure and temperature caused oversaturation of SiO_2, and thus precipitation of quartz within the Alpine fissures (Fig. 5b). The faster exhumation, erosion and cooling of the Alpine mountain belt took place, the faster quartz precipitated in Alpine fissures.

Conclusions

Combining different methods, the study of fluid inclusions leads to a model, relating crystal growth in Alpine extensional veins to plate tectonics (Fig. 5):

1. During a late stage of continent-continent collision around 20 Ma ago, the investigated extensional veins from the Gotthard and Aar massifs formed at a depth of approximately 13 to 17 km and at temperatures between 420 and 450 °C, probably close to the brittle-ductile transition.

2. Enhanced exhumation, erosion (P-decrease) and cooling (T-decrease) at Zinggenstock (southern Aar massif) are slightly retarded with respect to those of La Fibbia (southern Gotthard massif). This difference in time may be explained by post-collisional subplating evolving from south to north.

3. P- and T-decrease of 150 to 180 °C and 1.5 to 2.0 kbar is responsible for the main quartz precipitation between 21 to 13 Ma before present.

4. Tectonic events around 15 Ma ago deformed the vein system at Zinggenstock causing a fluid pressure drop, increase of CO_2 in the vein system, precipitation of the third quartz generation and crystallisation of a carbonate and rutile-rich mineral assemblage.
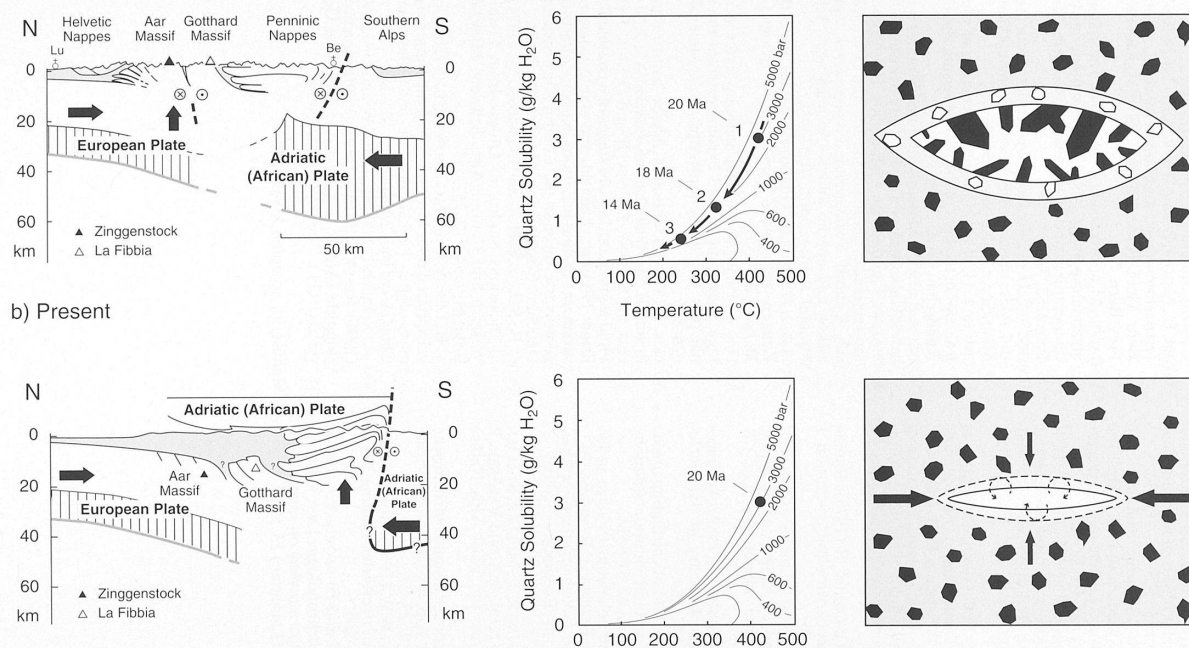
Fig. 5 Relationship between plate tectonics and crystal growth, illustrated with the Alpine fissure of La Fibbia.
a) Opening of the Alpine fissure 20 ± 1 Ma ago. Dissolution of quartz in the wall rock (leaching zone) as a consequence of high quartz solubility. Transport of dissolved quartz to the Alpine fissure.
b) Exhumation of the Alpine body. Erosion, cooling and crystallization of quartz in the Alpine fissure during the last 20 Ma.
(Slightly modified, after: MULLIS, 1995.)
The schematic tectonic cross section through the Central Alps, from Lucerne (N) to Bellinzona (S) is interpolated and modified after BERNOULLI et al. (1990), BERTOTTI (1991), BODMER and GUNZENHAUSER (1992), FREI et al. (1989), HEITZMANN (1991), LAUBSCHER (1990, 1994), MULLIS et al. (1994) and VALASEK et al. (1991). The northern part of the Adriatic-(African) plate wedges into the European plate and causes thickening of the crust and exhumation of the Central Alps. Triangles mark the positions of the investigated fissures in the cross section. The hatched area represents the lower crust, the white area is the crystalline basement of the upper crust, and the dotted area marks the sedimentary and metasedimentary rocks of the upper crust.

References

BERNOULLI, D., HEITZMANN, P. and ZINGG, A.A. (1990): Central and southern Alps in southern Switzerland: Tectonic evolution and first results of reflection seismics. Mém. Soc. géol. France, N.S. 156, 289–302.

