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Disequilibria in the Uranium Decay Series During Weathering of Organic-rich Shale: Implications for Radon Generation.

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Summary

Radon gas is a product of the Uranium decay series that poses a significant public health threat. The objective of this study is to better understand processes that take place during chemical weathering leading to fractionation in this decay series. Of particular interest are the fate of Thorium 230 and Radium 226, as Radon 222 is generated from these daughter products on a time scale applicable to the weathering environment.

Introduction

The focus of this study is to better understand the generation of radon gas as a results of processes that occur and alter the distribution of daughter products in the Uranium 238 (U238) decay series. In particular, processes that may occur during chemical weathering and formation of soils. Understanding processes responsible for the generation of Radon is important because radon gas is the second leading cause of lung cancer in Canada; radon in homes accounts for about 16 per cent of lung cancer deaths (Canadian Lung Association, 2015). A 2016 University of Calgary study by Dr. Aaron Goodarzi shows that many homes in and around Calgary have high radon gas levels. Low air pressure in a building draws radon in from the surrounding soil; Radon can enter homes through crawl spaces, cracks in foundations, sump pumps, etc. Radon 222 (Rn222) is a naturally occurring radioactive gas that is produced directly through the decay of Radium 226 (Ra226) well down the U238 decay series. Ra226 is likewise produced from the radioactive decay of Thorium 230 (Th230) on a time scale that is appropriate for the weathering environment.

Theory and Methods

Fractionation of uranium 238 (U238) and uranium 234 (U234) during chemical weathering is well established. However, fractionation of other daughter in the decay series, such as Thorium 230 (Th230) or Radium 226 (Ra226) is not. We used analyses from three different instruments to collect data at different scales to assess the fractionation of these daughter products:

1. ***X-Ray Fluorescence (XRF)***. A portable XRF instrument was used to determine the total Uranium content of materials. We selected samples with variable, but relatively high total Uranium content (7 to 19 ppm) for further analyses. Samples selected include five subsurface samples, three from the Cretaceous Colorado Group and two from the Devonian Duvernay Formation, as well as two weathered outcrop samples from the Devonian Horn River Group.
2. ***ICP-MS***. Relative abundances of U234, U235 and U234 were measured from splits of each of the seven samples using a Neptune ICP-MS. The relative proportion of U235 to U238 is constant at about 7.25E-5 atoms U235 per atom U238 in the absence of processes involving isotope mass fractionation. Values of the relative abundance of U235 from all seven samples are within experimental uncertainty of this indicating there are no processes involving isotope mass fractionation. Under isotopic equilibrium the relative proportion of U234 to U238 is about 5.5E-5 atoms U234 per atom U238. All five subsurface samples have this equilibrium U234 content. However, the relative proportion of U234 for multiple analyses of sample splits from outcrop samples range from 2.2E-5 to 3.3E-5. Preferential removal of U234 during chemical weathering is well

documented in the literature and is generally thought to result from radiation damage to the host material from energy released during radioactive decay.

3. ***Alpha Particle Detector***. A Durridge Instruments RAD7 was used to detect alpha particles emitted from the decay of Polonium 218 (Po218), the short lived daughter product of the decay of Rn222. We placed between 550 and 1000 grams of crushed material from each of the samples above into separate 1 litre glass mason jars. The jars contained between 4 and 18 mg of Uranium. Alpha particle decays in each jar were measured over a period of several weeks to determine the amount of Radon generated in each.

Results

The RAD7 instrument was calibrated at the factory for soil gas analyses in terms Bq (alpha particle decays per second) per cubic metre of air. This calibration is not appropriate for the less than one litre of air in our jar experiments. We employed data from the XRF and ICP-MS analyses along with theoretical knowledge of the U238 decay series (Table 1) to calibrate our experiments. Initial experiments in which we simply placed pieces of core samples in jars resulted in high relative humidity in the jars. Although the RAD7 can compensate for this at low levels these levels were higher than recommended. We decided to dry the sediments for our jar tests in a drying oven at 105 C. This resulted in driving off Radon gas in addition to the water. It is unlikely that we drove off other daughter products as these do not readily go into the gas phase. We made theoretical predictions of the generation of Radon gas in our experiments through knowledge of the total Uranium content of the jars and assuming the decay series remained intact to Ra226. The theoretical generation of Rn222 from the decay of Ra226 is illustrated in Figure 1.

