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ESR DATING OF MARINE BARITE IN CHIMNEYS DEPOSITED FROM HYDROTHERMAL VENTS

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Abstract: Electron Spin Resonance (ESR) dating of marine barite in chimneys deposited from hydrothermal vents was attempted to determine the time since hydrothermal activity occurred. In this study, we used Barite ($BaSO_4$) precipitated in icroenvironments in the chimneys deposited from the hydrothermal vents at the Archaean site in South Mariana spreading centre (12°56.4'N, 143°37.9'E) and at Hakurei site in the Izena caldron (27°15'N, 127°04'E) for ESR measurements. ESR spectrum of marine barite is characterized by an electron-type centre with g values of 2.0034, 2.0022 and 1.9995 attributed to SO_3^-. The signal intensity increased with gamma ray dose. The dose rates of hydrothermal chimneys from the Archaean site and from the Hakurei site were calculated using a model that assumed a grain size and that incorporation of radionuclides after ^{226}Ra in U series into the chimney, and assuming the efficiency of the defect formation by alpha particles to be the same as that for OSL. The ESR ages were estimated to be 470 years old for barite from the Archaean site and 5670 years old for one from the Hakurei site, although there is a considerable difference between the present ESR ages and the $^{210}Pb/^{226}Ra$ disequilibrium ages previously reported.

Keywords: marine barite, ESR, dating, hydrothermal chimney

1. INTRODUCTION

At the beginning of the discovery of the hydrothermal systems in the sea, their timescales were not of interest. The timescale became one of the issues when some huge hydrothermal plumes were found along with volcanic activities at the sea floor and sudden changes in the hydrothermal activities were reported. The long-term change of the hydrothermal activities also became of interest in the aspect of ore formations (e.g. Urabe, 1995). However, no systematic geochronological studies of the hydrothermal system at the sea floor have been possible so far due to lack of methods that cover the age ranges of interest. Recently, water circulation below the sea floor and the chemical interaction of sea water and fluid related with the hydrothermal activities have been a subject of the scientific study to investigate the transfer of the elements from the magma to the sea water and to inform on the biological systems sustained by the chemical species in those water flows (e.g. Macdonald *et al*., 1980).

Electron Spin Resonance (ESR) dating studies on oceanic materials have been limited to corals (e.g. Ikeda *et al*., 1992; Schellmann *et al*., 2004), shells (e.g. Radtke *et al*., 1982; Molodkov, 2001) and foraminifera (Sato, 1982; Mudelsee *et al*., 1992) as summarized by Ikeya (1993). These materials are useful for the studies on sea level change and related tectonic activities. However, no ESR studies on hydrothermal ore deposits in deep-sea floor have been reported so far.

Barite ($BaSO_4$), the most common barium mineral, occurs in depositional environments on sea floor, as well as in those on land including biogenic, hydrothermal, and evaporation on land. There were several ESR studies on the signals of barite (Ryabov *et al*., 1983) where Kasuya *et al*. (1991) suggested that barite is a mineral possibly suitable for ESR dating as indicated by the dose response and the thermal stability of the signal. However, so far there have been no reports on practical ESR dating of barite.

In this study, electron spin resonance (ESR) investigation of marine barite was carried out to evaluate its use as a dating for the evolution of hydrothermal systems, which

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are directly related to ore formation and to life activities in the sea floor.

2. SAMPLES

Two inactive chimney samples deposited from hydrothermal vents at different troughs of the see-floor were selected in this study.

Chimney 903-R7 from the South Mariana Trough was collected during the YK05-09 cruise, which was conducted in July and August 2005, by deep-sea submersible vehicle Shinkai 6500 performed by the Japan Agency for Marine-Earth Science and Technology (JAMSTEC). The sample was collected during dive 903 at the Archaean site (12°56.4'N, 143°37.9'E; depth ~3,000 m) (Ishibashi *et al*., 2006). This chimney mainly comprises barite, spharelite and pyrite. The age of this chimney has been estimated to be 31.1±1.5 years before 2005 using the $^{210}Pb/^{226}Ra$ disequilibrium method (Noguchi, 2007).

Chimney 220 was collected at Hakurei site (27°15‘N, 127°04‘E) in the Izena caldron, Okinawa Trough by ROV Hyper-Dolphin (dive 220) during the NT03-09 cruise performed by JAMSTEC in July and August 2003. This chimney mainly comprises barite, spharelite, pyrite and traces of sulfide bearing antimony and arsenic. The age of this chimney has been estimated to be 24-33 years before 2005 using the $^{210}Pb/^{226}Ra$ disequilibrium method (Noguchi, 2007).

