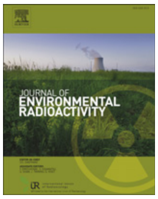
Journal of Environmental Radioactivity 120 (2013) 33–38

Contents lists available at SciVerse ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad



Investigation of the isotopic ratio ^{129}I/I in petrified wood

Tania Jabbar [a,*,1], Peter Steier [b], Gabriele Wallner [a], Otto Cichocki [c], Johannes H. Sterba [d]

[a] *Department of Inorganic Chemistry, University of Vienna, Währingerstr. 42, A-1090 Vienna, Austria*
[b] *VERA Laboratory, Faculty of Physics – Isotope Research, University of Vienna, Währingerstr. 17, A-1090 Vienna, Austria*
[c] *Department of Geology, University of Vienna, Althanstr. 14, A-1090 Vienna, Austria*
[d] *Atom Institute-Technical University of Vienna, Stadionallee 2, 1020 Vienna, Austria*

ARTICLE INFO

Article history:
Received 3 August 2012
Received in revised form
19 December 2012
Accepted 23 December 2012
Available online 13 February 2013

Keywords:
Petrified wood
^{129}I/^{127}I
^{238}U
Accelerator mass spectrometry
Instrumental neutron activation analysis
Dating

ABSTRACT

In fossil specimens, measurements of the natural isotopic ratio ^{129}I/I may provide a method to estimate the age of sample. The motivation for measuring the isotopic composition (^{129}I/I) of petrified wood samples collected from Austria was to check this feasibility. Alkaline fusion together with anion exchange was used to extract iodine from the sample. Typical sample size for this study was 10–90 g. An atomic ratio as low as 10^{-14} was determined using accelerator mass spectrometry (AMS). Uranium concentrations measured by instrumental neutron activation analysis (INAA) and α-spectrometry were found to be less than 3 mg kg^{-1}, therefore the contribution from fissiogenic ^{129}I was small and an estimation of ages was based on the decrease of the initial ratio (due to decay of the cosmogenic ^{129}I in a closed system) after subtraction of the fissiogenic ^{129}I. The value of the prenuclear ratio is crucial for the use of the ^{129}I system for dating purposes in the terrestrial environment. From the preanthropogenic (initial) ratio of 1.5×10^{-12} of the hydrosphere and the results of the present study for the samples from Altenburg (1.05×10^{-12}) and Fuerwald (6.16×10^{-13}), respective ages of 8 ± 2.2 and 20.2 ± 2.2 million years were derived. Since samples were collected from a stratum deposited in the Upper Oligocene/Ergerien period (~25–30 million years ago), it can be concluded that these isotopic ratios do not show ages but an elapsed time since fossil wood was isolated from mineral rich water. Paleontological investigation shows that samples from Altenburg had mixed characteristics of old and modern Tertiary plants, thus an origin from a younger stratum re-sedimented with Oligocene cannot be excluded. However, the sample from Drasenhofen reflects that the ^{129}I/I system might not always be suitable for the dating of petrified wood sample due to fixation of anthropogenic ^{129}I into surface fractures.

1. Introduction

Petrified wood is a type of fossil that forms in two different geological settings. Trees transported by streams and rivers can become buried in the fluvial sediments of river beds, deltas and floodplains or volcanic ash can bury them (sometimes as still upright trees). First, tissue undergoes decay in a moderately warm environment. Over time, mineral rich water passing through sediment fills all the cavities of the wood structure with silica without altering the overall cellular structure of wood. When this process occurs, and how it proceeds, is a matter of controversy. Buurman (1972) suggested that petrified wood can be formed either by replacement or through permineralization (filling), later Sigleo (1978) concluded that silicification is a process of impermeation (void filling) and not of inorganic replacement of organic cell walls (petrifiedwoodmuseum.org/PDF/Permineralization.pdf). Scurfield and Segnit (1984) described that petrification by silica involves penetration of wood via splits or checks caused by the permeation of cell walls via reticulated system. Researchers believe that several millions of years are necessary for the complete formation of solid petrified wood (Akahane et al., 2004).

^{129}I used for geological dating and as tracer of hydrologic and oceanographic systems has received increased attention in recent years (Fabryka-Martin et al., 1985; Fehn et al., 1994, 2000; Fehn and Snyder, 2003; Moran et al., 1995; Muramatsu et al., 2001; Tomaru et al., 2009). Production of natural ^{129}I ($t_{1/2} = 15.7$ Myr) takes place primarily by interaction of cosmic rays with Xe isotopes in the stratosphere and by spontaneous fission of ^{238}U in crustal rocks (induced fission of ^{235}U plays a minor role and can be neglected in most cases). Both of these processes contribute similar amounts of

---

* Corresponding author. Tel.: +43 1 4277 52623.
E-mail address: tania.jabbar@univie.ac.at (T. Jabbar).

[1] Pakistan Institute of Nuclear Science and Technology, Nilore, Islamabad, Pakistan.

0265-931X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jenvrad.2012.12.010

natural ^{129}I to the surface reservoir (Fabryka-Martin, 1988). In addition to these two natural production modes, large quantities of ^{129}I have been emitted by anthropogenic activities since the beginning of the nuclear age. The half life of ^{129}I together with the observed input ratios and the detection limit of accelerator mass spectrometry (AMS, $^{129}I/I = 10^{-14}$) allow the application of this dating method within a range of approximately 80 Ma, which is beyond the radiocarbon dating limit (Fehn et al., 2007a,b). Although theoretical detection limit of AMS is 2×10^{-15}, lack of the blank material with ratios below 10^{-14} establishes a practical detection limit of 10^{-14} (Fehn, 2012). The biophilic nature of iodine suggests that this isotopic system might be particularly useful for the dating of organic material (Fehn et al., 2007a).

