



Stable isotope properties of fluid inclusion waters as a tool for paleo-hydrogeological reconstructions: a viability study

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In this study we evaluated the viability of the method of isotope studies of waters recovered from fluid inclusions in minerals for deriving the paleo-hydrogeological information from diagenetic, catagenetic, and epigenetic mineral phases in carbonate rocks.

An analytical line for studying the isotope composition of fluid inclusion waters was designed at MTSN (Trento, Italy) and assembled at IGG-CNR (Pisa, Italy). The line, operating in continuous He flow mode, comprised an electromagnetic crushing cell, a gas interface with cryogenic trap, and a ThermoFinnigan TC/EA unit (glassy carbon pyrolysis reactor and a gas chromatographic column). The line was connected, via a ConFlo III interface, to a Thermo Finnigan Delta^{Plus}XP mass-spectrometer. To prevent adsorption of water, the line (from crushing cell to TC/EA) was thermostated at 150°C. Calibration by injecting standard waters into the crushing cell showed the reproducibility of δD measurements within ± 5 per mil.

One set of samples was from Conchodon Formation (Liassic peritidal carbonate platform that underwent multiphase burial dolomitization) collected from outcrops in Southern Alps and from cored boreholes in the Po Valley (Lombardy, Italy). Sampled phases included the massive replacement dolomite, dolomite showing different degrees of re-crystallization, as well as epigenetic dolomite cements. Previous fluid inclusion studies suggested that re-crystallization and cementation occurred within 75

to 130°C interval. Although the "pristine" replacement dolomite and its re-crystallized varieties showed significant difference in $\delta^{18}\text{O}_{dol}$ (-6.3 vs. -2.2 per mil V-PDB, respectively), the δD values of the fluid inclusion waters in them were indistinguishable (ca. -37 per mil V-SMOW). In contrast, inclusion waters from epigenetic dolomite cements returned substantially less negative values (-25 to -12 per mil V-SMOW). This indicates deposition of epigenetic cements from isotopically distinct waters.

The second set of samples comprised euhedral calcite crystals from solutional cavities in the Triassic Dolomia Ladinica and Dolomia Principale (Mezzolombardo, Trentino, Italy). Calcite was deposited as two consecutive phases characterized by evolving crystal morphology (from scalenohedral to rhombohedral+prismatic), fluid inclusion temperatures (from 58-70°C to less than ca. 50°C), $\delta^{18}\text{O}_{cat}$ (-17÷-20 per mil to -9÷-11 per mil V-PDB), $\delta^{13}\text{C}_{cat}$ (from 2.0÷2.7 per mil to -6.0÷-7.5 per mil V-PDB), and trace element compositions. The δD values of fluid inclusion waters were found to change from -68÷-76 per mil in early to -83÷-86 per mil V-SMOW in late calcite. Coupled with $\delta^{18}\text{O}_{wat}$ values (estimated from $\delta^{18}\text{O}_{cat}$ and fluid inclusion homogenization temperatures), the data indicate two isotopically distinct sources of mineral-forming solutions. Interestingly, on the $\delta^{18}\text{O}$ - δD graph the early, higher-temperature waters plot close to the Meteoric Water Line (within ± 1 per mil $\delta^{18}\text{O}$ -band), whereas later, relatively low-temperature waters exhibit substantial positive " $\delta^{18}\text{O}$ -shift".

Studies of the stable isotope properties of fluid inclusion waters show great promise for paleo-hydrogeological and sedimentological studies, as they can provide independent constraints on the paleo-hydrogeological models, particularly on sources of paleo-waters.