New dating method: Groundwater residence time estimated from the ^{4}He accumulation rate calibrated by using cosmogenic and subsurface-produced ^{36}Cl

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Abstract

Groundwater contains dissolved He, and its concentration increases with the residence time of the groundwater. Thus, if the ^{4}He accumulation rate is constant, the dissolved ^{4}He concentration in groundwater is equivalent to the residence time. Since accumulation mechanisms are not easily separated in the field, we estimate the total He accumulation rate during the half-life of ^{36}Cl (3.01×10^5 years). We estimated the ^{4}He accumulation rate, calibrated using both cosmogenic and subsurface-produced ^{36}Cl, in the Great Artesian Basin (GAB), Australia, and the subsurface-produced ^{36}Cl increase at the Äspö Hard Rock Laboratory, Sweden. ^{4}He accumulation rates range from $(1.9\pm0.3)\times10^{-11}$ to $(15\pm6)\times10^{-11}$ ccSTP·cm^{-3}·y^{-1} in GAB and

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$(1.8 \pm 0.7) \times 10^{-8}$ ccSTP·cm^{-3}·y^{-1} at Äspö. We confirmed a ground-water flow with a residence time of 0.7–1.06 Ma in GAB and stagnant groundwater with the long residence time of 4.5 Ma at Äspö. There-fore, the groundwater residence time can be deduced from the dissolved ^{4}He concentration and the ^{4}He accumulation rate calibrated by ^{36}Cl, provided that ^{4}He accumulation, groundwater flow, and other geo-environmental conditions have remained unchanged for the required amount of geological time.

1. Introduction

Long-term isolation of high-level radioactive wastes in deep, stable geological formations has been proposed as an effective way to protect human life and the human genetic effects from radiation, and sequestration of large amounts of CO_2 in such formations has been proposed for counteracting anthropogenic carbon dioxide emissions to reduce global warming. The key requirements for long-term subsurface storage of both high-level radioactive wastes and CO_2 are geochemical and hydrological stability and groundwater stagnancy.

In this paper, we discuss the estimation of groundwater stagnancy by measuring the groundwater residence time. We propose the use of dissolved chlorine-36 (^{36}Cl) and helium-4 (^{4}He) as environmental tracers for estimating groundwater residence times longer than 2 million years, a period long enough for all cosmogenic ^{36}Cl in groundwater to decay or to reach secular equilibrium with subsurface production of ^{36}Cl.

The sources of ^{36}Cl in groundwater are cosmogenic and subsurface pro-duction. The latter occurs by activation of ^{35}Cl by weak neutrons released in (α, n) reactions via α particles released from the decay of U and Th series radionuclides contained in the rock. Dissolved ^{4}He in groundwater has three different sources: atmospheric radiogenic and mantle helium. The concen-tration of ^{4}He of atmospheric origin in groundwater is almost constant and is determined by salinity and temperature of the recharge water. The ^{4}He concentration in groundwater is not constant but increases as the residence time increases, owing to the addition of radiogenic ^{4}He and accumulation due to the degassing crustal He flux, which includes a mantle component. The amount of radiogenic ^{4}He added to groundwater depends on the inten-sity of α radionuclide decay of U and Th, which depends on their contents in the rock, the He release rate (usually assumed to be 1.0, which is a factor of the relative number helium released into groundwater to the helium pro-duced *in situ*) from rock, and the rock's porosity [1–3]. On the other hand,

the accumulation rate from crustal He components depends on the diffusion rates of ancient He left in crustal rock and of the mantle component as well as advection by groundwater flow, which cannot be easily estimated in the field individually. However, the total He accumulation rate during the half-life of ^{36}Cl (3.01×10^5 years) can be estimated, provided that the ^{4}He accumulation mechanisms, groundwater flow conditions, and other geo-environmental conditions have not changed over the required amount of geological time. In addition, long residence times of groundwater on the order of millions of years can be estimated from the excess ^{4}He concentration and the ^{4}He accumulation rate. We can thus evaluate groundwater stagnancy at a candidate site for disposal of high-level radioactive waste or injection of CO_2 from the estimated groundwater residence time in combination with the results of other geo-hydrological investigations.