Isotope	Half Life minutes	atoms per atom U	mg per mg U	decays/sec per mg U
U 238	**2.35E+15**	**1**	**1**	**12.44**
Th 234	3.47E+04	1.48E-11	1.45E-11	12.44
Pa 234	1.20E+00	5.11E-16	5.02E-16	12.44
U 234	**1.29E+11**	**5.49E-05**	**5.40E-05**	**12.44**
Th 230	**3.96E+10**	**1.69E-05**	**1.63E-05**	**12.44**
Ra 226	8.42E+08	3.58E-07	3.40E-07	12.44
Rn 222	5.52E+03	2.35E-12	2.19E-12	12.44
Po 218	***3.10E+00***	***1.32E-15***	***1.21E-15***	***12.44***
Po 214	2.74E-06	1.17E-21	1.05E-21	12.44
Bi 214	1.99E+01	8.47E-15	7.61E-15	12.44
Pb 214	2.68E+01	1.14E-14	1.03E-14	12.44
Pb 210	5.52E+03	2.35E-12	2.07E-12	12.44
Bi 210	7.20E+03	3.06E-12	2.70E-12	12.44
Po 210	2.02E+05	8.58E-11	7.57E-11	12.44
Pb 206	stable			

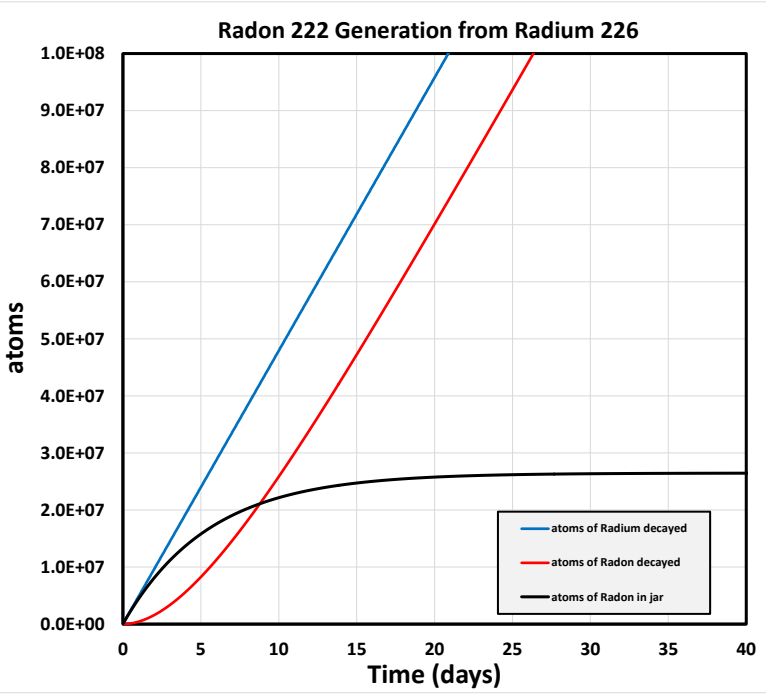

Table 1 and Figure 1. Table 1 contains data for the U238 decay series begininng with U238 working down to the stable Pb206. Under isotopic equilibrium the amount of a given daughter product is inversely proportional to its half life while the number of decays per second must be equal for all and are proportional to the amount of U238. Figure 1 illustrates the generation of Rn220 from Ra226. We dried the sediments for our jar tests driving off Radon gas in addition to the water; therefore, generation of Radon gas in our experiments follows the form of the black curve.

Results from one of the jar experiments performed on crushed core material from the Colorado Group are displayed in Figure 2. This jar contained 556 grams of core sediment with a total of 4.45 mg of Uranium as determined by XRF. ICP-MS analyses yielded equilibrium values for both the U235 and U234 content. Therefore, we expect the U238 decay series to be in isotopic equilibrium and be capable of generating a Radon gas level resulting in 55.4 Rn222 and Po218 decays per second (55.4 Bq). The sample was dried prior to being placed in the jar and sealed, so we expect the radon generation to follow the shape of the curve in Figure 1. The instrument measured far fewer decays than expected. All five jar experiments from subsurface samples showed the same trends. A calibration factor of 450 times the measured decays gave a very good fit to all (this may seem high, but considering the manufactures calibration factor for soil gas determinations is nearly 20,000 we think it reasonable).