BERTOTTI, G. (1991): Early mesozoic extension and alpine shortening in the western southern Alps: The geology of the area between Lugano and Menaggio. Mem. Sci. Geol. (Padova) XLIII, 17–123.

BODMER, PH. and GUNZENHAUSER, A.B. (1992): TGK Hydrocarbon Exploration in Central Switzerland: Experience with Alpine Reflection Seismics. Bull. Swiss. Assoc. Petroleum Geol. and Eng. 59/135, 15–22.

BOWERS, T.S. and HELGESON, H.C. (1983): Calculation of the thermodynamic and geochemical consequences of non ideal mixing in the system H_2O–CO_2–NaCl on phase relations in geologic systems. Equation of state for H_2O–CO_2–NaCl fluids at high pressures and temperatures. Geochim. Cosmochim. Acta 47, 1247–1275.

DELHAYE, M. and DHAMELINCOURT, P. (1975): Raman microprobe and microscope with laser excitation. J. Raman Spectrosc. 3, 33–43.

DEMPSTER, T.J. (1986): Isotope systematics in minerals: biotite rejuvenation and exchange during Alpine metamorphism. Earth and Planet. Sci. Let. 78, 355–367.

DUBESSY, J., POTY, B. and RAMBOZ, C. (1989): Advances in C–O–H–N–S fluid geochemistry of fluid inclusions. Eur. J. Mineral. 1, 517–534.

FOURNIER, R.O. (1983): A method of calculating quartz solubilities in aqueous sodium chloride solutions. Geochim. Cosmochim. Acta 47, 579–586.

FOURNIER, R.O. (1985): The behaviour of silica in hydrothermal solutions. In: BERGER, B.R. and BETHKE, P.M. (eds): Geology and Geochemistry of epithermal systems. Reviews in Economic Geology 2, 45–61.

FREI, W., HEITZMANN, P., LEHNER, P., MÜLLER, ST., OLIVIER, R., PFIFFNER, A., STECK, A.A. and VALASEK, P. (1989): Geotraverse across the Swiss Alps. Nature 340, 544–547.

HEITZMANN, P. (1991): Europäische und Afrikanische Platte in den Schweizer Alpen verzahnt. Spektrum der Wissenschaft, Sept. 91, 23–27.

HUBBERT, M.K. and RUBEY, W.W. (1959): Role of fluid pressures in mechanics of overthrust faulting. Geol. Soc. Amer. Bull. 70, 115–206.

HUNZIKER, J.C., DESMONS, J. and HURFORD, A.J. (1992): Thirty two years of geochronological work in the Central and Western Alps: a review on seven maps. Mémoires de Géologie (Lausanne) 13, 59 p.

HURFORD, A.J. (1986): Cooling and uplift patterns in the Lepontine Alps South Central Switzerland and an age of vertical movement on the Insubric fault line. Contrib. Mineral. Petrol. 92, 413–427.

JÄGER, E., NIGGLI, E. and WENK, A.E. (1967): Rb-Sr-Altersbestimmungen an Glimmern der Zentralalpen. Beitr. Geol. Karte Schweiz, NF 134, Kümmerly & Frey, Bern, 76 p.

LAGACHE, M. and WEISBROD, A. (1977): The system: two alkali feldspars-KCl–NaCl–H_2O at moderate to high temperatures and low pressures. Contrib. Mineral. Petrol. 62, 77–101.

LAUBSCHER, H. (1990): Deep seismic data from the Central Alps: mass distributions and their kinematics. Mém. Soc. Géol. France 156, 335–343.

LAUBSCHER, H. (1994): The deep structure of the Central Alps in the light of the newest seismic data. Geol. Rundschau 83, 237–248.

MAISSEN, F. (1955): Mineralklüfte und Strahler der Surselva. Universitätsverlag Freiburg Schweiz, 192 p.

MICHALSKI, I. and SOOM A.M. (1990): The Alpine thermo-tectonic evolution of the Aar and Gotthard massifs, Central Switzerland: Fission Track ages on zirkon and apatite and K–Ar mica ages. Schweiz. Mineral. Petrogr. Mitt. 70, 373–387.

MULLIS, J. (1976): Die Quarzkristalle des Val d'Illiez – Zeugen spätalpiner Bewegungen. Eclogae geol. Helv. 69, 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. (1995): Genesis of Alpine fissure minerals: Scientific and Technical Information XI., 2, 54–64.

MULLIS, J., DUBESSY, J., POTY, B. and O'NEIL, J. (1994): Fluid regimes during late stages of a continental collision: Physical, chemical, and stable isotope measurements of fluid inclusions in fissure quartz from a geotraverse through the Central Alps, Switzerland. Geochim. Cosmochim. Acta 58, 2239–2267.

POTY, B., STALDER, H.A. and WEISBROD, A. (1974): Fluid Inclusions Studies in Quartz from Fissures of Western and Central Alps. Schweiz. Mineral. Petrogr. Mitt. 54, 717–752.

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.

VALASEK, P., MUELLER, ST., FREY, W. and HOLLIGER, K. (1991): Results of NFP 20 seismic reflection profiling along the Alpine section of the European Geotraverse (EGT). Geophys. J. 105, 85–102.