In this paper, we summarize a new, practical ^{4}He–^{36}Cl dating method developed as part of our research activities in the Great Artesian Basin (GAB), Australia [4, 5] and at the Äspö Hard Rock Laboratory (HRL), Sweden [6, 7].

2. Mechanisms of the ^{36}Cl–^{4}He dating method

Chloride ions contain a radioactive ^{36}Cl "clock", which has a half-life of approximately 3.0×10^5 years. Radioactive decay and subsurface production control the number of ^{36}Cl atoms in groundwater during its residence time in the aquifer, which begin when it enters the aquifer as recharge. The number of ^{36}Cl atoms in groundwater can be deduced from the residence time as follows [8]:

$$^{36}Cl = Cl_0 \cdot R_0 \cdot e^{-\lambda \cdot t} + Cl_0 \cdot R_{eq} \cdot (1 - e^{-\lambda \cdot t}) + R_{eq} \cdot (Cl(t) - Cl_0), \quad (1)$$

where ^{36}Cl is the number of ^{36}Cl atoms per liter of groundwater; $Cl(t)$ is the number of stable chlorine atoms per liter of water at time t; t is the residence time; λ is the decay constant of ^{36}Cl ($2.31 \times 10^{-6}\,\mathrm{y}^{-1}$); Cl_0 is the initial number of stable chlorine atoms in the recharged groundwater; R_0 is the initial cosmogenic ^{36}Cl/Cl ratio, measured by accelerator mass spectrometry, in the recharged groundwater; and R_{eq} is the ^{36}Cl/Cl ratio at secular equilibrium within the rock matrix.

The first and second terms on the right-hand side of eq. (1) express the radioactive decay of the initial cosmogenic ^{36}Cl and the subsurface-produced ^{36}Cl of the initial stable chlorine in the recharged water, respectively. The third term expresses the addition of ^{36}Cl by dissolution from the rock matrix.

As shown by eq. (1), the number of ^{36}Cl atoms in groundwater reaches a constant value after a period of at least five times the ^{36}Cl half-life if no chlorine is added from the rock matrix. On the other hand, the number of helium atoms dissolved in groundwater increases over time if the accumulation rate is constant and mixing, dilution, diffusion, and degassing from groundwater do not occur. The excess ^{4}He concentration is thus proportional to the residence time. In other words, the ratio ($t = {}^4He_{(\mathrm{ex})}/\alpha$) of the dissolved excess ^{4}He concentration ($^4He_{(\mathrm{ex})}$) to the ^{4}He accumulation rate (α) can replace the residence time of the groundwater in eq. (1). Using the following equations (2) to (4), we can therefore rewrite equation (1) as eq. (5) to estimate the relationship between $^4He_{(\mathrm{ex})}/\alpha$ and the ^{36}Cl/Cl ratio (R):

$$Cl(t) = Cl_m, \tag{2}$$

$$^{36}Cl = R_m \cdot Cl_m, \tag{3}$$

$$(R_m - R_{eq}) \cdot Cl_m = Cl_0 \cdot (R_0 - R_{eq}) \cdot e^{-\lambda \cdot (He_{(\mathrm{ex})}/\alpha)}, \tag{4}$$

$$\frac{^4He_{(\mathrm{ex})}}{\alpha} = -\frac{1}{\lambda} \cdot \ln\left(\left(\frac{R_m - R_{eq}}{R_0 - R_{eq}}\right) \cdot \left(\frac{Cl_m}{Cl_0}\right)\right), \tag{5}$$

where Cl_m is the measured Cl ion concentration in groundwater, and R_m is the measured ^{36}Cl/Cl ratio in groundwater. We can estimate the He accumulation rate α from the slope of the correlation straight line drawn by plotting $^4He_{(\mathrm{ex})}$ to $[(R_m - R_{eq})/(R_0 - R_{eq})] \cdot (Cl_m/Cl_0)$ in a semi logarithmic diagram.

