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^{14}C in uranium and thorium minerals: a signature of cluster radioactivity?

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Abstract. Various uranium and thorium minerals have been analysed with accelerator mass spectrometry to determine their ^{14}C content. It is found that, whenever the contribution from secondary reactions such as the ^{11}B(α,p)^{14}C is sufficiently low, the ^{14}C concentration is consistent with that expected from ^{14}C (spontaneous) cluster radioactivity from radium isotopes of the uranium and thorium natural series.

1 Introduction

The spontaneous emission of heavy ions from members of natural radioactive series or from other heavy nuclides, called cluster radioactivity, has stimulated interest since its discovery [1, 2]. Moreover, the development of accelerator mass spectrometry (AMS) [3] has prompted several investigations in recent years of the subsurface production of long lived radioisotopes both from the theoretical and experimental point of view. A good example is ^{14}C, which, in addition to its well known importance in archaeometry and in environmental sciences, is of interest to hydrogeologists and hydrogeochemists, e.g. to establish the residence time of deep groundwaters [4–7].

Calculations of *in-situ* ^{14}C production in uranium rich minerals have been carried out by various groups [5–7]. These are based on different mechanisms such as neutron and alpha induced reactions and spontaneous emission of heavy ions such as ^{14}C from ^{223,4,6}Ra isotopes present in equilibrium within the uranium or thorium minerals. ^{14}C concentrations have been measured in several such minerals [8, 9] and compared with theoretical expectations.

However, no definite conclusion has been reached on the relative importance between such mechanisms, particularly cluster decay and the production due to the ^{11}B(α,p)^{14}C reaction, which recent studies [8, 9] have shown to be the most important in typical uranium minerals among the energetically possible n-and α-induced reactions.

In a recent work [10] we have pointed out that this unsatisfactory situation was due to the lack of a complete and consistent measurement of the ^{11}B(α,p) cross section, which we have thus measured in the energy range of interest (3–7.7 MeV). Moreover, and in contrast to previous studies [8, 9], we have shown that by using the known decay rates for ^{14}C emission from radium isotopes [1] and our measured cross section, the cluster decay contribution is comparable to the one due to the ^{11}B(α,p) reaction (and therefore measurable) only when the ^{11}B content of the mineral is $\leq$1 ppm.

In this paper we present the result of AMS measurements of ^{14}C concentrations in uranium and thorium minerals as well as a comparison with calculations performed on the basis of the above outlined recent achievements. Particular care is devoted to the boron content in choosing the minerals, which for a few of the analysed samples meets the above condition.

2 Sample preparation

U-ore samples of different origins were selected with U concentrations ranging from 2 to 90% and with boron content from 1 to 100 ppm. Samples were characterised for elemental composition by ICP-AES and by XRF and for mineral type by XRD. Sample masses of about 10 g were crushed (to a grain size of μm), loaded onto a recrystallised alumina boat and evacuated at 300°C in a tube furnace, to eliminate adsorbed atmospheric CO$_2$. Sample combustion was achieved by heating to 900°C in the presence of O$_2$ and the resulting gas fraction discarded. This fraction is a product of the decomposition of organic matter and carbonates [8]. The temperature was then raised

Table 1. Results obtained for the analyzed minerals. For each sample the description and origin (when known) are given, together with the measured U, Th and B concentration. The experimental values of ^{14}C content, obtained after the background subtraction, are compared with the calculated ones due to ^{11}B(α,p) reaction and to cluster radioactivity

acquisition	description	origin	M_{sample} (g)	M_{carbon} (mg)	^{14}C (pMC)	U (%)	Th (%)	B (ppm)	^{14}C atoms/g of mineral ($\times 10^6$)			
									exp	from ^{11}B	from cluster decay	^{11}B+ cluster decay
OZB000	Pitchblende	Zambia	9.5	0.13	44.36±0.44	87.3	–	47	0.32	8.69	0.168	8.86
OZB000-2	Pitchblende	Zambia	12.4	0.21	31.26±0.36	87.3	–	47	0.27	8.69	0.168	8.86
OZA996	Pitchblende	Zambia	10.54	0.19	14.47	88.8	–	45.1	0.086	8.48	0.171	8.66
OZA998	Uranite+ Thorianite	Madagascar	7.1	0.52	7.39±0.12	18	69	0.5	0.13	0.032	0.075	0.107
OZB005	Davidite+ Carnotite	South Australia	7.76	0.38	6.62±0.12	2.44	–	3.3	0.046	0.017	0.0047	0.0218
OZA989	Coffinite	Tasmania	9.64	0.22	31.38±0.41	81.2	–	118.2	0.37	20.3	0.156	20.5
OZA992	Coffinite	unknown	8.1	0.09	39.71±1.3	55	–	0.5	0.21	0.058	0.106	0.164
OZA013	Blank 9 Graphite	commercial	$2.6 \cdot 10^{-3}$	0.22	8.3±0.18	–	–	–				
OZA013	Blank 10 Graphite	commercial	$2.7 \cdot 10^{-3}$	0.04	24.88±1.31	–	–	–				
OZC365	Blank Granite	Australia	5.26	0.1	15.8	–	–	–				

to 1500°C, in presence of O_2, and the resulting gas was collected for analysis.

