Tracing time scales of fluid residence and migration in the crust

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Introduction: The Earth's crust is a vast reservoir of resources formed via natural geological processes. Furthermore, the crustal storage of substances undesirable for human beings, including nuclear wastes and carbon dioxide, has been considered. Crustal fluids (water, gas and oil) mediate chemical reactions, and they may transport, concentrate or disperse elements in the crust; the fluids are often valuable resources in their own right. Crustal fluids also play the role of messengers from the deep Earth through geothermal systems that may signal the activation of volcanism and/or earthquakes. In this context, determining the time scales of fluid transport and residence time is essential for understanding geochemical cycle of elements, as well as risk and resource management. The interactions between groundwater and gas or oil have been well studied, but the fluid migration rate or storage time of gas and oil in crustal reservoirs has rarely been determined due to the lack of optimal tracers. Combined studies of stable and radioactive noble gases will shed bright light on this field.

Geochemical analysis: Crustal fluids contain stable and radioactive noble gases indigenous to the fluid, which may be of magmatic or atmospheric origin of various ages. In addition, radiogenic and nucleogenic noble gases (both stable and radioactive) are continuously produced by the decay of U, Th and K and related nuclear reactions in the crust at known rates and in known relative proportions. They may be released from their production sites and incorporated into the fluid, acting as natural spikes to trace fluid flow. The concentrations of a noble gas isotope (^iC) in a crustal fluid in a system devoid of phase separation or mixing varies as:

$$\frac{d^iC_{Tot}}{dt} = -\lambda_i \cdot {}^iC_{Tot} + \frac{d^iC_{R}}{dt} \qquad (1)$$

The decay constant of an isotope *i* is λ_i. The subscripts *Tot* and *R* represent total and rock-derived, respectively. It leads to:

$${}^iC(t) = e^{-\lambda_i t}\left[{}^iC(0) + \int_0^t e^{\lambda_i x} \cdot f(x)dx\right] \qquad (2)$$

In this equation, $dC_R/dt=f(t)$. It is obvious that the concentration remains unchanged at $^iC(0)$ for a stable isotope ($\lambda_i=0$) that does not have a significant source in the crust ($dC_R/dt=0$). An isotopic ratio (R_{ij}) of a noble gas isotope, *i*, to a stable and indigenous isotope, *j*, evolves as:

$$\frac{R_{ij}(t)}{R_{ij}(0)} = e^{-\lambda_i t} \cdot \left[1 + \int_0^t e^{\lambda_i x} \cdot f(x)dx / {}^iC(0)\right] \qquad (3)$$

Assuming a constant input of in-situ produced isotopes ($f(t) = \kappa$), for first order

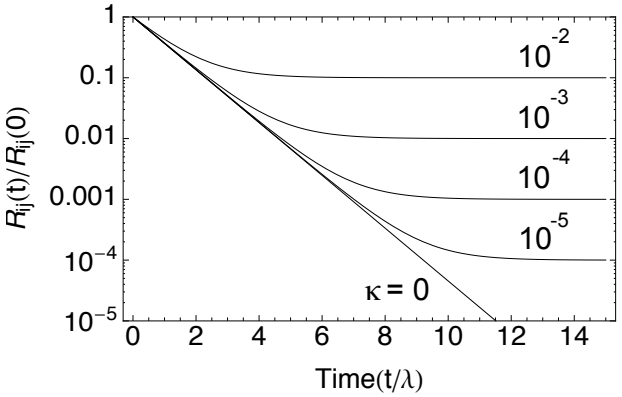

Figure 1: Model evolution curves of noble gas isotopic abundance based on Eq. (4). The x-axis represents the time normalized by the decay constant. The numbers adjacent to curves represent $\kappa/[\lambda_i \bullet {}^iC(0)]$.

approximation, this ratio evolves as (Figure 1):

$$\frac{R_{ij}(t)}{R_{ij}(0)} = e^{-\lambda_i t} + \frac{\kappa}{\lambda_i \cdot {}^{i}C(0)} \cdot (1 - e^{-\lambda_i t}) \qquad (4)$$

This equation contains two unknown parameters, κ and t. For κ = 0, i.e. absence of subsurface production and/or transfer of those isotopes into the fluid phase, the fluid migration time between two sites within a flow path can be determined simply by measuring the abundance of single radioactive isotope with an appropriate half-life. The best example of such geochemical tracer is ^{81}Kr. Otherwise, the migration time of the fluid between two points within single flow path needs to be determined using at least a couple of time-dependent isotopic abundances. Argon has one radioactive (^{39}Ar) and one stable (^{40}Ar) isotope produced in the crust, and provides an ideal isotope couple for tracing a relatively long fluid residence time in the crust (Yokochi et al., 2012). In practice, phase separations and/or mixing (including modern atmospheric contamination during sampling) can disturb the system. The relative abundances and isotopic compositions of stable noble gases are, however, good indicators of those processes and allow corrections for these effects in order to derive the original compositions. Krypton-85 is an unprecedented and unique tracer of atmospheric contamination that can distinguish the modern atmosphere from ancient one.

Potential applications: In the crust, fluid phases can obtain noble gas radionuclides either by experiencing gas exchange with meteoric water that contains atmosphere-derived components, or from reservoir rocks in which they are produced. They often contain abundant inorganic carbon, which compromises the use of cosmogenic ^{14}C isotopic abundance as a chronometer. Stable noble gases have been used for investigating the processes occurring in subsurface fluid reservoirs, during (i) migration of geothermal fluids (Sano and Wakita, 1985; Kennedy et al., 1987), (ii) evolution of hydrocarbon reservoirs (Ballentine et al., 1991; Pinti and Marty, 1995), and (iii) pilot or analogue studies of geological CO_2 sequestration (Gilfillan et al., 2008, Gilfillan et al., 2009). Noble gas radionuclides add enhanced capability of determining the time scales of these processes and fluid migration. Furthermore, the rate of release of radiogenic and nucleogenic noble gases from the production sites in minerals to the fluid phase may also be determined uniquely through the studies of noble gas radionuclides (Yokochi et al., 2012), which is fundamental to the behavior of volatile elements in geochemistry.

Case study: A pilot study of noble gas radionuclides in an active geothermal system was performed at Yellowstone National Park (Yokochi et al., 2012 in review). Prior studies of the Yellowstone system using stable noble gas isotopes show that the thermal fluids contain a mixture of atmospheric, mantle, and crustal components. ***Noble gas radionuclide measurements provide new chronometric constraints regarding the subsurface residence times of Yellowstone thermal fluids***. Upper limits on deep thermal fluid mean residence times, estimated from ^{39}Ar/^{40}Ar* ratios, range from 118 to 137 kyr for features in the Gibbon and Norris Geyser Basin areas, and are about 16 kyr in Lower Geyser Basin, with the key assumption that the fluid acquires its crustal component of Ar in Quaternary volcanic rock of the Yellowstone caldera. Krypton-81 isotopic abundances in the gas samples yield upper limits on residence time that are consistent with those obtained from ^{39}Ar/^{40}Ar* ratios.