

## Generation of thermogenic methane in the Central Alps (Switzerland) during Mid Miocene metamorphism – New insights from paired clumped isotopologues ( $^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$ )

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This paper reports analyses of ancient methane sealed in fluid inclusions of tectonic veins to document a widespread methanogenesis process during the Middle Miocene Alpine compression. The investigated fluid inclusions are dominated by co-genetic  $\text{H}_2\text{O}$ - and  $\text{CH}_4$ -inclusions. Molecular and isotopic analyses of the  $\text{CH}_4$ -bearing fluid inclusions ( $\delta^{13}\text{C}$ ,  $\delta\text{D}$ ,  $\Delta^{12}\text{CH}_2\text{D}_2$  and  $\Delta^{13}\text{CH}_3\text{D}$ ) indicate that entrapped methane is a dry thermogenic gas [ $\text{C}_1/(\text{C}_2+\text{C}_3) > 95\%$ ] generated at very high maturity ( $\delta^{13}\text{C} = -26/-30\text{‰}$  and  $\delta\text{D} = -126/-137\text{‰}$ ). This methane preserves internal isotopic equilibrium in  $\Delta^{13}\text{CH}_3\text{D}/\Delta^{12}\text{CH}_2\text{D}_2$  space, that translate into temperatures of  $243\pm 18^\circ\text{C}$  ( $\Delta^{13}\text{CH}_3\text{D}$ ;  $n=10$ ) and  $216\pm 14^\circ\text{C}$  ( $\Delta^{12}\text{CH}_2\text{D}_2$ ;  $n=10$ ). These “clumping” temperatures agree with the mineral precipitation temperatures derived from FI microthermometry ( $T_h = 227/260^\circ\text{C}$ ). Our findings reveal that a significant methanogenesis process occurred during peak metamorphic temperatures (c. 25 to 15Ma) from the catagenesis of the surrounding organic-rich flysch ( $R_o > 4-5\%$ ). Then, in a subsequent event during the Miocene (c. 17 to 10Ma), the nappe structure started to up dome and fracture, a process that may have favored significant emission of methane into the atmosphere in a time span overlapping the mid-Miocene climatic optimum event, i.e. a relatively warm period.