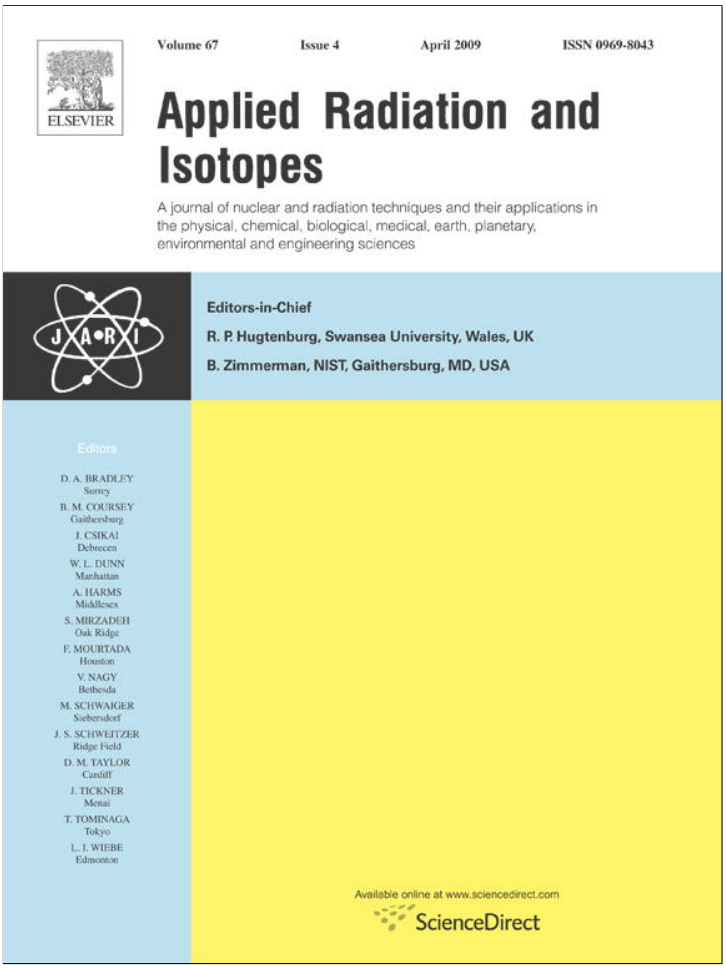

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Relationship between radioactivity of radium and concentrations of barium and lead in hokutolite

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ABSTRACT

Hokutolite consists of barite ($BaSO_4$) and anglesite ($PbSO_4$), and contains significant amounts of radium isotopes as a radioactive mineral. Photon activation and gamma-ray spectrometry were employed to determine Ba, Pb and ^{226}Ra contents in hokutolite samples and to investigate the correlation between ^{226}Ra activity and both Ba and Pb content. ^{226}Ra activity in 30 hokutolite samples were estimated in the range of 40–65 Bq/g and was positively related to Ba content ($r = 0.859$, $p < 0.001$), but independent of Pb content ($r = -0.236$, $p = 0.217$). Experimental results implied that ^{226}Ra preferably precipitated with Ba over Pb. The ^{226}Ra activity in hokutolite from the Peitou Hot Spring was experimentally estimated based on the Ba/Pb ratio and expressed as $^{226}Ra\ (Bq/g) = 14.67\ (Ba/Pb)_{molar} + 14.13$.

1. Introduction

Hokutolite, a lead-bearing barite, is a mixed solid solution of barite ($BaSO_4$) and anglesite ($PbSO_4$) (Chen and Yu, 1984; Sasaki and Minato, 1982; Sasaki et al., 1992), containing a considerable amount of radium and other alkaline earth elements (Momoshima et al., 1997; Takano and Watanuki, 1972). This radioactive sulfate mineral present in hot springs was first discovered in 1905 by Okamoto (Chang, 1961) at Peitou Hot Spring, a small town in northern Taiwan. It was also found at Tamagawa Spring in Akita, Japan (Sasaki et al., 1992). Numerous studies have been carried out to understand the crystal structure, chemical composition and growth rate of natural hokutolite, along with related environmental factors.