The isotopic ratio ($^{129}I/I$) below the zone of bioturbation has been calculated theoretically as 3.5×10^{-14} by Edwards (1962), 2.2×10^{-12} by Edwards and Rey (1968), $1^{-10} \times 10^{-13}$ by Burger (1980) and $3^{-30} \times 10^{-13}$ by Fabryka-Martin (1984) (all as cited by Fabryka-Martin, 1984) assuming iodine exchanges rapidly between all surface reservoirs such as the oceans, biosphere and atmosphere to produce constant preanthropogenic $^{129}I/^{127}I$ ratio. Once the iodine is removed from well mixed surface reservoir, the initial ratio will decrease due to continuous decay of ^{129}I. The ratio of $1.5 \times 10^{-12} \pm 10\%$ has been verified experimentally by AMS measurements of marine sediment samples off the coast of Carolina in the Atlantic Ocean and later in a series of samples from other marine locations and is used as the initial ratio for age determinations using ^{129}I in hydrosphere (Fehn et al., 1986; Schink et al., 1995). Although the average pre-anthropogenic ratio measured in marine sediments from Cape Hatteras is approximately 1.2×10^{-12}, there is a significant variation in the samples measured, with a range of $0.7–1.48 \times 10^{-12}$ (Moran et al., 1998). The observation of $^{129}I/^{127}I$ as low as 0.2×10^{-12} in the depth profiles from the Easter islands and Indian ocean and the results obtained by Ernst et al. (2003) of pre-nuclear iodine preparations of $(0.2 \times 1.4 \pm 1) \times 10^{-12}$ shed some doubt on previously proposed natural equilibrium isotopic ratio of 1.5×10^{-12} (Daraoui et al., 2012; Ernst et al., 2003). However, this issue is still not settled and ages are being calculated using isotopic ratio of 1.5×10^{-12}.

Up till now dating with ^{129}I mainly focused on marine samples (hydrates, brines and salt domes) with high concentrations of iodine. There are only two reports on dating of terrestrial samples because of the low iodine concentration and the uncertainty of the pre-nuclear ratio ($10^{-11}–10^{-13}$) (Szidat et al., 2000; Luo et al., 2011; Zhou et al., 2010). In this context, we have tried to date lignite, however, the lignite did not represent a closed system with respect to iodine (Wallner et al., 2007). Following our previous attempts we now investigated petrified wood. In general petrified wood is found in the silicified form, though this is not the only possible matrix. Because silicified wood is far more prevalent and probably better preserved (Kuczumow et al., 1999), it was adopted as an object of our research. Weathering products of rocks are probably the source of the non crystalline (or amorphous) form of hydrated silica ($SiO_2 \cdot nH_2O$). Continued crystallization and water losses transform the opal into chalcedony. Over time, re-crystallization occurs to convert chalcedony to quartz, the hardest form of silica (Suneson, 2010).

The present study aims to investigate pre-anthropogenic ratios and the possibility of dating petrified wood samples based on the decay of the cosmogenic ^{129}I component (after subtraction of the fissiogenic ^{129}I). Acid leaching with HF (Gao et al., 2007) and alkali fusion (Brown et al., 2005; Bienvenu et al., 2004; Chai and Muramatsu, 2007; Date and Stuart, 1988) are commonly used methods for separating trace iodine from silicate minerals. The drawback of acid digestion includes loss of iodine due to formation of volatile iodine compounds, and incomplete sample decomposition leading to the doubts as to whether the ^{129}I was completely released from the solid phase. Therefore we investigated the alkaline fusion method in more detail. Different salts have been used in the fusion process; we choose NaOH as fluxing agent which is applicable in samples containing silicates. The content of stable iodine in our samples was determined with instrumental neutron activation analysis (INAA). In order to estimate the amount of fissiongenic ^{129}I derived from decay of ^{238}U, wood samples were also analyzed for their uranium content by alpha counting and INAA. Finally, the $^{129}I/I$ isotopic ratio was determined by AMS. In addition, we checked the chemical composition of samples.

2. Material and methods

2.1. Description of samples

Three petrified wood samples used in this study were surface picked from northern Lower Austria in 1985 (Table 1). The petrified wood was found scattered over the sites and partially buried in the ground. Samples were mixed with remains of gravel layers deposited by Tertiary rivers, which also had erased the former floodplain forests and sedimented the stems for petrification. Two samples collected from Waldviertel were a semiring-porous wood (evergreen Mediterranean Oak type-Fuerwald) and a semiring-porous wood (hornbeam type-Altenburg). Both had been re-sedimented in the course of time and were preserved in a layer associated with the Upper Oligocene/Ergerien period, ~25–30 million years ago. The third piece stems from Drasenhofen, Weinviertel and is a ring-porous Oak type (modern deciduous Oak) as it still grows in Austria. It was found in a layer from the Pliocene period >3 million years ago and obviously was re-sedimented. As the paleontology of the Altenburg species spectrum shows mixed characteristics of old and modern Tertiary plants, the sample investigated might have been re-sedimented (condensed) into the layer where the Fuerwald sample was found (Cichocki, 1998, 1992).

The samples were sliced into 1-cm pieces with a diamond saw (water-cooled) perpendicular to the trunk axis, washed with Millipore water to remove surface contamination and air dried. The crushed and grinded samples were screened through a sieve. The fraction finer than 315-μm was used for further analysis. Composition of samples was checked using INAA and EDX (Energy Dispersive X-ray spectrometry). The results of elemental analysis are shown in Table 2.

