## Geochemical and carbon isotopic study in a karst groundwater system on Miyakojima Island, Japan

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Groundwater  $\delta^{13}$ C values and chemical compositions were employed to quantitatively evaluate the controlling processes and sources of dissolved inorganic carbon in a karst aquifer system on Miyakojima Island (MI), southwestern Japan. Most MI groundwater is Ca-HCO3 type water. The groundwater Ca/HCO3 ratio was relatively constant, as predicted by the dissolution processes of calcite and of CO<sub>2</sub> in the groundwater. WATEQ4F and PHREEQC calculations demonstrated that all groundwater samples, not only Ca-HCO<sub>3</sub> type groundwater but also groundwater of other types, were strongly influenced by dissolution of calcite and of soil CO<sub>2</sub> in this karst aquifer system. The system was open with respect to CO<sub>2</sub> with mostly around 10-50 matm as gas pressure, and most groundwater was saturated with respect to calcite. Detailed comparison of measured values and PHREEQC calculations for MI groundwater revealed that oxidation of ammonium sulfate (applied as fertilizer) played a key role in the groundwater chemistry by adding H<sup>+</sup>, which caused surplus calcite dissolution. Model calculations using the  $\delta^{13}$ C values and pH of the groundwater samples with PHREEQC were used to determine the mass fractions of DIC initially from calcite dissolution and from C3 and C4 organic materials, the origin of the soil CO2. On average, the contributions of calcite and C3 and C4 organic materials were estimated to be 46.4%, 18.5% and 35.1%, respectively. Of these, contribution of calcite was relatively constant in any groundwater, indicating easily occurrence of this process at anywhere in karst aquifer systems. The calculated mixing ratios of C3 and C4 organic materials, which explained the contribution of each to the DIC in the groundwater, were concordant with the land use on MI, that is, the distributions of forest and sugarcane fields. This fact indicates that the calculated mixing ratios from the model can be reasonably used to constrain groundwater information, such as its recharge area and flowpahts, in a specific study area where the distributions of organic materials in soil initially from C3 and C4 plants are clear.



**Fig.1:** The mass fractions initially from calcite and C3 and C4 organic materials by pie charts within the bubbles, expressing DIC contents in the MI groundwater.

## New time constraints on brittle faulting in the Toki Granite, central Japan

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Numerous studies [e.g. [1]] have highlighted the potential for determining the timing of near-surface brittle deformation using isotopic dating of authigenic illites in fault gouge. In recent years, precise size separation combined with mineral characterization of gouge samples has demonstrated the suitability of illite K-Ar dating for constraining the timing of brittle deformation [e.g. [2]], despite analytical difficulties such as contamination.

We discuss new K-Ar and fission-track age data from gouge samples collected from a fault in the Cretaceous Toki granite, central Japan. The fault occurs sub-vertically along the wall of a shaft exposing granite host rock. The minimum age of the fault deformation is estimated to be older than 20 Ma, as the Miocene sedimentary formation is not displaced by the fault. The gouge samples were separated into five grain-size fractions (<0.1, <0.4, <2, 2-6, 6-10 µm) and characterized by laser particle analyses, XRD, SEM, and TEM.

The fine fractions provide younger K-Ar ages, suggesting enrichment in more recently grown authigenic illites. The finest fractions (<0.1  $\mu$ m) give ages of 46 ±1 and 43 ±1 Ma (±2 sigma). The K-Ar ages of the fractions with no detectable contamination from detrital K-bearing minerals on XRD analysis, range from 53 to 43 Ma. The obtained illite age range is consistent with the stability field of illite and the main temperature field of brittle deformation within the cooling history of the host granite body of the fault, which was evaluated by apatite and zircon fission-track and K-Ar biotite ages from the host rock.

The internal consistency of the ages obtained from K-Ar dating of the two subsurface fault gouges, as well as their consistency with constraints from existing geochronological data demonstrate the potential of gouge dating in providing new data to constrain timing of brittle deformation in the Toki granite.

[1] Lyons and Snellenburg (1979), Geol. Soc. Amer. Bull. **82**, 1749-1752. [2] Zwingmann et al. (2010) Chem. Geol. **275**, 176-185.