

The laboratorial evaluation of the transfer of ^{234}U and ^{238}U to the waters interacting with carbonates and implications to the interpretation of field data

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Dissolution processes at the rock-water interface frequently result in $^{234}\text{U}/^{238}\text{U}$ activity ratios (AR's) greater than 1 for U dissolved in water. Alternative mechanisms which have been suggested for the generation of such enhanced AR's include preferential chemical dissolution of ^{234}U because of its oxidation during the decay processes by which it is formed or because of radiation damage to the crystal lattice in the vicinity of ^{238}U decay (Rosholt *et al.*, 1963; Fleischer, 1980), and α -recoil release of ^{234}Th at the rock-water interface (Kigoshi, 1971). Experimental etch/leach of Carboniferous Limestone gravels performed by Bonotto and Andrews (1993) demonstrated the generation of AR's greater than the radiochemical equilibrium value on a laboratory short time-scale. This abstract considers the effect of chemical etch/leach on the AR of dissolved U under various conditions involving carbonate matrices different of those referred by Bonotto and Andrews (1993).

Material and methods. The area considered in the present work for the application of the experimental data is the Mendip Hills district of England. Six samples were collected at Lime Kiln Quarry, Whatley Quarry and Burrington Combe almost in the center of the Mendip plateau, and consisted of grey to dark grey hard, massive, and fine-grained dolomite and limestones of marine origin, which belong to the Black Rock sedimentary facies, one main group of the Carboniferous Limestone Series extensively quarried in the area. Measurements of Ca, Mg, and U contents and AR were made on the acid-soluble (6M HCl) part of the rock matrix, but the U content and AR were also measured on the residues from such an attack, which were dissolved in HF + HClO₄. ^{238}U and ^{234}U were recovered by coprecipitation on Fe(OH)₃ and were subsequently separated from Fe³⁺, Ca²⁺ and Mg²⁺ by solvent extraction and anion-exchange procedures. They were then electrodeposited on stainless-steel planchets for assay by α -spectrometry.

Freshly crushed and sized samples were subjected to chemical dissolution in the laboratory under controlled conditions, where the gravels were initially washed with distilled water to remove any finely divided material. After drying, 3.5–15 kg aliquots were weighed into 5–20 litres glass bottles and subjected to chemical etch at room temperature ($\sim 20^\circ\text{C}$) under three conditions: etch with distilled water outgassed with N₂, etch with distilled water equilibrated with the atmosphere (pH = 5.65), and etch with distilled water saturated by CO₂ at 1 atm (pH = 2.15). The solutions were daily circulated through the rock aggregates, and they were periodically removed for analysis and replaced by a fresh one, where etching was continued in this sequential manner for up to 192 days. The etch solutions were filtered through a 0.45 μm Millipore membrane, an aliquot was reserved for Ca and Mg measurements, and the remainder was used for U and AR determinations.

The specific surface area S (cm^2g^{-1}) of the distribution of gravels was determined by the counting of a great number of particles (at least 600 randomly selected), and the weighing of this total amount. After evaluating the average mass m of each particle distribution, the value of S was calculated from the equation $S = (36\pi/\rho^2m)^{1/3}$, where ρ is the rock density (g cm^{-3}). The values ranged from 1.19 up to 6.14 cm^2g^{-1} , where the particle mass was lognormally distributed for one sample, yielding a modal value of 0.33 g and a median value of 0.46 g, which were determined in this case by individually weighing the fragments.

Analysis of the rock matrices. The Ca content in the 6 M HCl-soluble fraction of the limestones ranged from 30.75 up to 38.19%, whereas the Mg content varied between 0.15 and 2.5%; the dolomite sample showed a lower Ca content (21.38%) and a higher Mg content (11.06%). The results of the U content

for the analysed samples showed that their composition is variable, with the U content of the silicate (insoluble) fraction being significantly greater than that of the carbonate fraction. The non-calcareous residues exceeded 5% in two cases, and were composed of quartz with some feldspar and phyllosilicate minerals, the latter dominated by mica with minor amounts of kaolinite (Findlay, 1965). The weighted mean U content of the samples suggested that on average about 70% of the U is present in the 6 M HCl soluble fraction, where the lower value obtained in this fraction corresponded to 0.23 $\mu\text{g/g}$ for the dolomite sample. The highest U content corresponding to 14 $\mu\text{g/g}$ was found on the 6 M HCl-insoluble part of one limestone sample, whose AR value was 0.82 ± 0.08 , lower than unity. The other AR's values were equal to 1, within experimental errors, which indicated that secular radioactive equilibrium was established between ^{238}U and ^{234}U on the 6 M HCl-soluble and insoluble parts of the same rock matrices.

