## Fluid inclusions and stable isotope in calcite of Trostyanets volcanogenous complex (Ukrainian Carpathians)

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Results of fluid inclusions research and, for the first time, of the isotopic analysis of carbon and oxygen in hydrothermal calcite of the Trostyanets volcanogenous complex (Ukrainian Carpathians) are represented.

Early secondary fluid inclusions in calcite are homogenizing at temperature 300–330 °C; late secondary fluid inclusions homogenizing at 210–260 °C. Volatile phase of fluid inclusions is characterized by prevalence of methane and higher hydrocarbons.

Results of isotopic analysis of carbon and oxygen of calcite of veinlets and almonds show homogeneous values of  $\delta^{13}$ C and  $\delta^{18}$ O. For calcite in the veinlets and almonds from basalts  $\delta^{13}$ C changes ranging from 1.57 ‰ to 2.52 ‰ (PDB). Value  $\delta^{18}$ O changes ranging from 24.19 ‰ to 27.32 ‰ (SMOW). Except is quartz-calcite streak with organic matter, where the value of  $\delta^{13}$ C and  $\delta^{18}$ O are within 2.62 ‰ and 21.51 ‰, respectively.

For this type of carbonates of hydrothermal origin is a characteristic increase  $\delta^{13}$ C for the early stages of mineral formation with cooling. For the late calcite value of  $\delta^{13}$ C is from 5 % to 10 % [2]. Such data can be explained by the growing role of methane in the fluids, resulting in lower oxidation state of late fluids and slow crystallization and concentration of heavy isotopes in calcite [1].

Temperature features of calcite formation in veinlets and almonds, the predominance of methane and higher hydrocarbons in gas phase of fluid inclusions and peculiarities of distribution of isotopic composition of carbon and oxygen of calcite confirms our previous data [3] about deep-seated genesis of the hydrocarbon constituents of the fluid inclusions. It is a result of postmagmatic physical-chemical transformations of the deep-seated fluid saturated with the hydrocarbon constituents.

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## Fungi on the rocks!

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The transformation of rocks into soils by weathering forms the foundation of terrestrial ecosystems and it represents a major feedback on atmospheric  $CO_2$  levels and therefore climate. Over the last few decades, our understanding of weathering evolved from being essentially conceptualized in terms of inorganic aqueous dissolution reactions to now also integrate the role of micro-organisms and their secretions (i.e. organic acids and ligands). More recently, root-associated fungi (mycorrhizal networks) have come to the attention of geochemists because of (i) their ubiquitous presence in almost all forest ecosystems and (ii) their extremely large biomass which is fuelled by the plant photosynthesis. In return, mycorrhiza extract and transfer essential elements and nutrient from soil particles to the host plant roots. In doing so, mycorrhiza degrade minerals and helps to forms our soils.

Understanding and a fortiori quantifying fungal mineral weathering is a real challenge in many respects for experimental geochemists: we had to design a new experimental setup that replicates the physiological functioning of the plant-fungi symbiosis as well as the interactions with mineral surfaces under unsatured hydric conditions typically found in soils [1]. In addition, hypha are microscopic (only ~ 5  $\mu$ m wide but up 1 mm long) and they adhere strongly to mineral substrates. Using an array of cutting edge technique such as ion milling (FIB), transmission electron micro-spectroscopy (TEM/STEM-EDS), molecular probes and confocal microscopy and synchrotron-based X-ray microscopy (STXM) and  $\mu$ -FTIR we are now able to relate the nanometer scale alteration processes in the mineral with the chages in physiology and chemical micro-environments around the hypha and at the mineral-hyphae interface. This unique combination of approaches and the datasets produced shed new light onto the mechanism and rates of fungal weathering at the mineral surface and also allowed us to develop a first quantitative model of alteration at the hyphamineral interface.

[1] Bonneville et al. (2009) Geology 37, 615-618.