The Age Dating of Deep Paleogroundwater in Jijicao Preselected Site for High Level Radioactive Waste Geological Disposal

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Abstract. The geological disposal of high-level radioactive waste is concerned with the systematic characteristics of the long-time scale of groundwater. As part of the china site investigations and research associated with the disposal of high-level radioactive waste, the paleogroundwater in deep boreholes have been employed in order to characterize groundwater flow in the fractured bedrock at Jijicao preselected site. By obtaining the deep groundwater samples from deep borehole, this study focused on krypton isotope data, the groundwater mixing and relationship were analyzed, and the paleogroundwater dating results were corrected. It found that the age of deep groundwater is 25ka and 46ka, the characteristics of slow groundwater circulation rate and long residence time are conductive to the safe disposal of high-level radioactive waste.

1. Introduction
The safe disposal of high-level radioactive waste is a major issue related to the sustainable development of the nuclear energy industry, environmental protection, public health and safety. At present, deep geological disposal for high-level radioactive waste is the most technically feasible method [1]. For the high-level radioactive waste geological repository system, the groundwater is most likely to make the radionuclides release and enter the biosphere [2]. The geological disposal of high-level radioactive waste concerns ten thousand years scale time behaviors and performances in the deep groundwater, which as one of the core elements in the evaluation of disposal sites. The paleogroundwater dating is very important for determining the residence time of groundwater in the geological repository. The study has important application prospects and practical significance for the effective safety performance evaluation of the repository.

At present, there are isotopic methods developed for measuring paleogroundwater age, such as 14C, 36Cl, 81Kr, 39Ar, 4He, 234U/238U and so on, most of them need complex corrections when applied in groundwater age dating. The inert gas is evenly distributed in the atmosphere and the content of inert gas remains stable for a long time [3]. 81Kr is mainly produced in the upper atmosphere through the cosmic rays and nucleon reaction in atmosphere, and is distributed uniformly in the atmosphere, the isotopic abundance is (5.2±0.6)) ×10^{-13}, the half-life is 229ka [4], and it is suitable for the age dating of groundwater in the 20~100ka age range [5]. At the same time, the cosmic ray intensity fluctuation cycle caused by the influence of the solar activity is far less than the 81Kr half-life, which will not
cause significant changes to the $^{81}\text{Kr}$ concentration in the atmosphere [6], $^{81}\text{Kr}$ produced by nuclide and neutron-induced fission can be ignored [7]. In addition, $^{81}\text{Kr}$ is a stable radioisotope that is both chemically and physically stable, does not participate in chemical reactions in the environment, and the mixing transport process is simple [8, 9]. Therefore, the $^{81}\text{Kr}$ became an ideal tracer isotope for measuring paleogroundwater age.

2. Overview of the Study Area

The Jijicao rock mass is located in the pre-selected site of high-level radioactive waste repository in Beishan area (as shown in Figure.1), and is about 70km south from YuMen city, the altitude of this area is 1650 to 1700m. As to the arid climate, there are no perennial surface rivers in the area. The study area is lack of rainfall and the average annual temperature is about 4.4°C in the Mazong Mountains, and the annual evaporation capacity is more than 3000mm, the annual average temperature in the east is about 8.3°C, and the annual evaporation capacity is more than 3500mm, which is a typical inland arid climate.

The Jijicao rock mass is NW-SE trend and with the area about 40 km$^2$. The hercynian biotite monzonitic granite is the main rock; there are a small amount of metamorphic rock biorelicts and quaternary loose sediments around the rock mass. The metamorphic rock biorelicts is Proterozoic biotite schist, and the quaternary sediment is a mixture of gravel, sandy soil and clay layer, the average thickness is less than 2m.

![Figure 1. Sketch map of the study area](image)

3. $^{81}\text{Kr}$ Age Dating Principle

3.1. Krypton in the environment

The krypton has six stable isotopes in the natural environment, of which $^{84}\text{Kr}$ is the most abundant, and it is occupying 57% of krypton in the environment (as shown in Table 1), there are a total of
eleven krypton radioactive isotopes, but more than 2 days of half-life, and only $^{81}\text{Kr}$ and $^{85}\text{Kr}$ can be used for environmental process research, their half-lives are 229,000 and 10.76 years. In 1969, Loosli and Oeschger of the University of Berne in Switzerland discovered radioactive isotope $^{81}\text{Kr}$ in the air for the first time. This nuclide is produced by cosmic rays and is very evenly distributed in the atmosphere, and Natural abundance of isotope is about $6 \times 10^{-13}$.