The phase diagram of the U-O binary system [11, 12] is complicated by the presence of a number of non-stoichiometric compounds. The melting point of pure UO_2 is approximately 2800°C, far above our analytical selected temperature. For O/U ratio below 2, the presence of a liquid phase is evident over 1100°C; for O/U ratio above 2 a major phase transition is observed at 1123°C with the disappearance of U_4O_9. X-ray diffraction was unable to provide the exact composition of the U-oxides, preventing a precise determination of the melting temperature for these mixtures. Nevertheless, the presence of free O_2 at this temperature is likely to enhance U-oxide phase transitions and recrystallisations allowing the trapped C to be converted to CO_2 which subsequently evolves out of the matrix.

Combustion products were collected in a borosilicate glass tube over metallic Cu and Ag, using a liquid nitrogen cold trap. The sealed tube was then transferred to a conventional furnace at 550°C for CO_2 purification. Residual Gas Analysis of test samples verified the good performance of this purification method. The total mass of C collected between 900 to 1500°C was determined by pressure accurate measurement of the CO_2 in a closed vessel prior to graphitisation. Graphite targets for AMS analysis were obtained by CO_2 reduction over hot Zn using Fe powder as catalyst, using a modified procedure of Jacobsen *et al.* [13]. The pressure inside the graphitisation tube was monitored to assure complete reduction of the CO_2.

Blanks used for background correction were prepared from a commercial graphite (free of ^{14}C) and from a sample of granite processed as described in the above procedure.

The ^{14}C content of the samples were determined using the ANTARES accelerator mass spectrometer at the Lucas Heights Science and Technology Centre [14].

3 Results

Table 1 shows results for the selected samples. The ^{14}C concentration, measured by AMS, is expressed as Percent of Modern Carbon (pMC), after correcting for background.

The accelerator background was lower than 0.1 pMC and the chemistry background correction was determined according to the equation

$$^{14}\mathrm{C}_{\mathrm{bckgr}} = \mathrm{A} + \frac{\mathrm{B}}{\mathrm{M}_{\mathrm{blank}}} \tag{1}$$

where the parameters A and B are determined experimentally by preparing blank samples of different mass. Using the three blank samples shown in Table 1, values of A = 3.16 and B = 0.86 are obtained. This method for determining the appropriate background correction for samples with different C mass is described in [15].

pMC can be related to the concentration, in ^{14}C atoms per gram of mineral, according to the equation

$$\frac{^{14}C}{g} = \frac{pMC}{100} 1.2 \times 10^{-12} \frac{M_{\mathrm{carbon}}}{M_{\mathrm{sample}}} \frac{N_{\mathrm{Avo}}}{12} \tag{2}$$

where $\mathrm{N}_{\mathrm{Avo}}$ is the Avogadro number. The final ^{14}C concentration is given in column 10.

Columns 11 and 12 show the calculated ^{14}C concentrations due to the ^{11}B(α,p) reaction and cluster decay respectively. For the former, we used the equation

$$\frac{^{14}\mathrm{C}}{\mathrm{g}} = \rho \frac{\mathrm{N}_{\mathrm{Avo}}}{\mathrm{A}(^{11}\mathrm{B})} \mathrm{X}(^{11}\mathrm{B}) \sigma \mathrm{X}(\mathrm{U}) \phi \mathrm{R} \tau \tag{3}$$

where ρ is the average density of the mineral; A(^{11}B) is the atomic weight of ^{11}B; X(^{11}B) and X(U) are the ^{11}B and U fractions (by mass), σ is the effective cross section calculated by integrating the ^{11}B(α,p) excitation function from 0 to 7.7 MeV; R the corresponding α particle range; $\phi = 3.87 \times 10^{11}$ X(U) and 1.28×10^{11} X(Th) the α particle flux per year and per gram of mineral for uranium and thorium respectively; τ the mean life of ^{14}C.

In contrast to previous works [8, 9] which base their calculations on a constant value for the cross section, our calculations as discussed in [10] follow exactly the energy loss process of α particles within the mineral by using the differential ^{11}B(α,p) excitation function.

For cluster radioactivity, we assumed an equilibrium condition for ^{223,6}Ra in uranium minerals and for ^{224}Ra in thorium ones, and used the weighted averages of the corresponding ^{14}C/α branching ratios reported in the recent compilation of Hourany [1], with the result

$$\frac{^{14}\mathrm{C}}{\mathrm{g}} = 1.924 \times 10^5\,\mathrm{X(U)} + 5.92 \times 10^4\,\mathrm{X(Th)} \qquad (4)$$

4 Discussion and conclusions

We base our discussion on results shown in Table I, and compare first the experimental values of ^{14}C concentrations (column 10) with the theoretical estimates of summed cluster decay and ^{11}B contributions (column 13). At first glance, we clearly see on average a large discrepancy – the theoretical values greatly overestimating, in general, the experimental results. However, the two sets of values rapidly converge with decreasing boron concentration of the analysed minerals (see Table 1). Samples exhibiting the largest discrepancy such as OZA989 and OZA996 are characterised by the largest boron concentrations. In contrast the ratio of $^{14}\mathrm{C}_{\mathrm{theor}}/^{14}\mathrm{C}_{\mathrm{exp}}$ is ~0.5 for OZB005 which has a boron content of 3.3 ppm and only ~0.8 for OZA998 and OZA992 with ~0.5 ppm.

