Applications of ^{81}Kr and ^{85}Kr in Groundwater Hydrology

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Groundwater age is a parameter of fundamental importance in hydrological sciences. Groundwater age is usually defined as the mean subsurface residence time following isolation from the atmosphere, and it can be estimated either from Darcy's Law (based upon hydraulic conductivity and gradient) or from measurements of time-dependent abundances of natural isotopic tracers. It is one of the most elusive geologic parameters to quantify, despite its crucial significance for water resources, waste management, subsurface reactive transport, and paleoclimate reconstruction.

The optimal method for dating old groundwater is based on cosmogenic ^{81}Kr, which was difficult to measure before the recent development of the ATTA technique, owing to its low isotopic abundance ($^{81}Kr/Kr \sim 10^{-12}$). The ATTA technique has now been demonstrated to provide a practical approach for routine $^{81}Kr/Kr$ measurements of groundwater – this effectively opens the door for exploration of such measurements in a broad range of hydrologic systems where residence times are long. The only other quantitative tracer method for dating old (10^4–10^6 yr) groundwater involves measurement of cosmogenic ^{36}Cl ($t_{1/2} = 3.01\times10^5$ yr). The ^{36}Cl method is complicated by variations of the initial ^{36}Cl activity and by subsurface input of both stable chloride (Cl) and nucleogenic ^{36}Cl. Many groundwater aquifers do not meet the restrictive criteria for application of the ^{36}Cl dating method, e.g. those containing saline waters and brines, and therefore the ^{36}Cl method cannot be applied for dating such aquifers. The ^{81}Kr method can be used for dating brines.

In addition, ATTA can determine $^{85}Kr/Kr$ as well as $^{81}Kr/Kr$, and both measurements are readily performed on the same sample. This allows a number of unique applications in systems where old and young waters mix, or where short (< 50 yr) residence times occur but other tracers (e.g., tritium-helium or CFC's) do not yield coherent results because of gas loss.

Old Groundwater and ^{81}Kr. The first application of ATTA in an investigation of groundwater hydrology involved determining the residence times of old groundwater in the Nubian Aquifer located underneath the Sahara Desert in Western Egypt. The results of this study gave insights to the groundwater age and hydrologic behavior of this huge aquifer, with important implications for climate history and water resource management in the region. This study also demonstrated coherence of ^{81}Kr and ^{36}Cl activities. There were near-blank activities of ^{14}C and ^{85}Kr in these waters, as expected.

Other ^{81}Kr studies of old groundwater currently in progress, and for which preliminary data will be presented at TANGR2012, include: (1) the saline groundwaters of the Western Interior Plains Aquifer in Kansas and Missouri; (2) the brines of the Salado Formation near the Waste Isolation Pilot Plant in southeastern New Mexico; (3) the fossil fresh water of the Guarani Aquifer in Brazil and Argentina; and groundwaters of the Atacama Desert in Chile. Measurements of ^{81}Kr/Kr along with other solute and isotopic data in these systems will place strong constraints on flow rates and mixing processes, as well as insights into the general nature of continental scale aquifers and the long-term evolution of groundwater chemistry in such aquifers.

Young Groundwater and ^{85}Kr. The ability to determine residence times of young, shallow groundwaters is particularly important because of the fact that many shallow aquifers have been subject to contamination by hazardous and toxic substances such as solvents, heavy metals, pesticides, herbicides, endocrine disruptors, and radionuclides. Accurate residence time information for shallow groundwaters allows better understanding of the rates of natural attenuation of contaminants, as well as being useful for determining liability and implementing appropriate remediation strategies. The most successful methods available for determining residence times of young (<50 yr) groundwaters are: the tritium-^{3}He method, the CFC (chlorofluorocarbon) and SF_6 methods, and the ^{85}Kr method. The application of the ATTA method to measuring ^{85}Kr in young groundwater has several advantages over existing methods: (1) the CFC method and the tritium-helium method are becoming less useful because the decline of CFC input to the atmosphere and the decay of the bomb-produced tritium pulse have introduced ambiguity into residence time determinations by these methods; (2) Kr is unaffected by redox reactions such as those involved in biodegradation of CFCs; (3) there is a much smaller likelihood of local point sources of ^{85}Kr than is the case for tritium, CFCs and SF_6 (e.g. in landfills); and (4) ATTA measures the ratio ^{85}Kr/^{81}Kr, and this ratio is relatively insensitive to gas loss, recharge temperature or elevation, or to the presence of excess air, in contrast to the tritium-helium, CFC, or SF_6 methods. Results of an intercomparison study of ^{85}Kr/Kr measurements by ATTA-3 with CFCs and SF_6 (by GC) from a shallow young aquifer at Locust Grove, Maryland, will be presented.

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