Analysis of etch/leach solutions. The results of the analyses of etch/leach solutions demonstrated that significant reaction took place in each set of experiments. The U, Ca, and Mg dissolution showed to be a two-stage process characterized by parabolic and linear kinetics, in which the limestone/dolomite surfaces are dissolved by zero-order etch (constant etch rates with time) and first-order chemical leach (in general, decreasing leaching rates with time), confirming the previous data of Bonotto and Andrews (1993). Such a behaviour was independent of the type of etchant used, where the amount of U dissolved was strongly correlated with both Ca and Mg dissolution, and became linearly related as the process showed to be dominated by true zero-order etch.

The depth, d , of material which was removed by continuous surface etch was calculated from the mass, M_{Ca} , of Ca^{2+} dissolved and the specific surface area of the rock sample, using the equation $d = M_{\text{Ca}}/S_{\text{fp}}$, where f is the fractional mass of Ca in the rock. In the case of the relatively slow etch by N_2 - or air-saturated water, the depth of etch ranged from 13 up to 298 nm for the set of experiments performed with limestones, and from 112 up to 605 nm for the experiments performed with dolomite. However, higher values varying between 189 and 5578 nm were found for the more aggressive etchant, CO_2 -equilibrated water. Except for one limestone sample, the initial Ca^{2+} dissolution rates were much greater, not conforming to zero-order reaction rates, and being attributed to a gradual change from a first-order reaction (rate diminishing with time) to the constant rate zero-order process generally observed later.

The preference for U relative to Ca dissolution, $P_{\text{U/Ca}}$, was calculated from the equation $P_{\text{U/Ca}} = R_{\text{solution}}/R_{\text{rock}}$, where R is the molar ratio U/Ca, and yielded values between 1.7 and 19.5, confirming that uranium is etched/leached preferentially to Ca. A similarly defined preference ratio $P_{\text{U/Mg}}$ indicated values lower than 1 for the rapid etch of one limestone sample with CO_2 -equilibrated water, suggesting the preferential dissolution of Mg relative to U. However, high preference ratios $P_{\text{U/Mg}}$, between 20.3 and 34.9, were observed for the etch of dolomite with air-equilibrated water.

The AR of dissolved U in etch solutions generally increased as etch proceeded. However, the AR value for cumulative etch didn't approach of 1.3 as the Ca^{2+} content increased, as reported by Bonotto and Andrews (1993), since values corresponding to 1, 1.1, 1.2, 1.5, 1.6, and 1.8 were found. In contrast with these values showing equilibrium alpha-activity ratios of unity and the excess of ^{234}U , it was also possible to measure AR's of ~ 0.9 for all etchants of one limestone sample. Such an unusual AR value in solution must be related to the deficiency of ^{234}U in discrete fine particles of micaceous minerals in 6 M HCl-insoluble fraction, as identified in the analysis of the rock matrix; total dissolution of these fine particles during the initial etching period certainly provided the measured AR's values in solution. The observed cumulative AR's values were not related to the total surface area and total mass of rock matrices used for the etch/leach experiments; the different final values probably are being affected by the inhomogeneous U distribution in the multi-grain aggregates, a parameter difficult to be evaluated.

AR's in groundwater sources on the Mendip Hills. Groundwaters from the Mendip karst are low-temperature systems, have short residence times less than several days (Atkinson, 1977) and are reducing in character, despite the positive Eh values. Equilibrium AR's values and enhanced AR's between 1.3 and 2 have been observed, practically within the range of those found for the solutions in the laboratory experiments, suggesting that the lab data are reliable to interpret field data. The α -recoil process requires either a residence time of some hundreds of thousands of years or a large U enrichment by deposition at a redox boundary to significantly increase the AR of dissolved U within relatively short time-scales (some years to tens of years). Therefore, it is clear from the short duration of the laboratory experiments and from the short residence times for karstic groundwater that α -recoil processes cannot contribute to the generation of enhanced AR's in the groundwater.