### Table 1. Krypton in the environment

| Category/physical features | Value | Unit | Reference |
|----------------------------|-------|------|-----------|
| $^{81}\text{Kr}$ stable isotope concentration in the air | 1.1 | ppm | Aoki and Makide (2005) |
| $^{78}\text{Kr}$ | 0.35 | % | Ozima and Podosek (2002) |
| $^{80}\text{Kr}$ | 2.26 | % | Ozima and Podosek (2002) |
| $^{82}\text{Kr}$ | 11.52 | % | Ozima and Podosek (2002) |
| $^{83}\text{Kr}$ | 11.48 | % | Ozima and Podosek (2002) |
| $^{84}\text{Kr}$ | 57 | % | Ozima and Podosek (2002) |
| $^{86}\text{Kr}$ | 17.4 | % | Ozima and Podosek (2002) |
| $^{85}\text{Kr}$/Kr (2008) | 2.4 | $\times 10^{-11}$ | Winger et al. (2005) |
| $^{85}\text{Kr}$/Kr (air) | 5.2±0.6 | $\times 10^{-13}$ | Du et al. (2003); Collon et al. (1997) |
| $^{85}\text{Kr}$/Kr (2008) | 46.2 | | Du et al. (2003); Collon et al. (1997) |
| $^{81}\text{Kr}$ half-life | 10.76 a | | Firestone and Shirley (1996) |
| $^{81}\text{Kr}$ half-life | 229000 a | | Firestone and Shirley (1996) |
| $^{83}\text{Kr}$ atom/L water (2008) | 57845 | | Du et al. (2003); Collon et al. (1997) |
| $^{81}\text{Kr}$ atom/L (modern water) | 1253 | | Du et al. (2003); Collon et al. (1997) |
| soluble in water Kr (10°C) | 0.081 | cm$^3_{\text{atm}}$ cm$^{-3}_{\text{water}}$ | Weiss and Kyser (1978) |
| Kr diffusion coefficient in the air (20°C) | ~0.13 | cm$^2$/s | Weast (1981) |
| Kr diffusion coefficient in water (20°C) | ~6.2 | $10^{-5}$ cm$^2$/s | Weast (1981) |

#### 3.2. Atom trap trace analysis method

Atom trap trace analysis is a good method for direct detection of single atom. It is based on the technology of laser cooling and trapping atom; its basic principle is to use the magneto-optical trap method to selectively trap atoms of specific isotopes. The test equipment (as shown in Figure 2), low-pressure krypton (0.1Pa) passes through a section of 1cm diameter quartz tube from the gas source chamber, it is ionized by radio-frequency discharge, generates metastable state krypton atoms into the lateral cooling chamber, it is compressed by the transverse 811 nm resonant laser beam, reduce the divergence angle of the atomic beam and increase the flow of the atomic beam. The atomic beam passes through Zeeman slow-speed tube, which is decelerated by the laser and then enters the magneto-optical trap. In this magneto-optical trap, it is cooled by six slightly red detuned 811 nm lasers and trapped in a magneto-optical trap, and emitted resonance fluorescence is detected by the detector, by precisely tuning the laser frequency, only certain isotope atoms can be cooled and trapped by the laser. Only one atom can occur in the magneto-optical trap, at the same time, and its fluorescence signal is also very weak. Through the imaging system, the single-atom fluorescence signal is efficiently collected to a highly sensitive single-photon detector, and the background scattered light signal is filtered as much as possible, thereby improving the signal-to-noise ratio of single-atom signals and achieving single atom measurement [14-15].

From the radioactive Kr atom content in the sample, the age of the sample can be determined by the following formula:

$$t_{Kr} = \frac{T}{\ln 2} \cdot \ln \left( \frac{R_{air}}{R} \right)$$

The half-life of $T^{81}\text{Kr}$ (about 2.29 × 10$^5$ a); $R_{air}$-the atomic ratio of $81\text{Kr}$ isotope atom in atmospheric precipitation of the supply area; $R$-the $^{81}\text{Kr}$ isotope ratio in the groundwater.
4. $^{81}$Kr Sampling and Testing

As the $^{81}$Kr content in groundwater is extremely low, in order to measure the $^{81}$Kr age in groundwater, it is necessary to extract more than one hundred litres of original groundwater sample based on the double packer hydrogeological system (as shown in Figure 3). The fluorescein sodium spectrophotometer was used to detect the concentration of tracer in the groundwater sample. After collecting enough groundwater samples, the krypton gas is separated in the laboratory by low temperature fractionation and chromatography technology, then the krypton gas was measured by atomic trap trace analysis method which established by the team of University of Science and Technology of China, the atomic number of $^{81}$Kr can be collected, and the concentration ratio and other data of isotope can be obtained [16,17].