2.2. Extraction method

Iodine isotopes were extracted by alkaline fusion following procedures from literature (Nishiizumi et al., 1983; Schmidt et al., 1998) after some modifications. About 10–90 g of sample was mixed with NaOH (1:3) as fluxing agent in a porcelain crucible, spiked with 2.5–5 mg of iodide (in-house standard Vienna-NaI-78, isotopic ratio 10^{-14} from Isotrace Laboratory) and was fused at 300 °C. The fused solid was then extracted with 100–200 mL of hot water and the residual was dissolved using a mixture of 1 mL of concentrated H_2SO_4 and 1-mL 1-M $NaHSO_3$ solution. In the beginning of the acidification of the filtered leachate, a large amount of precipitate were produced, however, with the addition of acid, most of these precipitates can be dissolved (Hou et al., 1999). Remaining steps are the same as given in literature (Jabbar

Table 1
Sampling site specifications.

Sampling site	Latitude (N°)	Longitude (E°)
Altenburg	48.64	15.58
Fuerwald	48.68	15.53
Drasenhofen	48.78	16.64

Table 2
Elemental analysis of petrified wood samples.

Element	Concentration (mg kg-1)		
	Altenburg	Drasenhofen	Fuerwald
Si[a]	420 ± 39	467 ± 23	450 ± 40
Na	68.23 ± 4.09	74.54 ± 4.47	67.97 ± 4.07
K	n.d.	n.d.	n.d.
Ca	393 ± 70	507 ± 91	283 ± 45
Mn	20.07 ± 0.30	16.15 ± 0.32	7.51 ± 0.15
Al	6804 ± 34	6328 ± 53	1983 ± 40
Sc	0.180 ± 0.003	0.180 ± 0.003	0.170 ± 0.003
Cr	14.59 ± 0.72	14.92 ± 0.72	13.43 ± 0.68
Fe	1478 ± 38	1459 ± 38	1396 ± 36
Co	0.87 ± 0.03	0.71 ± 0.02	0.68 ± 0.02
Ni	2.48 ± 0.16	3.86 ± 0.24	3.99 ± 0.76
Zn	12.4 ± 0.5	481.9 ± 13.4	460.7 ± 12.8
As	0.40 ± 0.03	0.81 ± 0.04	0.34 ± 0.01
Rb	n.d.	n.d.	n.d.
Sr	3.79 ± 1.70	n.d.	n.d.
Zr	23.80 ± 3.09	90.75 ± 6.57	80.01 ± 3.52
Sb	0.06 ± 0.01	0.29 ± 0.01	0.29 ± 0.01
Cs	n.d.	n.d.	n.d.
Ba	483 ± 9	1793 ± 48	1671 ± 45
La	2.37 ± 0.09	10.10 ± 0.30	0.45 ± 0.02
Ce	2.76 ± 0.08	13.57 ± 0.40	12.93 ± 0.50
Nd	n.d.	11.70 ± 2.80	10.94 ± 2.73
Sm	1.54 ± 0.07	2.54 ± 0.12	0.39 ± 0.02
Eu	0.27 ± 0.01	0.56 ± 0.01	0.53 ± 0.01
Tb	0.14 ± 0.01	0.31 ± 0.01	0.28 ± 0.01
Yb	0.50 ± 0.03	0.67 ± 0.09	0.57 ± 0.07
Lu	0.08 ± 0.01	0.11 ± 0.01	0.031 ± 0.002
Hf	0.57 ± 0.02	2.85 ± 0.08	2.67 ± 0.07
Ta	n.d.	n.d.	n.d.
W	0.84 ± 0.10	0.26 ± 0.09	3.79 ± 0.34
Th	0.11 ± 0.01	0.15 ± 0.01	0.15 ± 0.01

n.d. (not detected).
[a] mg/g.

et al., 2011, 2012). The clear solution was loaded onto the column packed with already conditioned 5–40 g of Dowex 1 × 8 (100–200 mesh Cl^{-} form) and was washed with 50-mL 0.1-M HNO_3. Iodide was eluted with 200 mL of 0.5-M HNO_3. Subsequently, iodine was precipitated as AgI by addition of 4-mL of 0.01-M $AgNO_3$. Silver iodide was thereafter isolated by centrifugation. The precipitates were washed with 25% NH_3 and twice with Millipore water in order to dissolve other halides that may have co-precipitated with AgI. The contamination introduced in the process was determined by the preparation of blank samples processed in the same way as real samples and was found insignificant.

The percentage recovery of iodine was also investigated as a function of concentration of NaOH and fusion temperature. For this purpose, petrified wood samples were placed in crucibles, 1 mL of iodine carrier (2.5 mg mL^{-1}) was added and different amounts (2-mL, 3-mL, 4-mL, 5-mL and 6-mL) of saturated NaOH solution were mixed with the samples. The fusion time was varied from 300-°C for 5 h (Schmidt et al., 1998), 450 °C for 4 h (Chao et al., 1999) and 550 °C for 1 h (Brown et al., 2005) after 30 min heating at 150-°C in each case. The maximum recovery of iodine was obtained for fusion with NaOH (1:3) at 300-°C for 5 h as determined by inductive couple plasma mass spectroscopy (ICP-MS) after filtration.

One drawback of alkali fusion is that a large amount of flux to sample (3:1) is required which is not suitable for analyzing a big sample. The advantages of this method are its simplicity and that it does not require any special equipment.

2.3. Total stable iodine

The iodine content of petrified wood was determined by INAA. Typically 200-mg of powdered samples were sealed in a polythene vial. The samples were irradiated with pneumatic transport system of the TRIGA Mark II research reactor at the Atominstitut (Tech. Uni. Vienna) at a thermal neutron flux density of 1×10^{12} cm^{-2} s^{-1} for 2 min, followed by 10 min decay and then counting for 10 min. The irradiation and counting period are limited due to the short half-life of ^{128}I ($t_{1/2} = 25$ min). Any chemical treatment which could lead to a contamination of the sample was avoided as well as the surface of the sample container was cleaned after irradiation to get rid of any surface contamination. The 443 keV gamma line of ^{128}I was used for measuring the iodine content with a 151 cm^{3} HPGe detector, a loss-free counting system and a PC (Hou et al., 1998). The resolution of this system is 1.8 keV for the 1332 keV gamma line of ^{60}Co and the relative detection efficiency is 50.1%. The advantages of INAA are high sensitivity, good accuracy and precision, and only small amounts of samples are needed.