Based on the analysis of the crystal structure in hokutolite, the Ba and Pb cations are in a fully disordered arrangement for mutual substitution in lattice (Chen and Yu, 1984; Su et al., 2002). The ratio of Ba to Pb in hokutolite has frequently been used to elucidate the chemical composition of hokutolite and to understand environmental factors that control the growth of hokutolite crystal (Chen and Yu, 1984; Takano and Watanuki, 1974). The chloride concentration and temperature of a hot spring water are major factors in controlling the lead content in hokutolite during the formation processes (Takano, 1969; Takano and Watanuki, 1974). The increased amount of lead-chloro-complexes is believed to reduce the formation of $PbSO_4$ in thermal solution. Additionally, $BaSO_4$ precipitates before $PbSO_4$ in hot spring water as the temperature declines, which leads to increasing the fraction of $PbSO_4$ in hokutolites that precipitate downstream (Takano, 1969; Takano and Watanuki, 1972).

Takano and Watanuki (1972) observed that the contents of minor elements Sr and Ca are positively related to Pb content in hokutolite. They attributed this finding to the fact that the crystal chemical properties of $SrSO_4$ and $CaSO_4$ are more similar to those of $PbSO_4$ than those of $BaSO_4$. Based on the similarity between the chemistries of alkaline earth elements and Pb, the radium atoms are supposed to co-precipitate with Ba and Pb in the crystallization process. The radioactivity of two main radium isotopes, ^{226}Ra and ^{228}Ra, in hokutolite has been measured to estimate the growth rate of hokutolite (Momoshima et al., 1997; Saito and Nagai, 2007). However, the relationship between the distribution of radium and the two major elements, Ba and Pb, has not been well studied, and their correlation during formation is unknown.

Non-destructive elemental analysis of hokutolite with an electron probe micro-analyzer (EPMA) or X-ray fluorescence (XRF) analysis is the most common method for determining Ba and Pb contents (Chen and Yu, 1984; Momoshima et al., 1997; Sasaki and Watanuki, 1983; Sasaki et al., 1992). However, it can only be performed on the surface of a sample, rather than throughout a bulk sample. Estimating the Ba and Pb fractions in

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an intact hoktolite specimen is typically difficult because the specimen may incorporate mineral impurities and the Ba/Pb ratio may be non-uniform. Moreover, mechanically separating pure hokutolite from an andesite block and other incorporated materials prior to elemental and radionuclide analyses is difficult. Neutron activation analysis (NAA) is the most popular non-destructive method and can be applied to a bulk sample, but it suffers from being insensitive to Pb.

This study presents photon activation analysis (PAA) using a medical accelerator for elemental analysis. PAA is desirable for determining Ba and Pb contents in hokutolite as their sensitivities through photon nuclear reactions are adequate and the activated nuclides ^{135m}Ba and ^{203}Pb have suitable half lives that facilitate measurement. The activities of the activated radionuclides and ^{226}Ra were simultaneously measured using a gamma-ray spectrometer. The ^{226}Ra activity in hokutolite in relation to Ba and Pb was statistically analyzed to explain the behavior of radium in the precipitation process. The ^{226}Ra content in relation to Ba/Pb ratio was also investigated.

2. Materials and methods

2.1. Sample preparation

Thirty hokutolite specimens of mass 0.2–1.0 g were randomly selected for this experiment. These samples were collected along Peitou River during 1980–2001, when they were isolated from the hot spring water. The water temperature has been reduced by introducing a cold flow, and hokutolite has not been precipitated for a long time. Two areas A and B are known for hokutolite deposits at around 300 and 150–250 m from the vent of the hot spring. The actual location of the samples from area B was not recorded. To simulate the chemical composition of hokutolite, powder chemicals (purity >99%) of $BaSO_4$ (0.24 g) and $PbSO_4$ (0.16 g) were mixed and pressed into a tablet for use as a comparative standard.

2.2. Photon irradiation

Photoirradiation was conducted using an 18 MV medical accelerator (Precise, Elekta) at E-Da Hospital. The hokutolite samples and the standard were placed immediately outside the treatment head with a source-to-sample distance of 53 cm. The accelerator was operated to provide 20 consecutive exposures of 1000 monitor units (MUs) for 1 h for a field size of 40 cm × 40 cm. The total radiation at maximum depth in a water-equivalent phantom with a source-to-surface distance of 100 cm was calibrated as 200 Gy while the actual radiation dose at the sample position was estimated with a QED photodiode detector (Model 1135, Sun Nuclear Corporation) to be 698 Gy during the 1 h irradiation (Chao et al., 2009).

2.3. Photon activation reactions

Table 1 presents possible photon activation reactions for analysis of Ba and Pb in hokutolite. The reaction ^{136}Ba(γ,n)^{135m}Ba may provide the highest sensitivity for Ba determination (Chao et al., 2009). The reaction ^{204}Pb(γ,n)^{203}Pb is the only one that can be exploited for determining Pb. The half lives of ^{135m}Ba ($t_{1/2}$ = 28.7 h) and ^{203}Pb ($t_{1/2}$ = 52 h) suffice for gamma-ray measurement within one week after photon irradiation.