Chimney samples were cut into slice perpendicular to the growth orientation. Samples numbered 903-R7-2 and 220-E (see Noguchi, 2007) were used in this study.

3. EXPERIMENTAL PROCEDURES

Barite was separated from the chimney using a sequential leaching procedure. Approximately 2 g (dry weight) of a fragment hewed from core of chimney sample approx. 14 cm in diameter, was crushed using a mortar and placed in a 300 ml beaker. To separate sulfides from the chimney, the sample was treated by 20 ml of 12M HCl for 24 h at room temperature. Then sulfides as sphalerite and pyrite were removed from the residue by treating it with 10 ml of 13M NHO_3 for 24 h at room temperature. The residue then was leached by 10 ml of 6M HCl and 10 ml distilled water. The sample was dried using heater at 40°C and then sieved to obtain a 75-300 μm grain fraction. The sample was analyzed using X-ray diffraction (XRD) and Scanning Electron Microscope-Energy Dispersive X-ray System (SEM-EDS) at Okayama University of Science after the impurities such as remaining sulfide, were handpicked and removed. Extracted barite was ~30-35% in weight percent of a chimney sample.

All samples were measured with a JEOL PX-2300 ESR spectrometer at Okayama University of Science. The measurement was carried out under following conditions; microwave power 1 mW, width of the magnetic field 10 mT scanned in 1 min. with accumulation of 5 scans, modulation amplitude 0.1 mT, modulation frequency of 100 kHz, time constant 0.03 s at room temperature.

The dose response of ESR signals in barite was obtained by irradiating the samples using a ^{60}Co gamma ray source at doses ranging from approx. 50 to 2600 Gy at a dose rate of approx. 100 Gy/h at Takasaki Advanced Radiation Research Institute of Japan Atomic Energy Agency. ESR measurements were made about a week storage after the irradiation.

In order to estimate dose rate for the chimney samples, at first two-dimensional measurement of radiation produced by natural irradiation of the chimney was performed by the use of an imaging plate (for more details see Hareyama *et al*., 2000; Toyoda *et al*., 2010) and then radionuclide concentrations of U and Th series, and potassium (K_2O) were measured using gamma-ray spectrometry at Okayama University of Science with a low background germanium semiconductor detector system (CANBERRA GC1520).

4. RESULTS AND DISCUSSION

ESR signals

ESR spectra of marine barites in 903-R7-2 from the South Mariana Trough and in 220-E from Izena caldron, Okinawa, at room temperature, are shown in **Figs. 1** and **2**, respectively. A set of signals is observed in both samples. The observed signal is attributed to the electronic SO_3^- centre (Ryabov *et al*., 1983; Kasuya *et al*., 1991) with a structure similar to the E' centre in SiO_2 and CO_2^- centre in $CaCO_3$ (Kasuya *et al*., 1991). The g factors are 2.0034, 2.0022, and 1.9995, and are consistent with those reported by Ryabov *et al*. (1983), 2.0032, 2.0023, and 1.9995. The ESR intensity of SO_3^- centre in both samples was enhanced by gamma irradiation of approx. 2000 Gy as shown in **Figs. 1** and **2**. The shapes of two curves did not change by irradiation. However, o hole-type O_2^{3-} centre (g = 2.0191, 2.0127, and 2.0103 reported by Kasuya *et al*., 1991) was detected in either sample. The O_2^{3-} centre observed in anhydrite ($CaSO_4$) is stabilized by a

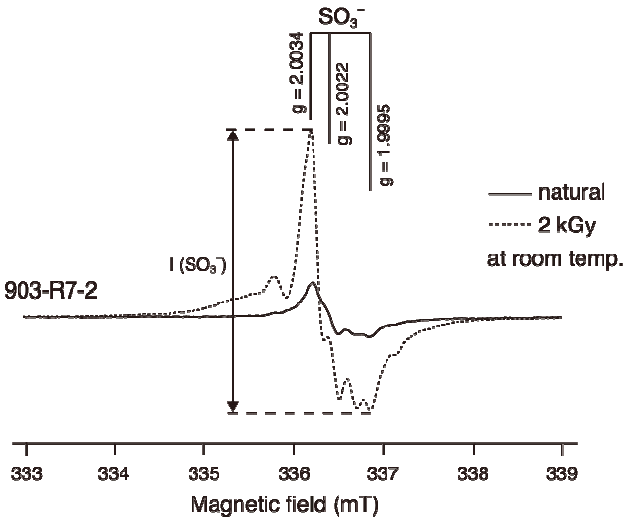

Fig. 1. *The ESR spectra due to SO_3^- observed in a marine barite sample, 903-R7 chimney, solid line is for natural sample and broken line after irradiation. I denotes the intensity of the SO_3^- signal, peak height between g = 2.0034 and g = 1.9995.*