It is interesting to note that if we compare the experimental results with the calculations based on cluster decay contribution only, we get quite a reasonable agreement, generally within a factor ~2.

The most striking conclusion one can draw from the above analysis is that our experimental results are generally not correlated at all with the boron content of the measured samples, an effect that becomes now particularly meaningful due to the above described improvements in the boron channel calculations.

A possible explanation lies in the spatial distribution of the boron atoms in the uranium or thorium matrix. It is clear that only if the boron atoms were uniformly distributed within the radioactive material would our calculated concentrations be realistic. If not, they will only represent an upper limit on the basis of the assumption that each alpha particle has equal probability to interact with a ^{11}B nucleus. The scale of what we define to be a "uniform distribution" is given by the maximum range of alpha particles emitted by members of the radioactive series in uranium or thorium oxide, i.e. about 25μm.

On the other hand, at very low boron concentrations ($\leq$1 ppm), it is more likely that the ^{14}C content is mainly represented by the radiogenic (cluster decay) contribution [10], which depends only on the quantity of uranium and thorium.

Indeed, as remarked above, these are just the samples which agree rather well with the theoretical predictions shown in column 13.

We now compare our results with those of Barker *et al.* [8] and Jull *et al.* [9]. These authors measured ^{14}C concentrations in several uranium minerals with the AMS facility of the University of Arizona, together with their boron and uranium contents. Although both their and our data have been obtained with similar techniques on similar minerals, our ^{14}C concentrations are, in general, one order of magnitude smaller than those of [8] and [9]. It is not easy to understand the origin of this difference. It is possible that microscopic differences in the distribution of boron densities or inhomogeneities of the minerals analysed in the two laboratories could result in large differences in measured ^{14}C concentrations even under conditions of equal bulk density. Another explanation may lie in the fact that we employed a different temperature regime to extract trapped carbon atoms from our mineral samples: 1500°C vs 1150°C in the case of [8] and [9]. However, without knowledge of B inhomogeneities our explanations are only speculative. Efforts to map boron distribution in a few selected samples by means of a Scanning Electron Microprobe (SEM-EDS) have, up to now, been unsuccessful because of the small signal to noise ratio we obtained.

On the other hand, understanding the reasons of the discrepancy in theoretical predictions between the present and the earlier work is less speculative. A major reason is the ^{11}B(α,p) cross section. In [8] a constant value of 20 mb was used, while a higher value, 100 mb, was used in the subsequent paper [9]. We have, on the other hand, used our recently measured, strongly energy-varying, cross section [10] to obtain a more realistic estimate of the production due to boron impurity. A second reason is in the formula which has been used to evaluate the above contribution: if the fraction of boron content X(^{11}B) is expressed in ppm (μg/g), the boron atomic weight has to be used in the denominator of formula (3), while in [8] the average atomic weight was incorrectly adopted.

In conclusion, we have shown that uranium and thorium rich minerals with a low level ($\leq$1 ppm) of boron contamination have a ^{14}C content which is consistent with the one predicted for ^{14}C cluster radioactivity for the various radium isotopes of the uranium and thorium natural radioactive series. On the other hand, by inverting this reasoning, one could consider the above result as a completely independent measure of the ^{14}C decay rates, which do agree within ~20% with existing data.

In the case of higher boron content, the cluster decay contribution is expected to be overwhelmed by the one due to the ^{11}B(α,p) reaction. However, most probably because of the non-uniform spatial distribution of boron atoms, this prediction is only partially verified by data, which are still very close (within a factor ∼2) to the cluster decay contribution only.

Apart from the nuclear physics implications, our result is relevant for hydrogeology. The "*in situ*" production of radionuclides has been deeply investigated because of its possible influence on groundwater age estimations. Andrew and Fontes [7] concluded that "*in situ*" radiocarbon production could become significant in hydrogeological environments where soil-generated Total Dissolved Inorganic Carbon (TDIC) is not present and where uranium and thorium concentrations are high. This is the case for example of low fracture flows in crystalline acid rocks. In addition, groundwaters with an "*in-situ*" ^{14}C-labelled TDIC could exchange with calcite in the fractures and raise their ^{14}C content [17]. Fracture filling material analysis is currently used in the safety assessment of underground waste disposal sites, to prove the absence of recent groundwater circulation. Calculations of the equilibrium ratio are made on the basis of bulk analysis of high cross section elements, regardless of their distribution in the rock. This might lead to an overestimation of the production rates in the case of alpha induced reactions like the one on boron.

In conclusion, our study stresses the importance of performing direct measurements instead of using calculated estimates in cases where the "*in situ*" production of radionuclides could be relevant, in order to avoid erroneous interpretation of goundwater flow and residence time.

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