

**Negative  $\delta^{18}\text{O}$  signatures in morphologically complex zircons: evidence for Proterozoic cold-climate water/rock interaction in the Qinglongshan UHP meta-granite (Sulu terrain, China)**

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Oxygen stable isotope analyses of bulk zircon grains and cores (isolated by air-abrasion) from ultra-high pressure (UHP) meta-granite from the Qinglongshan region of China, yield negative  $\delta^{18}\text{O}$  values ranging from  $-0.2$  to  $-7.3$  ‰. Sample characterization using back-scattered electron and cathodoluminescence reveals a complex multistage zircon growth history. Pre-metamorphic cores contain inclusions of biotite, quartz (no coesite), K-feldspar, magnetite and apatite whereas the UHP rim overgrowths are inclusion-free. Pre-metamorphic allanite-(Ce) is chemically heterogeneous with complex internal structures and, together with the unusual zircon core morphology and inclusion-rich cores, suggests crystallization within a fluid-rich environment. The mineral inclusions in the zircon cores account for small  $\delta^{18}\text{O}$  differences (0.2 to 1.0‰) between abraded and non-abraded zircons, indicating that cores and rims have nearly the same negative  $\delta^{18}\text{O}$  signature. The pre-UHP metamorphic zircon cores probably acquired their negative  $\delta^{18}\text{O}$  values during subsolidus crystallization in a peculiar hydrothermal context, where rocks (or magma) interacted with cold-climate meteoric water during late Proterozoic times.

#### References

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**Isotopic study of  $\text{CO}_2$  and  $\text{CH}_4$  out-gassed from argillites investigated for radioactive waste repository**

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#### Context and objective

The Callovo-Oxfordian (C-O) argillites, presently lying at ca. 500 m depth, in the eastern part of the Paris basin are being considered as a potential repository site for radioactive waste. As a result, this formation is the object of numerous detailed studies. One objective of on-going work is to reconstruct the chemical and isotopic signature of the argillites pore water, in order to constrain the nature and intensity of water-rock interactions that might have occurred in the past. With this purpose in mind, a methodology was designed to recover  $\text{CO}_2$  (dissolved in pore water) and  $\text{CH}_4$  (adsorbed on clays) gas naturally liberated from C-O core samples under vacuum in a confined inert atmosphere ( $\text{N}_2$  or He). Stable isotope compositions of these gases were then determined by IRMS and GC-IRMS conventional techniques and provided valuable information about their origin.

#### Results and interpretation

$\text{CO}_2$  gas recovered from four cores of C-O argillites yielded reproducible and consistent isotopic compositions, averaging  $-6.3 \pm 1.7$  ‰ PDB for  $\delta^{13}\text{C}$  and  $+35.4 \pm 0.3$  ‰ SMOW for  $\delta^{18}\text{O}$ . This isotopic signature is not compatible with  $\text{CO}_2$  sources such as atmosphere, mantle, degradation of organic matter or bacterial processes. It is best explained as reflecting isotopic equilibrium with dissolved bicarbonate (for C) and with pore water (for O). It further indicates that dissolved carbonate is of inorganic marine source and that pore water is of meteoric origin.

$\text{CH}_4$  gas recovered from seven C-O cores yielded  $\delta^{13}\text{C}$  values ranging mostly between  $-53$  and  $-43$  ‰ PDB (except for one sample yielded ca.  $-61$  ‰). These values, along with the presence of significant amounts of higher alkanes ( $\text{C}_2$  to  $\text{C}_4$ ) associated to  $\text{CH}_4$ , suggest that adsorbed methane in the studied argillites has a thermogenic origin. Because maximum burial temperature in the C-O argillites did not exceed ca.  $50^\circ\text{C}$ , the thermogenic nature of methane further implies that it originated from an external source and migrated into the argillites subsequently. This agrees with the existence of accumulations of natural gas in the vicinity (about 30 km) of the sampled site.

#### Conclusion

The results of this study suggest that C-O argillites interacted with meteoric waters and with externally-derived gaseous hydrocarbons, and were not the locus of significant post-depositional bacterial activity. Another implication is that  $\text{pCO}_2$  was primarily controlled by mineral equilibria.