5. Results

Compared with the test results (as shown in Table 2), it can be seen from the measurement results of $^{85}$Kr and $^{81}$Kr, CY-02 samples are close to the value of modern air, this indicates that the CY-02 sample may have been contaminated during the extraction of the water sample or groundwater dissolves gas. The concentration of $^{81}$Kr in the CY-01 sample is relatively low, but the value of $^{85}$Kr is relatively high, it may be contaminated in the $^{85}$Kr test process or influenced by the mixing effect of younger groundwater. The $^{85}$Kr content of CY-03 was measured to be $12.9 \pm 1.4$ dpm/cc, the ratio of $^{81}$Kr content to the corresponding content in the modern atmosphere is $1.08 \pm 0.09$, the groundwater sample of CY-03 maybe a mixed sample, therefore, $^{85}$Kr data can be used to correct test results.

The CY-02 sample measurement result is selected as the initial concentration of $^{85}$Kr, use the $^{85}$Kr test results to calculate the mixing ratio of younger groundwater, assume that the deep paleogroundwater mixed by shallow groundwater and the piston flow is main mechanism, namely the young groundwater is mixed during sampling in piston flow type of paleogroundwater system, the age distribution function of the sampling point water is:

$$g(t) = \sum a_k \delta(t-t_k)$$

The $a_k$ age is the share of $t_k$ groundwater ($\sum a_k$), and $\delta$ is the Dirac delta function.
Figure 3. Device of the groundwater sampling and gas separation
Table 2. Results of krypton isotopes in groundwater

| Sample | CY-01 | CY-02 | CY-03 |
|--------|-------|-------|-------|
| Sample depth /m | 390~ | 330~340 | 390~ |
| Krypton / microlitre | 1 | 1.3 | 6 |
| Sample time | 2013-11-04 | 2013-10-21 | 2013-10-30 |
| Count time /hour | 4.5 | 5 | 4.5 |
| \(^{83}\text{Kr}:^{85}\text{Kr}:^{81}\text{Kr}\) measurement time | 1:2:4 | 2:5:15 | 1:2:4 |
| \(^{85}\text{Kr}\) counting | 192 | 304 | 170 |
| \(^{85}\text{Kr}(\text{dpm/cc})\) | 67.8±5.8 | 75.6±5.8 | 12.9±1.4 |
| \(^{81}\text{Kr}\) counting | 45 | 85 | 188 |
| \(^{81}\text{Kr}_{\text{sample}}:^{81}\text{Kr}_{\text{air}}\) | 0.87±0.14 | 1.15±0.13 | 1.08±0.09 |

According to formula (2), the proportion of younger groundwater in the samples can be calculated. The high value of \(^{85}\text{Kr}\) in CY-03 is a mixed sample of groundwater, the corrected groundwater mixed ratio and age data can be obtained based on the \(^{85}\text{Kr}\) mixed model, the depth of groundwater age of CY-01 and CY03 is 46ka and 25ka, the paleogroundwater ratio of CY-03 is about 83% (as shown in Table.3).

Table 3. The results of paleo-groundwater dating corrected by 85Kr

| Sample | \(^{85}\text{Kr}(\text{dpm/cc})\) | \(^{81}\text{Kr}_{\text{sample}}:^{81}\text{Kr}_{\text{air}}\) | Ratio of paleogroundwater | Ratio of young water | Corrected age/ka |
|--------|-----------------|-----------------|-------------------------|----------------------|------------------|
| CY-01  | 67.8±5.8        | 0.87±0.14       | 100%                    | 0                    | 46               |
| CY-02  | 75.6±5.8        | 1.15±0.13       | 0                       | 100%                 | modern           |
| CY-03  | 12.9±1.4        | 1.08±0.09       | 83%                     | 17%                  | 25               |

6. Conclusion

The krypton isotope can be used to carry out dating research on the deep groundwater, the results show that the \(^{81}\text{Kr}\) ages of the deep groundwater in Jijiao preslected site are 25ka and 46ka, respectively, it shows that the deep environmental groundwater circulation rate is extremely slow, this feature is conducive to the safe disposal of high-level radioactive waste.

The use of \(^{85}\text{Kr}\) isotope can effectively determine the mixing effect and ratio of younger groundwater and paleogroundwater, and can be applied to the correction of the \(^{81}\text{Kr}\) age.

Considering the harsh conditions of the krypton isotope dating method, the uncertainty of the isotope dating method, and the complexity of the deep geological environment, isotope dating studies are needed to verify its credibility further, and various dating methods need be used for comparative studies, then the characteristics of the deep groundwater system can be described more accurately and reliably, thus providing a reliable reference for the suitability evaluation of the high-level radioactive waste repository.

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