3. Case studies for estimation of groundwater residence time

3.1 Groundwater with mainly cosmogenic ^{36}Cl: The Coonamble Embayment in the GAB, Australia

The Coonamble Embayment is a small basin located at the south-eastern edge of the GAB. The confined aquifer consists of Pilliga Sandstone, a porous quartzose sandstone formation with 20%–30% porosity and high groundwater conductivity (*i.e.*, 10^{-5} m·s^{-1}). Since the variation of the chloride ion concentration in the groundwater from the upstream to the downstream end of the surveyed flow line was very small, we can assume that the chloride ion concentration is almost constant. Since the (^{36}Cl/Cl)$_{eq}$ ratio, estimated as $(8 \pm 0.7) \times 10^{-15}$ from the average U ($1.5 \pm 0.2\,\mu$g·g^{-1}) and Th ($6 \pm 2\,\mu$g·g^{-1}) contents of the Pilliga Sandstone, is negligibly small compared to the initial
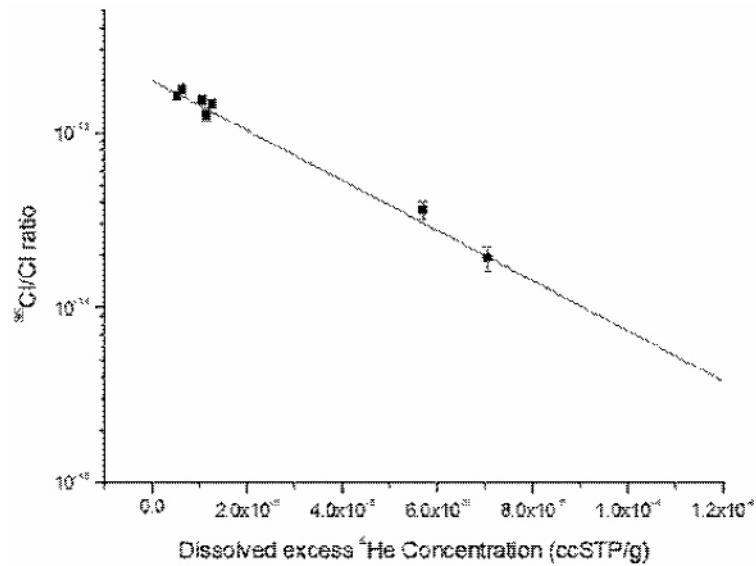
Figure 1: Groundwater with mainly cosmogenic ^{36}Cl (subsurface production of ^{36}Cl was neglected): correlation between the ^{36}Cl/Cl ratio and the excess ^{4}He concentration dissolved in groundwater of the Coonamble Embayment Basin in the GAB, Australia.

cosmogenic ratio, the number of ^{36}Cl atoms in the recharge area is controlled by the cosmogenic source.

We fitted equation (5) to the data (fig. 1) and estimated the ^{4}He accumulation rate to be 6.9×10^{-11} ccSTP $\mathrm{g}_{water}^{-1} \cdot \mathrm{y}^{-1}$ ($r^2 = 0.75$) from the slope of the linear correlation line, using $24\,\mathrm{mg \cdot L^{-1}}$ as the constant chloride concentration in the recharge area 241×10^{-15} as the initial cosmogenic ^{36}Cl/Cl ratio and neglecting the secular equilibrium ^{36}Cl/Cl ratio in the Pilliga Sandstone. We thus estimated the longest residence time, at the downstream end of the survey line, to be $1.12\,\mathrm{Ma}$.