2.4. Gamma-ray measurement

The irradiated hokutolites were transferred to the radioactivity measurement laboratory (National Tsing Hua University) for counting using a well-type Ge detector (GCW6023, Canberra) equipped with a multi-channel analyzer (35-Plus, Canberra). Gamma-ray spectra were analyzed using the Sampo 90 gamma-ray spectrum software package. The activities of the photon-activated nuclides ^{135m}Ba and ^{203}Pb, as well as of ^{226}Ra were measured together. The activity of ^{226}Ra was determined in terms of its daughter nuclide ^{214}Bi at 609 keV.

2.5. Statistical analysis

Data were analyzed using SPSS for Windows version 13.0. Pearson correlation was used to analyze the correlation of ^{226}Ra with $BaSO_4$ or $PbSO_4$. Multiple regression analysis based on the stepwise method was performed to evaluate the contribution of $BaSO_4$ and $PbSO_4$ to ^{226}Ra after adjusting for confounding variables. A two-tailed p-value <0.05 was considered significant.

3. Results and discussion

3.1. Distribution of ^{226}Ra and Ba/Pb ratio in hokutolite

The Ba and Pb in hokutolite are assumed to have been formed as $BaSO_4$ and $PbSO_4$, respectively; their masses were determined by the photon activation technique and their masses were summed as the mass of "pure hokutolite" in the samples. The activity of ^{226}Ra, based on "pure hokutolite", was therefore determined, and ranged from 40 to 65 Bq/g, approximating the published values of 28–86 (Momoshima et al., 1997) and 56–69 (Tomita et al., 2006) in Peitou, and 52–85 Bq/g (Saito and Nagai, 2007) in Tamagawa. Table 2 summarizes ^{226}Ra and the respective Ba/Pb molar ratios of these samples from areas A and B. The results revealed that both ^{226}Ra and the Ba/Pb ratio in the hokutolite samples from the upstream area (B) exceeded those from the downstream area (A).

Table 1
Photon activated nuclides of Ba, Pb and the respective gamma rays.

Element	Photonuclear reactions	Q value (MeV)	Abundance (%)	Half-life ($t_{1/2}$)	$E_\gamma(I_\gamma)$ (keV) (%)
Ba	^{132}Ba(γ,n)^{131}Ba	9.80	0.101	12.0 d	124 (29.2); 496 (47.1)
	^{134}Ba(γ,n)^{133m}Ba	9.76	2.42	38.9 h	276 (17.5)
	^{136}Ba(γ,n)^{135m}Ba	9.38	7.85	28.7 h	268[a] (17.5)
Pb	^{204}Pb(γ,n)^{203}Pb	7.75	1.42	52.0 h	279[a] (80.1)

[a] The gamma rays used for the determination.

3.2. Correlation of ^{226}Ra activity with Ba and Pb contents

Bivariate analysis of the Pearson correlation showed that ^{226}Ra activity was individually associated with Ba ($r = 0.989$, $p < 0.001$) or Pb ($r = 0.960$, $p < 0.001$) (Table 3, Fig. 1(a)). However, after controlling for the contribution of Pb to ^{226}Ra, ^{226}Ra was strongly correlated with Ba content ($r = 0.859$, $p < 0.001$; Table 3 and Fig. 1(b)). On the contrary, ^{226}Ra was not independently correlated with Pb ($r = -0.236$, $p = 0.217$; Table 3 and Fig. 1(c)). Since Pb was obviously correlated with Ba ($r = 0.978$, $p < 0.001$), it is the reason that there was correlation between Pb level and ^{226}Ra activity in bivariate analysis ($r = 0.960$) but no correlation in partial analysis adjusted to Ba ($r = -0.236$). These results meant Pb was a confounding factor to interfere with the evaluation of Ba level referred to ^{226}Ra activity. It is difficult to experimentally distinguish the contribution of ^{226}Ra activity from Ba and/or Pb because they exist together in hokutolite. This statistical logic implied that Pb may theoretically interfere with the accuracy in evaluating ^{226}Ra activity attributed to Ba ($r = 0.989$ down to 0.859). Based on statistical analysis, it suggested that Pb happen to occur with Ba in the hokutolite, and Ba was the crucial element that contributed to ^{226}Ra activity. If Ba and Pb were considered together in determining ^{226}Ra activity, the correlation between ^{226}Ra and Ba would be overestimated. According to the stimulated regression equation, every gram of $BaSO_4$ was accompanied by 83 Bq of ^{226}Ra activity.