2.4. ^{129}I/I ratio

For the determination of the ^{129}I/I ratio, the dried AgI precipitates were mixed with silver powder (AgI: Ag 1:1 by weight) and pressed into copper targets for AMS measurements carried out at the Vienna Environmental Research Accelerator (VERA). Negative ions from the Cesium sputter source were mass analyzed, stripped at the terminal of 3 MW Tandem Accelerator and 4+ charge state was chosen for the measurement, where ^{127}I4^{+} was measured as current using a Faraday cup and ^{129}I was measured using gas ionization detector. To avoid cross contamination from high ratio reference materials, the samples were normalized to our in-house standard Vienna-AgI-111, which was calibrated to be $(1.8 \pm 0.2) \times 10^{-13}$ in previous measurements.

2.5. Uranium concentration

Samples were homogenized by grinding, dried at 105-°C to constant weight and ashed at 450-°C overnight to destroy organic matter. Samples were then digested by the radiochemical procedure given in (Eichrom Technologies, 2005) with slight modifications. The samples were leached in 10-mL 14-M HNO_3 and 5-mL 12-M HCl in a Teflon beaker, and ^{232}U tracer (13.85 ± 0.20 mBq) was added. After boiling the mixture for 3 h, the sample was centrifuged for 30 min at 4000 rpm (relative centrifugal force (RCF) is 1646). The residue was leached twice with 20-mL 14-M HNO_3 and 15-mL 40% HF for 3 h and was then rejected. The combined solutions were evaporated till dryness, and fumed three times with 5-mL boric acid (c = 5 g/100 mL), 5-mL 12-M HCl and 5-mL 14-M HNO_3 respectively. The residue was dissolved in 80-mL of 8-M HCl and uranium was separated by anion exchange and measured α-spectrometrically after micro precipitation with neodymium fluoride (Wallner et al., 2007).

Uranium was also determined by INAA. The samples were irradiated at a thermal neutron flux density of 1 × 1013 cm^{-2} s^{-1} for 36 h, followed by cooling for 5 days and then counting for 30 min. Here the 277.7 keV photopeak of ^{239}Np (half-life 2.4 days) produced by neutron capture of ^{238}U was used (El-Ghawi et al., 2005).

3. Results and discussion

The energy dispersive X-ray spectrometry and INAA revealed the main composition of the samples. Silicon dioxide was the most prevalent component, with other elements (Al, Fe, Ba, Ca, Zn, Na) at low levels but clearly noticeable (Table 2). The respective Si and Fe concentrations were similar in all samples, while Ca gave differing values for all three samples investigated; lowest Al concentration was observed in Fuerwald, whereas Zn and Ba were considerably lower in the Altenburg sample. Differences in sample composition from Fuerwald and Altenburg were unexpected as they were collected from a single stratum of limited geographic extent. On the other hand, compositional similarity between Fuerwald and Drasenhofen is not surprising since similar characteristics in specimens from different localities have also reported (Kuczumow et al., 1999; Mustoe, 2008). We observed that the samples from Altenburg and Fuerwald were easier to cut and crush than the sample from Drasenhofen though organic matter as measured by loss on ignition was found to be nearly the same (0.05–0.07%) in all three samples. However, the fact that the highest concentration of Zr was detected in the Drasenhofen sample supports our observation (Debsikdar and Sowemimo, 1992).

Our samples showed iodine concentrations (mg kg^{-1}) of 5.5 ± 0.4 (Altenburg), 9.7 ± 0.4 (Fuerwald) and 0.32 ± 0.03 (Drasenhofen) as detected by INAA (Table 3). The concentration of iodine in the first two samples is much higher than the average iodine concentration of 0.12 mg kg^{-1} in bulk continental crust (Muramatsu and Wedepohl, 1998) and higher than the range of 0.1–0.5 mg kg^{-1} found in rock-forming minerals and in igneous rocks (Fabryka-Martin, 1984).

Our first measurements of the ^{129}I/I ratio with only 10 g sample mass gave too high values on the order of 10^{-10}, which we thought might be due to contamination. The presence of small quantities of recent material could cause a substantial shift in isotopic ratios as shown in Fig. 1. For excess ^{129}I, there are three potential sources of contamination (two anthropogenic and one natural):

(i) ^{129}I introduced from air during sample preparation
(ii) ^{129}I introduced to fissures or fractures of samples from (modern) atmospheric precipitation and from ground moisture on the collection spot
(iii) Fissiogenic ^{129}I built up in the sample itself or incorporated after leaching from nearby U bearing geologic formations before the end of petrification

Since contamination is an important problem for low level iodine analysis, some chemical blanks were prepared by taking 5 mg of iodine carrier (NaI) and carrying out the entire sample preparation for AMS analysis. The average amount of ^{129}I in these blanks was 5.25 ± 2.54 × 10^{-16} g which is one order of magnitude higher than NaI precipitated as AgI without sample preparation steps. This may be related to presence of ^{129}I in some chemicals. Still the concentration of ^{129}I found in different blanks prepared by varying amount of chemicals has same order of magnitude and would not affect isotopic ratio considerably. Considering surface contamination, we washed all samples with Millipore water, but excess ^{129}I might have accumulated in open voids and structural fractures. This sort of contamination could be overcome by washing the surface of the samples and by increasing the sample size. At the same time we decreased the amount of iodine carrier, thus enhancing the ^{129}I/I ratio measured. We continued to increase the sample mass until we got constant ^{129}I/I ratios below pre-anthropogenic level for the samples Fuerwald and Altenburg. However, this did not work for the sample from Drasenhofen. Thus, the very hard and compact sample from Drasenhofen with a ratio of 6.5 × 10^{-12} might contain fissiogenic ^{129}I taken up from the environment during the period of petrification. Re-crystallization and physical deformation of the fossil wood from the weight of overlying sediments or from tectonic events may lead to brittle fissures that may allow for deposition of minerals at a later stage (Trostle, 2009). These processes may add fissiogenic ^{129}I or natural iodine (with the above given initial ^{129}I/I ratio) to the samples long after the end of petrification.