3.2 Groundwater with mainly subsurface-produced ^{36}Cl: The Äspö HRL, Sweden

The HRL was constructed as the *in situ* testing site for disposal of high-level radioactive waste in the Äspö Island. The Äspö Island consists of 1.8-billion-year-old granite. Although tunnel excavation has caused severe groundwater disturbance, which is gradually extending deeper into the tunnel as modern Baltic seawater intrudes through fractures connecting to the surface, palaeo-hydrogeochemical conditions are partially preserved in deep, highly saline
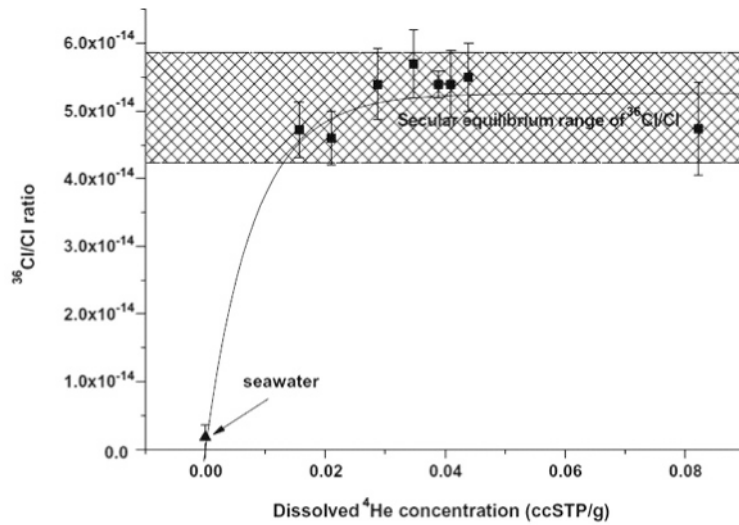
Figure 2: Groundwater with mainly subsurface-produced ^{36}Cl: correlation between the ^{36}Cl/Cl ratio and the ^{4}He concentration dissolved in groundwater. The theoretical growth curve of ^{36}Cl/Cl and the secular equilibrium range for the granites of Äspö are shown (after Mahara *et al.* [7]).

waters of seawater origin that remain unmixed. At Äspö, the dissolved ^{4}He concentration is positively correlated with the ^{36}Cl/Cl ratio, which have been measured every two years from 1995 to 2001, just like an activation curve observed in a nuclear reactor.

Subsurface production is responsible for the majority of the ^{36}Cl and excess dissolved ^{4}He in interstitial groundwater in fractures. The secular equilibrium ratio of ^{36}Cl/Cl in rock was theoretically estimated to be $(5.1 \pm 0.8) \times 10^{-14}$ from the neutron flux intensity, a value comparable to the measured ^{36}Cl/Cl ratio in rock and groundwater. The degassing crustal ^{4}He flux was estimated to be 1.3×10^{-6} (ccSTP cm^{-2}·y^{-1}), which is only one-third the value (3.6×10^{-6} ccSTP cm^{-2}·y^{-1}) estimated in the GAB, Australia. The estimated ^{4}He accumulation rate therefore ranges from 6.8×10^{-10} (the *in situ* accumulation rate) to 7.0×10^{-9} (ccSTP g$^{-1}_{water}$·y^{-1}) (considering both *in situ* ^{4}He production and the degassing flux), if a constant accumulation rate of ^{4}He in groundwater is assumed. Thus, by comparing the subsurface ^{36}Cl increase with the ^{4}He concentration in groundwater, the ^{4}He accumulation rate can be determined for groundwater in which ^{36}Cl/Cl has reached its secular equilibrium value. In this way, an ^{4}He accumulation rate of $(1.8 \pm 0.7) \times 10^{-8}$ ccSTP g$^{-1}_{water}$·y^{-1} could be es-

timated from the relationship between the dissolved ^{4}He concentration and the ^{36}Cl/Cl secular ratio in rock without determining the magnitude of the degassing ^{4}He flux (fig. 2). The longest residence time of the groundwater was then estimated to be 1.2–4.5 Ma in the area isolated from intrusion of modern Baltic seawater.