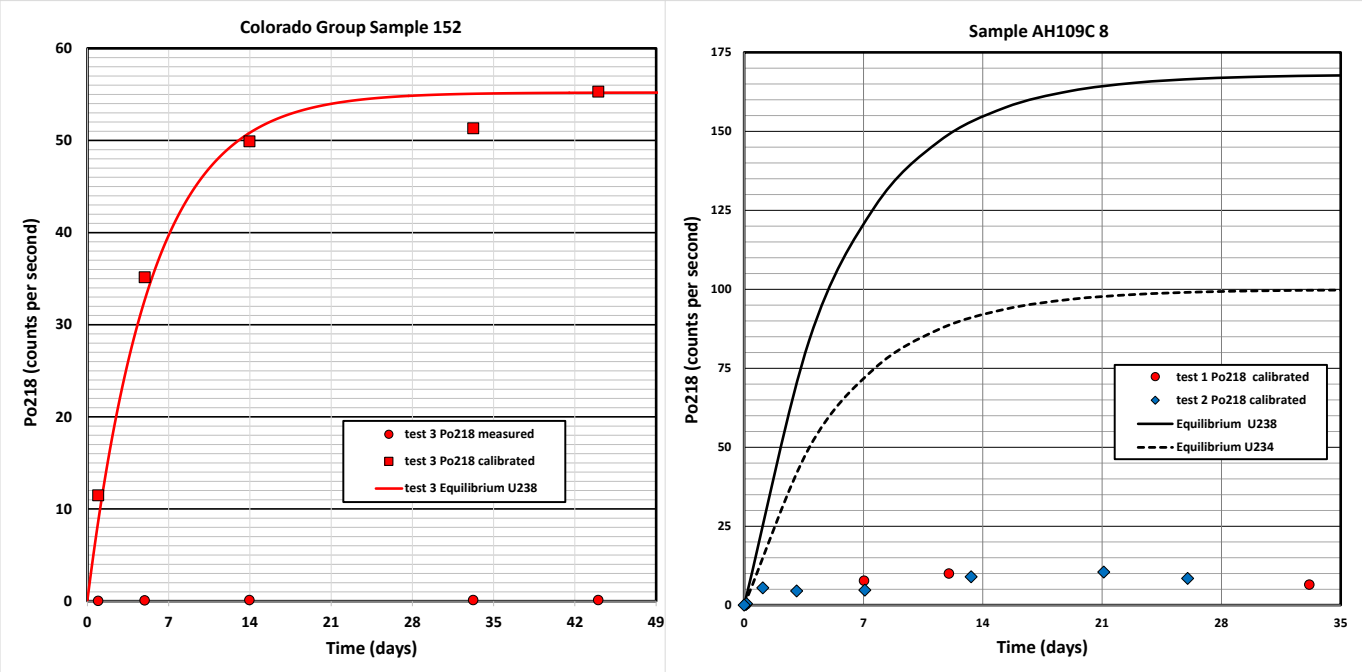

Figure 2 and Figure 3. Figure 2 (left) contains data from one of the subsurface samples where the U238 decay series is thought to be in isotopic equilibrium. Circles represent actual counts per second, red curve is theoretical value and red squares are actual counts times a calibration factor of 450. Figure 3 (right) contains data from one of the outcrop samples where the U238 decay series is not in isotopic equilibrium. Curves are for U238 and U234 equilibria theoretical value and symbols are actual counts times a calibration factor of 450.

Results from jar experiments performed on crushed outcrop material collected along the Alaska Highway from the Horn River Group are displayed in Figure 3. This jar contained 750 grams of sediment with a total of 13.44 mg of Uranium as determined by XRF. ICP-MS analyses yielded equilibrium values for the U235, but not for the U234 content. We do not expect the U238 decay series to be in isotopic equilibrium, nor do we expect the system to be in isotopic equilibrium with the U234 content as it would take several hundred thousand years to establish this and we do not believe these rocks have undergone chemical weathering over this time span. If only U234 but not Th230 or Ra226 were removed the sample should be capable of generating a Radon gas level between the U238 and U234 equilibria values and likely closer to the U238 value. For U238 this is 168 Rn222 and Po218 decays per second (168 Bq) and for U234 equilibria it is 99 Rn222 and Po218 decays per second (99 Bq). Again, the sample was dried prior to being placed in the jar and sealed, so we expect the radon generation to follow the shape of the curve in Figure 1. The instrument measured far fewer decays. Applying the calibration factor of 450 times the measured decays yields values of 5 to 10 decays per second. The results indicate substantial removal of both Th230 and Ra226 from the system during chemical weathering.

Implications

Radon generation experiments on weathered samples show that in addition to the well established preferential removal of U234 from the host during chemical weathering that both Th230 and Ra226 are prefentially removed in even higher proportions. No soil is forming on the weathered bedrock samples from the Horn River Group and it is likely that these daughter products of the Uranium decay series are removed in the creek that flows over them. However, the experiments here lead to several questions as to the fate of Th230 and Ra226 in other weathering environments such as those forming soils. The experiments above show that these radioactive daughter products are preferentially removed from the host. Both Thorium and Radium are thought to have high affinity for adsorption onto clay minerals. We feel it likely that as these isotopes are preferentially leached from their host they may be adsorbed on clay minerals (or other materials) and become enriched in some horizons. If so, this could be a mechanism for the generation of high levels of Radon gas.