Table 3
Iodine concentration and isotopic ratios of petrified wood samples.

Sample	Amount (g)	^{127}I (ppm)	^{129}I/^{127}I × 10^{-12}	Corrected[a] ^{129}I/^{127}I × 10^{-12}
Altenburg	90	5.5 ± 0.4	1.15 ± 0.19	1.06 ± 0.11
Drasenhofen	32	0.32 ± 0.03	6.49 ± 0.89	6.13 ± 0.70
Fuerwald	60	9.7 ± 0.4	0.63 ± 0.12	0.62 ± 0.03

[a] After substraction of the fissiogenic ^{129}I, considering only spontaneous fission of ^{238}U as given in (Fabryka-Martin, 1988). ^{129}I (atoms/g) = 1470 × ^{238}U concentration (ppm).

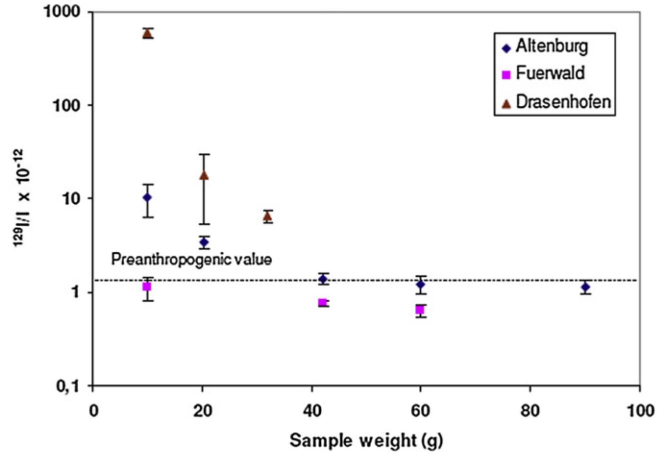


Fig. 1. Correlation between sample size and isotopic ratio (log scale) for petrified wood samples. Dotted line shows preanthropogenic value of 1.5 × 10^{-12}.

So the ^{129}I/I ratios of the samples with high stable iodine concentration (Fuerwald and Altenburg) were found below the measured pre-anthropogenic input ratio of 1.5 × 10^{-12} for the hydrosphere indicating the absence of anthropogenic contributions, while the Drasenhofen sample with low stable iodine concentration had a ratio above the prenuclear threshold and therefore was rejected. In Fig. 2 we compared our results with other data from the literature. Iodine chemicals from the nitrate deposits in Atacama Desert, Chile, which had been stored from times before the onset of the nuclear age, and iodine bearing minerals had clearly lower average ^{129}I/I ratios of approximately 0.2 × 10^{-12} (Fehn et al., 2007b). Similarly for the first time in soil sample (at depth of 10 cm) from Eastern Islands, isotopic ratio below 10^{-12} was observed (Daraoui et al., 2012). Assuming 1.5 × 10^{-12} as pre-nuclear

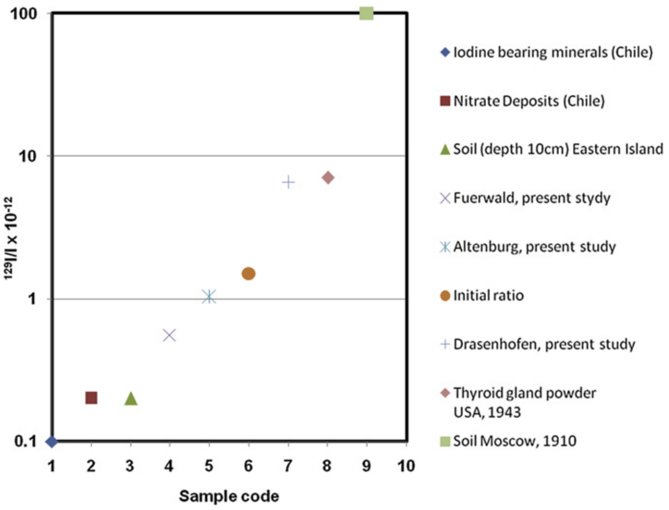


Fig. 2. Comparison of present results with published data.

value, the nitrate deposits as well as the minerals might have been formed about 3 half-lives of ^{129}I ago. On the other hand, the values measured for the petrified wood from Fuerwald and Altenburg are much lower than the reported values of 7×10^{-12} and 1×10^{-10} (5–66 times higher than pre-nuclear value) of a thyroid gland powder from USA, 1943 and of soil from Moscow, 1910 respectively (Szidat et al., 2000).

