

***In situ* U-Pb dating, oxygen isotope and trace element analyses of zircons from quartz vein and host UHP eclogite in the Dabie orogen**

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In situ SIMS analyses of oxygen and U-Pb isotopes as well as LA-ICPMS analysis of trace elements in zircon were carried out for a quartz-vein and its host UHP eclogite in the Dabie orogen, China. The results are used to trace the origin of metamorphic fluid and its isotopic and chemical alteration of protolith zircon during continental subduction-zone metamorphism. In CL images, most zircons separated from the vein and eclogite have distinct core-mantle-rim structures. The cores show clear oscillatory or patchy zonation and Th/U ratios of 0.13 to 2.12 typical of magmatic origin, and they have concordant or discordant U-Pb ages with upper intercept ages at 805 ± 30 Ma for the vein and 785 ± 41 Ma for the eclogite. The mantle and rim domains are characterized by no or weak zoning and Th/U ratios of 0.003 to 0.06, indicating their growth from metamorphic fluid. They have concordant U-Pb ages of 215 ± 2 Ma for the vein, and 220 ± 3 and 208 ± 3 Ma for the eclogite.

Most cores have largely variable positive $\delta^{18}\text{O}$ values of 1.92 to 4.76‰ for the vein and 0.19 to 6.9‰ for the eclogite with a few domains as low as -1.28‰. The cores with discordant U-Pb ages show variably depletion in ^{18}O , but the relationship between discordance and $\delta^{18}\text{O}$ is not systematic, indicating the isotopic alteration of the protolith zircon by metamorphic fluid to the two isotopic systems is not identical. The $\delta^{18}\text{O}$ values up to 4.76‰ with concordant U-Pb ages would approximately represent the original $\delta^{18}\text{O}$ values for magmatic zircons. Thus, the cores crystallized from an ^{18}O depleted magma in the Neoproterozoic, and then interacted with a much more depleted ^{18}O fluid of metamorphic origin in the Triassic. The mantle-rim domains have relatively uniform negative $\delta^{18}\text{O}$ values of -1.23 to -2.59‰ for the vein and -0.46 to -3.37‰ for the eclogite, suggesting their growth from the same origin of metamorphic fluid. The few cores suffered replacement recrystallization due to invasion of metamorphic fluid, resulting in slightly negative $\delta^{18}\text{O}$ values, and cloudy or chaotic zoning in the CL images. But they still have high Th/U values of 0.40 to 0.59, steep MREE-HREE patterns and high REE contents, indicating that zircon oxygen isotopes are susceptible to fluid action.

Moving beyond tracers: ^{13}C insights into carbon sequestration

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Science and society are faced with the inextricably linked challenges of fossil fuel energy dependence and rising atmospheric CO_2 levels. There is growing recognition that management of remaining hydrocarbon resources, exploration of less CO_2 -emitting 'cleaner' CH_4 and natural gas fuels, and investigation of subsurface capture and storage of anthropogenic CO_2 require a better understanding of the deep terrestrial carbon cycle [1]. Noble gases provide a tracer set that preserves a signal of fluid origin, transport, and age. Coupling this tracer set with carbon isotope geochemistry enables resolution of the inorganic and organic reactions controlling carbon mobility.

Prediction of the subsurface behaviour of CO_2 on a decadal time scale can be achieved through careful combination of laboratory and field experiments in engineered systems and modeling. Understanding the fate of injected CO_2 on the millennia time scale needed to assure reservoir competence and safety remains a challenge. A key unknown is the CO_2 residence time and mobility once injected. Addressing this requires understanding how much CO_2 ultimately reacts with the rock to form immobile carbonate rocks; how much remains in a near pure, but buoyant, CO_2 gas phase; and how much is dissolved into the groundwater.

Traditional use of carbon isotope signatures in investigations of CO_2 sequestration in saline aquifers and oil field brines focuses on injected tracer study approaches, are dependent on having a sufficiently different carbon isotopic signature between injected CO_2 and background CO_2 and dissolved inorganic carbon species (DIC) in the subsurface, and yield information on a timescale of years to decades. Recently the use of *in situ* carbon isotope studies in naturally occurring CO_2 -rich gas fields has demonstrated the insights available on CO_2 trapping mechanisms and water-rock interactions over millennial timescales from geologic analog sites worldwide.

[1] Sherwood Lollar & Ballentine (2009) *Nature Geoscience* 2, 543–547.