3.3 Groundwater with both cosmogenic and subsurface-produced ^{36}Cl: The central GAB, Australia

We tested the validity of the method for dating groundwater that cannot be reliably measured by ^{36}Cl dating alone, based on ^{4}He accumulation rates calibrated with ^{36}Cl. We sampled groundwater from confined aquifers along six inferred regional groundwater flow paths in the GAB, and then selected three groundwater paths along which the decrease in ^{36}Cl was mainly controlled by cosmogenic ^{36}Cl radioactive decay without any significant increase in the chloride concentration, taking account for the condition of the secular
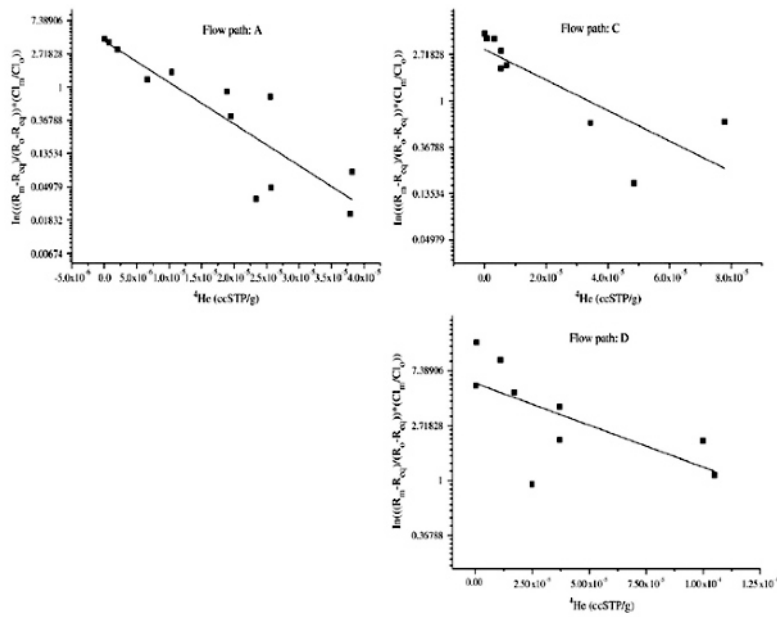

Figure 3: Groundwater with both cosmogenic and subsurface-produced ^{36}Cl: correlation between the excess ^{4}He concentration and the transformed function of the ^{36}Cl/Cl ratio along selected flow paths A, C, and D in the GAB, Australia (after Mahara *et al.* [5]).

^{36}Cl/Cl ratio. The selected three paths have neither strong evaporation nor strong effects of mixing with chloride ion having a low ^{36}Cl/Cl ratio supplied from dissolution from aquifer rock and diffusion from adjoining aquitards. Along these paths, the ^{4}He concentration can therefore be approximated by eq. (5) in the semi logarithmic diagram with a constant accumulation rate.

The estimated ^{4}He accumulation rate ranged from $(1.9 \pm 0.3) \times 10^{-11}$ ccSTP cm^{-3}· y in the central GAB to $(1.5 \pm 0.6) \times 10^{-10}$ ccSTP cm^{-3}· y^{-1} in the western GAB (fig. 3). These rates are from one-half to 1/15 the previously reported rates [9]. However, our estimated rate of 1.51×10^{-10} ccSTP cm^{-3}· y^{-1} in the western GAB is compatible with previous estimates of $(0.2–1.9) \times 10^{-10}$ ccSTP cm^{-3}· y^{-1} based on ^{81}Kr ages [10]. The residence time was estimated to be approximately 7×10^{5} y, based on the ^{4}He accumulation rate near Lake Eyre. Finally, we can extend this method to estimate residence times after secular equilibrium of ^{36}Cl has been reached if the groundwater velocity and the ^{4}He accumulation rate are constant.

4. Conclusion

We can deduce groundwater residence times from the dissolved ^{4}He concentration and the ^{4}He accumulation rate calibrated by ^{36}Cl provided that ^{4}He accumulation mechanisms, groundwater flow, and other geo-environmental conditions have remained unchanged for the required amount of geological time. Furthermore, this proposed ^{4}He–^{36}Cl dating method can probably be used to estimate very long groundwater residence times of more than 2 Ma, which cannot be estimated by using ^{36}Cl alone, from the dissolved excess ^{4}He concentration, even after cosmogenic ^{36}Cl has decayed or subsurface-produced ^{36}Cl has reached secular equilibrium.

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