

## Redox reactions at the end of the CH<sub>4</sub>-zone in the external part of the Central Alps, Switzerland

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Fluid inclusion studies in the Central Alps (Switzerland) distinguished four different fluid zones (HHC, CH<sub>4</sub>, H<sub>2</sub>O and CO<sub>2</sub>) from diagenesis to greenschist facies metamorphism (i.e. Stalder & Touray 1970; Frey et al. 1980; Mullis 1979, 1987; Mullis et al. 1994). This work investigate the conditions and mechanisms 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.

Fluid inclusions trapped within crack-seal fibre quartz during prograde opening of Alpine fissures record increasing temperature conditions during burial and nappe stacking. Incipient metamorphism in the Helvetic domain of the Central Alps in Switzerland led to the formation of dry gas in the CH<sub>4</sub>-zone by hydrocarbon cracking. Fluid immiscibility is observed in the H<sub>2</sub>O-CH<sub>4</sub>-(CO<sub>2</sub>)-NaCl system and fluid inclusions are either CH<sub>4</sub>- or H<sub>2</sub>O-rich. The upper temperature limit of formation of this zone is 270 ± 5°C for pressures between 1.5 and 2.5 kbar. With increasing temperature as indicated by vitrinite reflectance and illite "crystallinity", in the H<sub>2</sub>O-zone, the total amount of volatiles in the fluid inclusions falls below 1 mol%. In response, homogenisation temperatures decrease systematically below 180°C. The end of the CH<sub>4</sub>-zone is marked by an increase in CO<sub>2</sub> in the volatile part of fluid inclusions. The sudden decrease of the amount of the volatile content in the H<sub>2</sub>O-zone coincides with the presence of calcite, filling the Alpine fissures and overgrowing the previously formed, syn-kinematic fibre quartz.

In the CH<sub>4</sub>-zone, just before the transition to the H<sub>2</sub>O-zone, methane-calcite C-isotope fractionations indicate temperatures of 250-270°C, in agreement with the homogenisation temperatures of unmixed methane-bearing water-rich fluid inclusions. At the transition to the H<sub>2</sub>O-zone, δ<sup>13</sup>C(CH<sub>4</sub>) values decrease and isotopic equilibrium with calcite is not shown anymore due to later equilibration with CO<sub>2</sub> within fluid inclusions after trapping.

In the CH<sub>4</sub>-zone, δD(H<sub>2</sub>O) values are consistent with isotopic equilibrium with phyllosilicates of the surrounding rocks. δD(CH<sub>4</sub>) values less than -100‰ reflect an origin by cracking of hydrocarbons and in isotopic disequilibrium with water. The strong decrease of δD(H<sub>2</sub>O) values at the CH<sub>4</sub> / H<sub>2</sub>O-(CO<sub>2</sub>) transition reveals a contribution of methane-derived water. δD values increase again within the H<sub>2</sub>O-zone, in isotopic equilibrium with phyllosilicates of the host rock.

Although δ<sup>13</sup>C(CO<sub>2</sub>) values indicate isotope disequilibrium with methane and calcite, they nevertheless suggest a <sup>12</sup>C contribution through methane oxidation. Stable isotope compositions of fluid phases in the fluid inclusions support a model where the end of the methane zone is directly related to local oxidation of methane without an external supply of water.

This reaction in the fluid is controlled by iron reduction of solid reacting phases of the host-rock. Petrographic investigations of the North-Helvetic Flysch show the presence of detrital biotite in the CH<sub>4</sub>-zone. The increase of CO<sub>2</sub> in the fluid is associated by the first appearance of newly formed chlorite and muscovite at direct proximity of biotite. In the H<sub>2</sub>O-zone, no biotite is observed: they are totally replaced by muscovite-chlorite interlayered stacks. As no oxides or sulfides other than pyrite are present in the rock, this reaction between Fe-bearing sheet silicates must control the fluid composition. Mössbauer spectroscopy investigations measure a decrease of 18 to 9% of Fe<sup>3+</sup>/Fe<sub>tot</sub> from the CH<sub>4</sub>- to the H<sub>2</sub>O-zone. Reduction of iron is also expressed by EELS on single isolated Fe-rich sheet silicate. Such a reaction of Fe reduction permits to oxidize up to 85 moles of CH<sub>4</sub> per cubic meter corresponding to a porosity of 0.5 to 1.5 vol% in the bulk rock of the North-Helvetic Flysch.

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