U/Pb age spectra of detrital rutile as a powerful tool for provenance analysis

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Compared with zircon, rutile is assumed to be unstable during low-grade metamorphic conditions, so that rutile grown under prograde metamorphic conditions should not contain inherited cores of older metamorphic events. Therefore rutile predominantly reflects the age of the latest metamorphic overprint. In general, metamorphic overprint is orogen-wide with similar ages in large areas. We therefore propose that detrital rutile age spectra can be utilized to distinguish between local sources (unimodal age distribution) and continent-wide catchment areas (several age peaks).

As part of a larger project aiming at detrital rutile of subgreenschist facies meta-psammitic rocks, several samples from the Saxo-Thuringian Zone of the Variscan Orogen have been dated. All detrital rutiles from the Neoproterozoic to Lower Silurian depositional ages show pre-depositional ages indicating that the rutiles are detrital and that the Variscan overprint has not reset the ages. Most samples show an unimodal age distribution, with Pan African ages between 600 and 800 Ma. However, rutiles out of one meta-sandstone with Late Ordovician / Early Silurian depositional age show a multimodal age spectrum. 30 % of the ages are > 1000 Ma and reaching a maximal age of 2200 Ma. This age distribution suggests erosion of other metamorphic domains and transport of the eroded material at the same time and to the same sedimentary environment as those from the Pan African Orogen. The Late Ordovician of the Saxo-Thuringian strata characterizes the transition from rift basin to a passive margin setting on the northern periphery from Gondwana [1]. The age spectrum indicates a direct sedimentary connection between Saxo-Thuringia and Gondwana during that period, perhaps by a continent-wide river system.

Alternatively, another source of multimodal detrital rutiles can be deposits of the Late Ordovician Hirnantian glaciation of Gondwana, which are found stratigraphically below the meta-sandstones [1]. However, this possibility would still imply a sedimentary connection between Gondwana and Saxothuringia.

[1] Linnemann et al. (2004) Int J Earth Sci 93, 683–705.

Reactivity of mafic and ultramafic rocks with CO_2 -charged fluids and the autocatalytic reduction of CO_2 to form CH_4

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Mafic and ultramafic rocks are highly reactive to carbon dioxide (CO₂). They may be potential repositories for sequestering CO₂ because of their capacity for trapping CO₂ in carbonate minerals. They are also capable of reducing CO2 to form CH₄ via molecular hydrogen (H₂) from serpentinization reactions. Geochemical laboratory experiments, reacting tholeite, picrite, and olivine with CO₂-charged fluids over a range of temperature (50 - 200°C) and pressure (100 - 300 bar) conditions, resulted in a high degree of rock alteration, secondary mineral formation and gas synthesis. In tholeite and picrite experiments, CO₂ is taken up from solution at all temperatures but the maximum extent and rate of reaction occurs at 100°C and 300 bar. The amount of CO₂ uptake at 100°C, 300 bar ranged from 8 wt% for a typical tholeite to 26 wt% for a picrite, where the amount of uptake coincides with the Mg content of the rock as a reaction limiting factor. Although geochemical modeling predicts an equilibrium carbonate alteration assemblage of calcite, magnesite, and siderite, only secondary ferroan magnesite was identified in the residual solids.

An alternate fate for CO_2 when reacted with ultramafic rocks is conversion to CH_4 . In olivine hydrolysis experiments (200°C, 300 bar), Fe^{2+} from olivine is incorporated into carbonates more rapidly than Fe^{2+} oxidation (and concomitant H_2 formation) leading to diminished yields of H_2 and H_2 -dependent CH_4 production. At carbonate equilibrium or under-saturated conditions, the experimental data suggest that produced magnetite catalyzes the reduction of CO_2 to form CH_4 . Rate calculations suggest that the kinetic balance between the production of H_2 and CH_4 in natural systems undergoing serpentinization may serve to discriminate between abiotic and biotic processes.

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