The uranium contents and isotopic ratios ^{234}U/^{238}U measured in petrified wood samples are presented in Table 4. The ^{234}U/ U activity ratios of the samples were close to unity, suggesting that the material has not been strongly leached (Kanai et al., 2006). The uranium concentrations measured by INAA are also shown. These values were used further, considering INAA results are more reliable as no chemical separation is involved. ^{129}I can also be produced by spontaneous fission of ^{238}U, with minor production by neutron induced fission of ^{235}U depending on rock types. However, the uranium concentrations of 1 and 2.2 mg kg^{-1} are rather low in our samples, so the amount of fissiogenic ^{129}I built up in the already petrified wood is negligible (the fissiogenic ^{129}I from 1 mg kg^{-1} uranium corresponds only to 2% of the ^{129}I/I ratios, considering 50% of the atoms have already decayed in case of Fuerwald). But, as already mentioned, potentially complicating the interpretation is the migration of fissiogenic ^{129}I (from nearby geological formation) dissolved in mineral rich water during the silication process that might lead to fixation of iodine within the wood structure together with scavenging of Fe, Al oxides and organic matter (a removal of iodine might also be possible, but would not alter the isotopic ratio).

Assuming that (stable as well as radioactive) iodine was fixed in the petrified wood, the decay of ^{129}I provides an elapsed time since the end of the petrification process:

$$R_{\mathrm{obs}} = R_i e^{-\lambda_{129} t}$$

Where

R_{obs} = observed ^{129}I/I ratio,
R_i = initial ^{129}I/I ratio of 1.5×10^{-12},
λ_{129} = decay constant of ^{129}I (4.41×10^{-8} y^{-1}), and
t = years since iodine-129 deposition.

Obviously, the age values calculated strongly depend from the assumed initial ^{129}I/I ratio. With older samples like Fuerwald, however, at least the order of magnitude of the derived age should be correct. According to the standard decay equation, Fuerwald and Altenburg reflect the respective end of the petrification process at about 20.2 ± 2.2 and 7.95 ± 2.20 million years ago (Fig. 3), whereas the depositional formation that contained the samples belongs to Upper Oligocene/Ergerien period, (~25–30 million years ago). We must consider that the duration of the mineralization process of the silicified wood must be added to get the real age of the wood, and that also later processes influencing the surrounding strata and resulting in deformation and alteration of the wood may have an influence on the ^{129}I/I ratio and therefore on the derived age. Considering the paleontological determination and hardness of the trunk pieces collected from Altenburg it is not surprising that the sample from Altenburg is much younger than Fuerwald and might have its origin from a younger stratum mixed with the underlying Oligocene.

Table 4
Uranium concentration of petrified wood samples.

Sample	Method	^{238}U (ppm)	^{234}U/^{238}U
Altenburg	INAA	2.24 ± 0.13	1.2 ± 0.1
	α-Spectrometry	3.7 ± 0.1	
Drasenhofen	INAA	0.32 ± 0.02	1 ± 0.1
	α- Spectrometry	0.5 ± 0.1	
Fuerwald	INAA	1.1 ± 0.1	1 ± 0.06
	α-Spectrometry	1.4 ± 0.1	

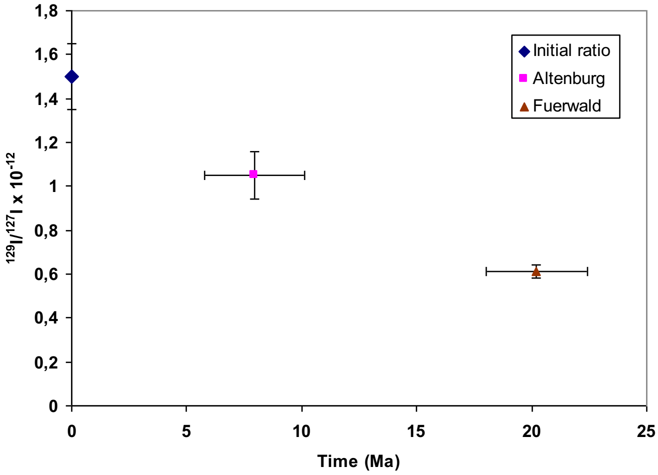


Fig. 3. Correlation between isotopic ratios and estimated elapsed time.

4. Conclusions and perspective

The ratio ^{129}I/I as well as stable iodine and uranium concentrations were measured in three samples of petrified wood with AMS and INAA, respectively. The sample from Drasenhofen did not yield isotopic ratios independent from sample size and gave a ratio higher than the pre-anthropogenic level (1.5×10^{-12}) used as the initial ratio for age determinations; we think that this sample does not represent a closed system. The other two samples, however, gave ratios smaller than this value, and so we were able to estimate a time elapsed since the end of the petrification process by using the decay of the cosmogenic ^{129}I (the amount of fissiogenic ^{129}I was calculated from the uranium concentration and was subtracted from the total ^{129}I measured). Both samples (Altenburg and Fuerwald) had been collected from the same stratum deposited during Upper Oligocene/Ergerien period (~25–30 million years) and gave post mineralization ages of 8 ± 2.20 and 20.2 ± 2.2 million years, respectively. These differences in ages may be explained by paleontological determination of species giving a hint to a possible resedimentation of the “younger” sample on the underlying older layer. Taking into account that several millions of years might be necessary for the complete formation of silicified wood, our data show a reasonably good correspondence to the ages of the surrounding geological stratum. Still the ages calculated are nominal due to ambiguity in initial isotopic ratio and discrepancy in mineralization process of the silicified wood. So for the first time a research protocol for dating silicified wood from the isotopic ratio ^{129}I/I has been established. However, due to funding constraint, only a representative sample from each location was analyzed. A much more extensive study regarding larger numbers and masses of subsamples, analysis in fractions (outer and inner rings) and site characterization (^{129}I/I and uranium concentrations in underground water) is suggested.

Acknowledgment

Authors would like to thank Mag. Siegfried Fürtauer, Institute of Inorganic chemistry/material chemistry and Mag. Dr. Stephan Puchegger, Faculty Center for Nanostructure Research, University of Vienna for their help in sample preparation and Silicon analysis by EDX spectrometry.

References

Akahane, H., Furuno, T., Miyajima, H., Yoshikawa, T., Yamamoto, S., 2004. Rapid wood silicification in hot spring water; an explanation of silicification of wood during the Earth's history. Sediment Geol. 169 (3–4), 219–228.

