Rapid hydrogen isotopic exchange between aqueous hydrocarbons and water under hydrothermal conditions

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Numerous experimental studies have investigated D/^{1}H isotopic exchange between sedimentary organic matter (*e.g.* kerogen/oil) and ambient water during thermal maturation (Schimmelmann *et al.*, 2006). However, isotopic exchange involving low molecular weight hydrocarbons and water has received relatively little attention. Due to its high activation energy for exchange, alkyl-bound hydrogen (H) is widely considered to be isotopically conservative and incorporation of water-derived H is assumed to be limited to cracking reactions during catagenesis.

We conducted experiments to investigate D/^{1}H exchange between aqueous *n*-alkanes and water using a Au-TiO_2 flexible cell hydrothermal apparatus. C_1–C_5 *n*-alkanes were heated at 325ºC and 350 bar in aqueous solutions of varying initial D/^{1}H ratio (δD) in the presence of a pyrite-pyrrhotite-magnetite (PPM) mineral redox buffer. Extensive incorporation of water-derived H into C_2–C_5 *n*-alkanes was observed on timescales of months. In contrast, relatively minor incorporation was observed for CH_4. Isotopic exchange appears to be facilitated by reversible equilibration of *n*-alkanes and their corresponding alkenes by the reaction:

$$C_nH_{2n+2(aq)} = C_nH_{2n(aq)} + H_{2(aq)} \qquad (1)$$

Where $H_{2(aq)}$ is derived from water. The lack of substantial *n*-alkane decomposition on the timescale of observation, combined with an approach to steady-state isotopic composition, suggests that *n*-alkane δD values may reflect an approach to isotopic equilibrium rather than kinetically-controlled fractionation effects associated with degradation reactions. Substantially lower amounts of exchange were observed for ethane relative to C_3–C_5 *n*-alkanes, suggesting that alkene isomerization may enhance incorporation of water-derived H in these compounds. Thus, in reducing aqueous environments, reaction mechanisms exist that allow rapid D/^{1}H exchange of alkyl-H with water at elevated temperatures and pressures on timescales much shorter than previously assumed.

Reference

Schimmelmann, A., Sessions, A.L., Mastalerz, M., 2006, *Ann. Rev. Earth Planetary Sci.* **34**, 501–533.

Nickel isotope anomalies in iron and chondritic meteorites

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^{60}Fe decays to ^{60}Ni with a half-life of 1.49 Ma, and can be used to obtain relative ages for meteorites and processes that occurred within the first ~10 Ma of the formation of the Solar System. Radiogenic ^{60}Ni variations of <50 ppm are expected in iron meteorites, given ^{182}W core formation ages of asteroids and an initial ^{60}Fe/^{56}Fe ratio of 4 x 10^{-7}. However, previous studies have not been able to resolve the predicted variations in ^{60}Ni between magmatic iron groups having different Fe/Ni.

We have developed methods for high-precision Ni isotope analysis of metal and silicate samples. Ni is separated using a 3-stage ion exchange procedure, which includes dimethylglyoxime to yield a Ni fraction free of impurities, in particular Fe, Ti, Sn that potentially form interferences on Ni masses. Ni isotope ratios are measured using a Finnigan Neptune MC-ICPMS in medium resolution mode in order to resolve ^{40}Ar^{16}O from ^{56}Fe and correct for ^{58}Fe on ^{58}Ni (<5 ppm). ^{58}Ni signals of 900pA are measured on a Faraday detector equipped with a 10^{10} Ω resistor. Each sample was analysed a minimum of 4 times. Using this procedure we obtain a reproducibility of ~5 ppm on the ^{60}Ni/^{61}Ni ratio. Terrestrial samples (JP-1, BHVO-2, NIST 361 steel) have Ni isotope compositions that are identical within error of the SRM 986 standard.

Our results show that magmatic iron meteorites have variable ^{60}Ni/^{61}Ni, ranging from a terrestrial value in high Fe/Ni group IIAB, to ~15 ppm deficits of ^{60}Ni in low Fe/Ni group IVB samples. Although a positive Fe/Ni-^{60}Ni/^{61}Ni correlation is consistent with ^{60}Fe decay, we find that ^{60}Ni/^{61}Ni ratios are inversely correlated with variations in ^{62}Ni/^{61}Ni, which are likely to be of nucleosynthetic origin. Moreover, ordinary chondrites (LL) and volatile poor (CV) carbonaceous chondrites cover the same range in Ni isotopic composition as seen in the magmatic iron meteorites. These combined observations show that Ni isotopic heterogeneity within bulk planetary samples is widespread, but do not yield clear evidence of live ^{60}Fe during planetesimal core formation. Bizzarro *et al*. (2006) have previously noted variable ^{62}Ni/^{61}Ni in bulk meteoritic material but our different sample set illustrates several contrasting systematics. In particular, we find that iron meteorites have ^{62}Ni/^{61}Ni both higher and lower than terrestrial values. We suggest that Ni isotopes may provide a valuable means to link iron and chondrite groups, with IVB samples apparently derived from a CV-like parent body and IIAB from LL chondrite. Interestingly, the only meteorite group we have found to have Ni isotopic systematics identical to Earth are the enstatite chondrites.