Table 2
Comparison of ^{226}Ra and Ba/Pb ratio in the hokutolite samples from A and B areas.

Sampling area (sample number)	^{226}Ra (Bq/g)		$(Ba/Pb)_{molar}$ ratio	
	Range	Mean	Range	Mean
A (13)	40.4–48.8	43.9	1.81–2.54	2.07
B (17)	42.8–64.7	55.1	2.39–3.24	2.77

Table 3
Pearson correlation of ^{226}Ra with Ba and Pb.

	Pearson correlation			
	Bivariate		Partial (adjusted)[a]	
	$BaSO_4$ (g)	$PbSO_4$ (g)	$BaSO_4$ (g)	$PbSO_4$ (g)
^{226}Ra (Bq)	0.989 ($p < 0.001$)	0.960 ($p < 0.001$)	0.859 ($p < 0.001$)	−0.236 ($p = 0.217$)

[a] Regression equation: ^{226}Ra (Bq) = 0.56+82.62 $BaSO_4$ (g)–17.41 $PbSO_4$ (g) ($R^2 = 0.979$).

3.3. Estimation of ^{226}Ra activity from Ba/Pb ratio

The Ba/Pb ratio has been commonly used to characterize the chemical composition of hokutolite. To express ^{226}Ra activity in hokutolite simply, the ^{226}Ra activities of all samples were plotted against Ba/Pb ratio in Fig. 2. The relationship between ^{226}Ra activity and Ba/Pb demonstrated that ^{226}Ra preferentially co-precipitated with Ba. The equation ^{226}Ra(Bq/g) = 14.67 $(Ba/Pb)_{molar}$+14.13 can be applied to evaluate the ^{226}Ra activity in hokutolite (Ba/Pb = 1.8–3.3) from Peitou Hot Spring.

3.4. Other remarks

The formation of the hokutolite crystal is governed by several factors such as source material, flow rate of hydrothermal solution, pH value, chloride concentration, temperature and others. Therefore, the Ba/Pb ratio in hokutolite may vary in time and among domains. The advantage of using PAA and gamma-ray spectrometry to determine Ba, Pb and ^{226}Ra contents simultaneously is to obtain more representative and reliable information, even when the composition of samples is non-uniform. Notably, the photon activated nuclides and ^{226}Ra in the hokutolite samples were measured together under the same counting geometry and

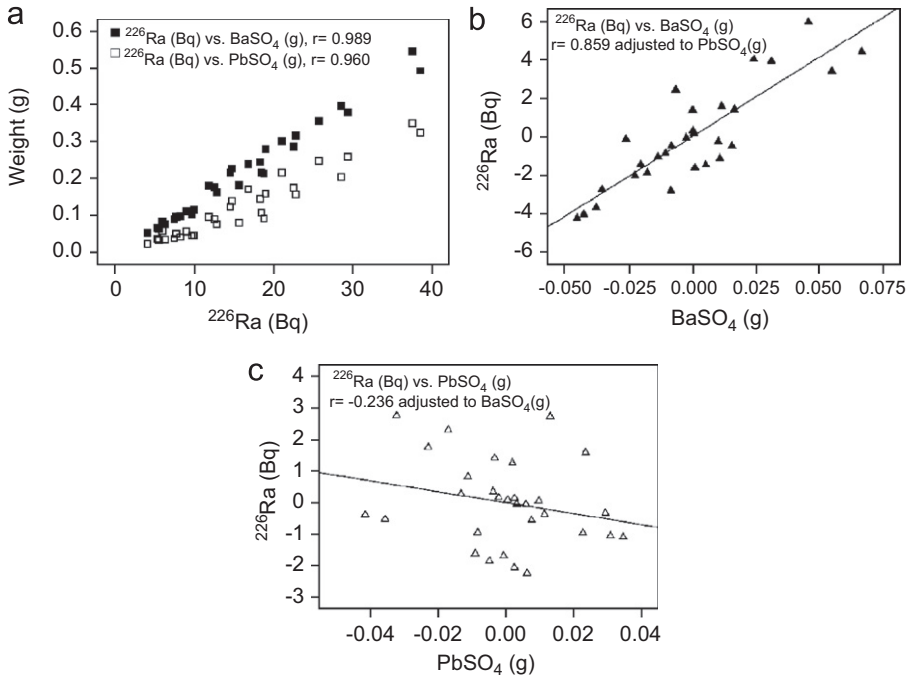

Fig. 1. Correlation of ^{226}Ra activity with Ba or/and Pb contents illustrated in scatter plot and partial regression plots. Scatter plot of ^{226}Ra and Ba, and ^{226}Ra and Pb (a). Partial regression plots of ^{226}Ra and Ba adjusted for Pb (b), and ^{226}Ra and Pb adjusted for Ba (c).