Bienvenu, P., Brochard, E., Excoffier, E., Piccione, M., 2004. Determination of iodine-129 by ICP-QMS in environmental samples. Can. J. Anal. Sci. Spectrosc. 49 (6), 423–428.

Brown, C.F., Geiszler, K.N., Vickerman, T.S., 2005. Extraction and quantitative analysis of iodine in solid and solution matrixes. Anal. Chem. 77, 7062–7066.

Buurman, P., 1972. Mineralization of fossil wood. Scripta Geologica 12, 1–43.

Chai, J.Y., Muramatsu, Y., 2007. Determination of bromine and iodine in twenty-three geochemical reference materials by ICP-MS. Geostand. Geoanal. Res. 31 (2), 143–150.

Chao, J.H., Tseng, C.L., Lee, C.J., Hsia, C.C., Teng, S.P., 1999. Analysis of I-129 in radwastes by neutron activation. Appl. Radiat. Isot 51, 137–143.

Cichocki, O., 1988. Zur Histologie tertiärer Hölzer Österreichs. Diss. form. naturw. Fak., Univ. Wien.

Cichocki, O., 1992. Fossile Hölzer aus tertiären und quartären Sedimenten des Mühl-, Wald- und Weinviertels und der Molasse: Vergleichende Untersuchungen über deren Histologie, Paläökologie und Altersstellung. In: Paneurop Palaeobot Conf 1991, Tagungsband, Ann.d. Naturhist. Mus., Wien, pp. 117–120.

Date, A.R., Stuart, M.E., 1988. Application of inductively coupled plasma mass spectrometry to the simultaneous determination of chlorine, bromine and iodine in the national bureau of standard reference material 1648 urban particulate. J. Anal. Atm. Spectrom. 3, 659–665.

Daraoui, A., Michel, R., Gorny, M., Jakob, D., Sache, R., Synal, H.-A., Alfimov, V., 2012. Iodine-129, Iodine-127 and Caesium-137 in the environment: soils from Germany and Chile. J. Environ. Radioact. 112, 8–22.

Debsikdar, J.C., Sowemimo, O.S., 1992. Effect of zirconia addition on crystallinity, hardness, and microstructure of gel-derived barium aluminosilicate, $BaAl_2$-Si_2O_8. J. Mat. Sci. 27, 5320–5324.

Eichrom Technologies, Inc, 2005. Uranium in Soil (2 Gram Samples), Analytical Procedures. ACS07, Rev. 1.5.

El-Ghawi, U.M., Bejey, M.M., Al-Fakhri, S.M., Al-Sadeq, A.A., Doubali, K.K., 2005. Analysis of Libyan Arable soils by means of thermal and epithermal NAA. Arab. J. Sci. Tech. 30 (1A), 147–153.

Ernst, T., Szidat, S., Handl, J., Jakob, D., Michel, R., Schnabel, C., Synal, H.-A., Santos Arevalo, F.J., Benne, I., Boess, J., Gehrt, E., Capelle, A., Schneider, J., Schafer, W., Bottcher, J., 2003. Migration of iodine-129 and iodine-127 in soils. Kerntechnik 68, 155–167.

Fabryka-Martin, J.T., 1984. Natural Iodine-129 as ground water tracer. Master dissertation, The University of Arizona.

Fabryka-Martin, J., Bentley, H., Elmore, D., Airey, P.L., 1985. Naural iodine-129 as an environmental tracer. Geochim. Cosmochim. Acta 49, 337–347.

Fabryka-Martin, J.T., 1988. Production of radionuclides in the earth and their hydrogeologic significance, with emphasis on chlorine-36 and iodine-129. Ph.D. dissertation, The University of Arizona.

Fehn, U., Holdren, G.R., Elmore, D., Brunelle, T., Teng, R., Kubik, P.W., 1986. Determination of natural and anthropogenic 129I in marine sediments. Geophys. Res. Lett. 13, 137–139.

Fehn, U., Moran, J.E., Teng, R.T.D., Rao, U., 1994. Dating and tracing of fluids using ^{129}I and ^{36}Cl: results from geothermal fluids, oil field brines and formation waters. Nucl. Instrum. Methods Phys. Res. Sect. B 92, 380–384.

Fehn, U., Synder, G.T., Egeberg, P.K., 2000. Dating of pore waters with ^{129}I: relevance for the origin of marine gas hydrates. Science 289, 2332–2335.

Fehn, U., Synder, G.T., 2003. Origin of Iodine and ^{129}I in volcanic and geothermal fluids from the North island of New Zealand: Implications for subduction zone processes. Soc. Econ. Geol. 10, 159–170.

Fehn, U., Synder, G.T., Muramatsu, Y., 2007a. Iodine as tracer of organic material: ^{129}I results from gas hydrate systems and fore arc fluids. J. Geochem. Explor. 95, 66–80.

Fehn, U., Moran, J.E., Synder, G.T., Muramatsu, Y., 2007b. The initial ^{129}I/I and the presence of old iodine in continental margins. Nucl. Instrum. Methods Phys. Res. Sect. B 259, 496–502.

Fehn, U., 2012. Tracing crustal fluids: applications of natural ^{129}I and ^{36}Cl. Annu. Rev. Earth Planet. Sci. 40, 45–67.

Gao, Y.C., Gao, Q.F., Sunb, M.X., Zhub, Z.X., Chenb, Z.H., 2007. Simultaneous measurements of arsenic, bromine, and iodine in coal and coke by inductively coupled plasma-mass spectrometer. Chin. J. Anal. Chem. 35 (8), 1175–1178.

Hou, X., Feng, X., Qian, Q., Chai, C., 1998. A study of iodine loss during the preparation and analysis of samples using ^{131}I tracer and neutron activation analysis. Analyst 123, 2209–2213.

