

Targeted drilling for Re-Os geochronology to decipher complex history of overmature source rocks and migrated hydrocarbons

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Successful Re-Os geochronology depends on acquisition of samples with identical age and initial ¹⁸⁷Os/¹⁸⁸Os (Os_i), but varied Re/Os concentration ratios. Black shales and migrated hydrocarbons present unique challenges. Sampling strategy must be grounded in knowledge of the local sedimentology and maturation history, as these factors contribute to small-scale heterogeneity.

Two sampling strategies were employed for Re-Os geochronology using core from ICDP FAR-DEEP drillhole 13A, intersecting the ca. 2 Ga Zaonezhskaya Formation black siltstones near Shunga village in the Onega Basin, Russian Fennoscandia [1, 2]. First, six 7-9 g samples were taken from discrete segments spanning 5 m of drill core; each sample was pulverized and homogenized to minimize any Os_i heterogeneity. These samples yield an errorchron of 1852 ± 300 Ma (Os_i = 1.5 ± 2.0, MSWD = 40). Scatter is likely caused by migration of hydrocarbons in the section. Vitreous 'shungite', up to 70% carbon, is visible under a binocular microscope. These large 7-9 g samples contain both primary organic matter and locally migrated hydrocarbons, and thus are heterogeneous mixtures with variable Os_i and age.

Second, using the binocular scope, eight much smaller 450-500 mg samples were taken from drillhole 13A by targeted drilling of homogeneous black C-rich siltstone within a 3-cm section. These samples yield a Model 3 isochron age of ~1730 Ma with an Os_i of 5. Four additional samples from a new 3-cm section (0.5 m up section) improve the isochron statistics without a change in the nominal age or Os_i. We interpret this as the age of isotopic homogenization (maturation?) for the fossil hydrocarbons. This age is consistent with younger phases of the Svecofennian orogeny [3], known to have impacted the siltstones.

This is but one of many localities yielding meaningful ages by targeted drilling of heterogeneous shale-hydrocarbon sequences. Small samples (500 mg) can yield big results.

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[1] Melezhik *et al.* (2009) *Terra Nova* **21**, 119–126.
[2] Hannah *et al.* (2008) *33rd IGC*, Oslo, #1352701. [3] Stein (2006) *Lithos* **87**, 300–327.

Using hydrogen isotopes to assess proton flux during biological hydrogen production: Part 1

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Biological hydrogen production is mainly mediated by hydrogenase (H₂ase) enzymes, which combine protons from water with electrons to generate H₂. One major impediment to improving our understanding of H₂ metabolism is our inability to define adequately the regulation of and the flux through key pathways involved in H₂ production. To fill this need, we are developing the use of hydrogen isotopes as a tool to address fundamental questions related to hydrogenases and intracellular proton trafficking.

In the first phase of the project, we have overexpressed and purified a number of different H₂ases under anaerobic conditions, quantified the specific activity of the purified H₂ases, and constructed a custom-built GC-IRMS system to measure the isotope ratio of the collected H₂ with good precision (error ≤ 3‰) and sensitivity (0.2 μM in 1 mL headspace). As predicted, isotopic analysis of the H₂ generated by 7 different enzymes (including one nitrogenase) revealed that each H₂ase has a unique fractionation factor and produces H₂ with a distinct isotopic signature. In addition, our research will provide the first fractionation factors for these classes of enzymes.

In a second phase of the project, we are also performing *in vivo* experiments (see accompanying poster). Preliminary results indicate that the isotopic content of H₂ produced *in vitro* is remarkably similar to that measured *in vivo*. Together our results provide compelling evidence that hydrogen isotopes can be used to study biological H₂ production.