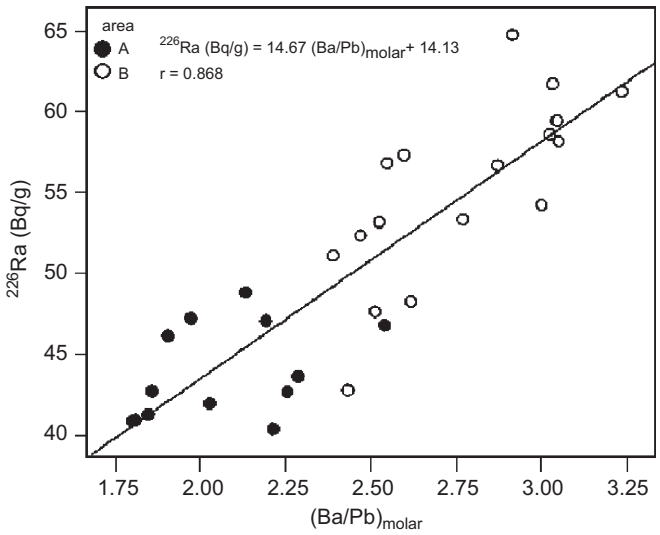

Fig. 2. Activity of ^{226}Ra as a function of Ba/Pb ratio for hokutolite samples.

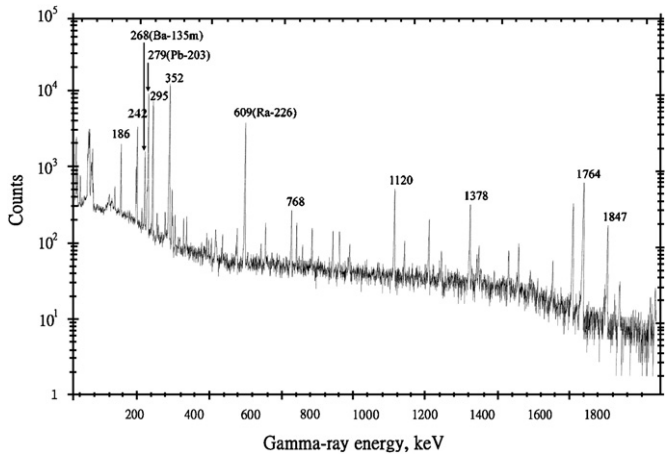

Fig. 3. Gamma-ray spectrum of hokutolite sample irradiated with 18 MeV bremmstrahlung photons. Peaks other than the photopeaks from ^{135m}Ba (268 keV) and ^{203}Pb (279 keV), with indicated energy (keV), are from ^{226}Ra.

conditions, and the concentrations of Ba, Pb and ^{226}Ra in the hokutolite samples can therefore be precisely related, avoiding uncertainties associated with the use of different analysis processes. Fig. 3 displays a typical gamma-ray spectrum after photon irradiation.

For 1 g of pure hokutolite specimen with a Ba/Pb ratio of 2, the photon-induced activities of ^{135m}Ba and ^{203}Pb were estimated to be 55 and 58 Bq, respectively, at the end of irradiation. These activities are close to that from the ^{226}Ra that they contained. Additionally, these levels are far below the exempt limits on the activities for ^{203}Pb (10^6 Bq), ^{135m}Ba (10^6 Bq) and ^{226}Ra (10^4 Bq) (IAEA, 1996; AEC, 2006), suggesting that handling and delivering such samples poses no radiation risk.

4. Conclusion

(1) The combination of photon activation and gamma-ray spectrometry constitutes a practical and reliable method for determining Ba, Pb and ^{226}Ra contents in hokutolite, although the amount of radium by weight is much lower than that of Ba or Pb.
(2) Barium content is strongly correlated with ^{226}Ra activity, and is the crucial element that co-precipitates with ^{226}Ra during the formation of hokutolite.
(3) Both ^{226}Ra and Ba/Pb ratio in hokutolites that were collected from the Peitou River decline as the distance from the vent increases. The activity of ^{226}Ra can be derived from the experimentally determined Ba/Pb ratio.

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