Hou, X., Dahlgaard, H., Rietz, B., Jacobsen, U., Nielsen, S.P., Aarkrog, A., 1999. Determination of ^{129}I in seawater and some environmental materials by neutron activation analysis. Analyst 124, 1109–1114.

Jabbar, T., Steier, P., Wallner, G., Kandler, N., Katzlberger, C., 2011. AMS analysis of iodine-129 in aerosols from Austria. Nucl. Instrum. Methods Phys. Res. Sect. B 269 (24), 3183–3187.

Jabbar, T., Wallner, G., Steier, P., Katzlberger, C., Kandler, N., 2012. Retrospective measurements of airborne ^{129}Iodine in Austria. J. Environ. Radioact. 112, 90–95.

Kanai, Y., Kamioka, H., Nakajima, T., Tsukamoto, H., 2006. Characterization and geochemical behaviour of uranium series nuclides in sandy sediments at Kanamaru area, Yamagata and Niigata Prefectures, Japan. Geochem. Explor. Environ. Anal. 6 (1), 57–67.

Kuczumow, A., Vekemans, B., Olivier, S., Dorrine, W., Chevallier, P., Dillmann, P., Ro, C.U., Janssen, K., Grieken, R.V., 1999. Analysis of petrified wood by electron, X-ray and optical micro probes. J. Anal. Atom. Spectrom. 141, 435–446.

Luo, M.Y., Zhou, W.J., Hou, X.L., Chen, N., Zhang, L.Y., Liu, Q., He, C.H., Fan, Y.K., Liang, W.G., Wang, Z.W., Fu, Y.C., 2011. Determination of low level ^{129}I in soil samples using coprecipitation separation of carrier free iodine and accelerator mass spectrometry measurement. Chin. J. Anal. Chem. 39 (2), 193–197.

Moran, J.E., Fehn, U., Hanor, J.S., 1995. Determination of source ages and migration patterns of brines from US Gulf Coast basin using ^{129}iodine. Geochim. Cosmochim. Acta 59, 5055–5069.

Moran, J.E., Fehn, U., Teng, R.T.D., 1998. Variations in ^{129}I/^{127}I ratios in recent marine sediments: evidence for a fossil organic component. Chem. Geol. 152, 193–203.

Muramatsu, Y., Wedepohl, K.H., 1998. The distribution of iodine in Earth's crust. Chem. Geol. 147, 201–216.

Muramatsu, Y., Fehn, U., Yoshida, S., 2001. Recycling of iodine in fore arc areas: evidence from the iodine brines in Chiba, Japan. Earth Planet. Sci. Lett. 192, 583–593.

Mustoe, G.E., 2008. Mineralogy and geochemistry of late Eocene silicified wood from Florissant fossils beds national monument, Colorado. Geo. Soc. Amer. Special Paper 435, 127–140.

Nishiizumi, K., Elmore, D., Honda, M., Arnold, J.R., Gove, H.E., 1983. Measurement of ^{129}I in meteorites and lunar rock by tandem accelerator mass spectrometry. Nature 305, 611–612.

Schink, D.R., Sanstaschi, P.H., Corapcioglu, O., Sharma, P., Fehn, U., 1995. ^{129}I in Gulf of Mexico waters. Earth Planet. Sci. Lett. 135, 131–138.

Schmidt, A., Schnabel, Ch., Handl, J., Jakob, D., Michel, R., Synal, H.-A., Lopez, J.M., Suter, M., 1998. On the analysis of iodine-129 and iodine-127 in environmental materials by accelerator mass spectrometry and ion chromatography. Sci. Total Environ. 223, 131–156.

Scurfield, G., Segnit, E.R., 1984. Petrification of wood by silica minerals. Sediment Geol. 39, 149–167.

Sigleo, A.C., 1978. Organic geochemistry of silicified wood, petrified forest National Park, Arizona. Geochim. Cosmochim. Acta 42, 1397–1405.

Suneson, N.H., 2010. Petrified wood in Oklahoma. The Shale Shaker 60, 259–274.

Szidat, S., Schmidt, A., Handl, J., Jakob, D., Botsch, W., Michel, R., Synal, H.-A., Schnabel, C., Suter, M., López-Gutiérrez, J.M., Städe, W., 2000. Iodine-129: sample preparation, quality control and analyses of pre-nuclear materials and of natural waters from Lower Saxony, Germany. Nucl. Instrum. Methods Phys. Res. Sect. B 172, 699–710.

Tomaru, H., Lu, Z., Fehn, U., Muramatsu, Y., 2009. Origin of hydrocarbons in the Green Tuff region of Japan: ^{129}I results from oil field brines and hot springs in the Akita and Niigata Basins. Chem. Geol. 264, 221–231.

Trostle, K., 2009. Diagenetic History of Fossil Wood from the Paleocene Chickaloon Formation, MatanuskaValley, Alaska. Graduate thesis, Franklin and Marshall College.

Viney, M. The Silicification of Wood by Permineralization. (petrifiedwoodmuseum.org/PDF/Permineralization.pdf).

Wallner, G., Steier, P., Brandl, T., Friesacher, M.E., Hille, P., Kutschera, W., Tatzber, M., Ayromlou, S., 2007. Development towards the measurement of I-129 in lignite. Nucl. Instrum. Methods Phys. Res. Sect. B 259, 714–720.

Zhou, W.J., Hou, X.L., Che, N., Zhang, L.Y., Liu, Q., He, C.H., Luo, M.Y., Liang, W.G., Fan, Y.K., Wang, Z.W., Fu, Y.C., Li, H.B., 2010. Preliminary study of radioisotope ^{129}I application in China using Xi'an accelerator mass spectrometer. INCS News 25 (1), 9–23.