

## THE CH<sub>4</sub>/H<sub>2</sub>O-(CO<sub>2</sub>) TRANSITION ZONE IN THE EXTERNAL PART OF THE CENTRAL ALPS, SWITZERLAND: A LOW-GRADE METAMORPHIC FLUID EVOLUTION STUDY.

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Many fluid inclusion studies in the Central Alps, Switzerland, i.e. (Frey et al., 1980); (Mullis, 1979, 1987); (Mullis et al., 1994), distinguish four different fluid zones (HHC, CH<sub>4</sub>, H<sub>2</sub>O and CO<sub>2</sub>) from diagenesis to medium-grade metamorphism. The aim of this study is to show the conditions under which the transition from the CH<sub>4</sub> to the H<sub>2</sub>O-(CO<sub>2</sub>) dominated fluid zone occurs. Alpine cavities and their quartz crystals represent the basis of this work. These were investigated on several cross-sections through the external part of the Central Alps. Actual results on two profiles in the Linth and Sernf valleys of the Glarus area (a classical field for low-grade metamorphic studies) are presented here. They are situated in the same lithology (North-Helvetic Flysch).

Fluids are trapped within crack-seal fibre quartz during prograde opening of Alpine fissures. Such fluid inclusions record increasing temperature conditions encountered by the rock during burial and nappe stacking. High-density CH<sub>4</sub>-rich fluid inclusions will tend to decrepitate with increasing temperature. Thus, non-decrepitated early fluid inclusions must have been formed close to the maximum temperature attained by the rock (Mullis et al, 2002).

Thermal maturation as a function of increasing temperature led to the formation of dry gas and to the so-called methane zone. This zone is characterized by an over-saturation of methane. Fluid immiscibility is often observed and fluid inclusions are either CH<sub>4</sub>- or H<sub>2</sub>O-rich. The volatile part of the methane-rich fluid inclusions is composed of  $\geq 97$  mol% CH<sub>4</sub>,  $\leq 1$  mol% HHC and  $\leq 2$  mol% CO<sub>2</sub>. In contrast, the H<sub>2</sub>O-rich fluid inclusions contain  $\leq 3$  mol% CH<sub>4</sub>. The upper temperature limit of formation of this zone is 270°C. With increasing temperature, in the water zone, the total amount of volatiles in the fluid inclusions drops below 1 mol%, while methane tends to disappear totally. In response to that, the homogenisation temperatures fall systematically below 180°C although formation temperatures are increasing. Vitrinite reflectance investigations along the same cross-sections show an evolution of R<sub>max</sub> from 6.1 % in the methane zone to 7.5 % in the water zone, confirming increasing temperature for the transition from the CH<sub>4</sub> to the H<sub>2</sub>O-(CO<sub>2</sub>) zone.

The transition from the methane to the water zone is marked by an increase of CO<sub>2</sub> within the volatile part of fluid inclusions, some localities showing even more than 15 mol% of CO<sub>2</sub> in CH<sub>4</sub>-rich fluid inclusions. Oxidation is thought to be the main mechanism of the CH<sub>4</sub> breakdown yielding CO<sub>2</sub> and H<sub>2</sub>O. The sudden decrease of the total amount of volatile components to below 1 mol%, inducing a decrease of the homogenisation and clathrate dissociation temperatures, is contemporaneous with the precipitation of calcite, filling completely the Alpine fissures.

The question of the origin of O<sub>2</sub> is a key topic of this study. This will be discussed with the help of stable isotope investigations. The constant salinity along the profiles leads to suppose a more or less close system with respect to the water. Dilution by dehydration reactions can practically be excluded.

### References

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