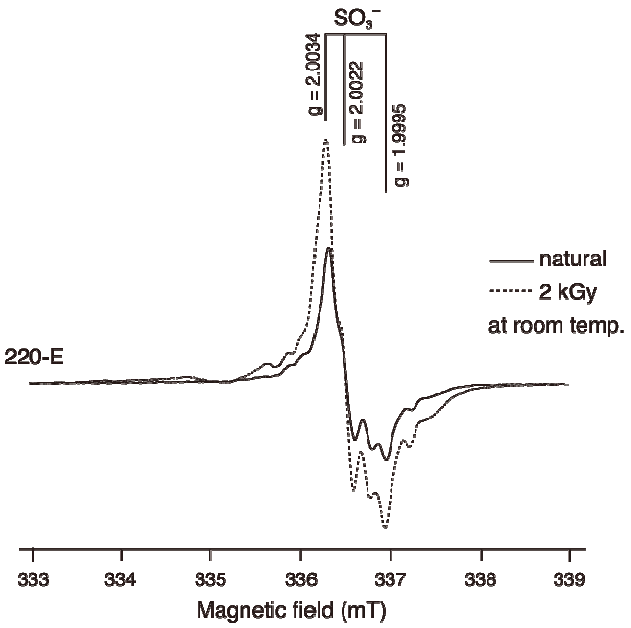

Fig. 2. *The ESR spectra due to SO_3^- observed in a marine barite sample, 220-E chimney, solid line is for natural sample and broken line after irradiation. I denotes the intensity of the SO_3^- signal, peak height between g = 2.0034 and g = 1.9995.*

trivalent metallic ion (M^{3+}) such as Y^{3+} (Bershov *et al*., 1971). Therefore, the contents of a M^{3+} ion in marine barite may be different from that in natural barite on land.

Dose response

In this study, the amplitude between the peaks at g = 2.0034 and g = 1.9995 was taken as the intensities of the SO_3^- signal. Additive dose responses for the two samples are shown in **Figs. 3** and **4**. The intensities were enhanced at least up to approx. 2600 Gy. According to Kasuya *et al*. (1991), the thermal annealing experiment indicated that these electron-type centres in barite are stable up to 330°C and more stable than the hole-type centres. Moreover, they reported that the electron centres could be applicable to ESR dating.

The dose responses were fitted to a saturating exponential function to extrapolate the curve to the zero ordinate in order to determine the equivalent doses (D_e). For each sample, D_e values were obtained to be 231 Gy for 903-R7-2 and 1730 Gy for 220-E as shown in **Table 1**. The errors of D_e's were calculated by considering the errors of the parameters of the saturating exponential curves and the correlation between the errors. The reproducibility of the signal on repeated measurements was about 5%. One could see a possible kink at the middle of the dose responses. This issue should be one of the topics to be further investigated whether a single saturation exponential curve is appropriate for fitting the dose responses of the barite signal.

Distribution of radioactive elements

Polarized microscopic observation of thin section sample was conducted, and then the distribution of radioactivity in samples was examined with an imaging plate (Toyoda *et al*., 2010). A typical example of natural radioactivity mapping of core part of chimney 903-R7-2 sample is shown in **Fig. 5**. The darker areas in **Fig. 5c** correspond to those with relatively higher radioactivity. As a result of comparing autoradiograph with optical microphotograph, it was confirmed that radioactive sources within the chimney corresponds to marine barite (bright area in **Fig. 5b** and dark area in **Fig. 5c**) where the barite is strewn in the whole sample (**Fig. 5a**). The shape of marine barite is a rectangle and its grain size is approx. 100 × 40 × 20 μm in the core of the sample. In this study, we used barite in the core part of the sample rather than those in the vein. The ^{226}Ra activities of the barite were measured by gamma ray spectrometry assuming radioactive equilibrium. The bulk Ra concentrations were 7.72 Bq/g for chimney 903-R7-2 and 4.77 Bq/g for chimney 220-E, while the decay members of Th series and K_2O were not detected.

For the above observation, we considered how much energy of α, β and γ ray emitted from barite is absorbed within the sample based on a model that a grain of barite is an infinite plate (layer) with 20 μm in thickness. The range of alpha particles in barite of density of 4.5 g/cm^3

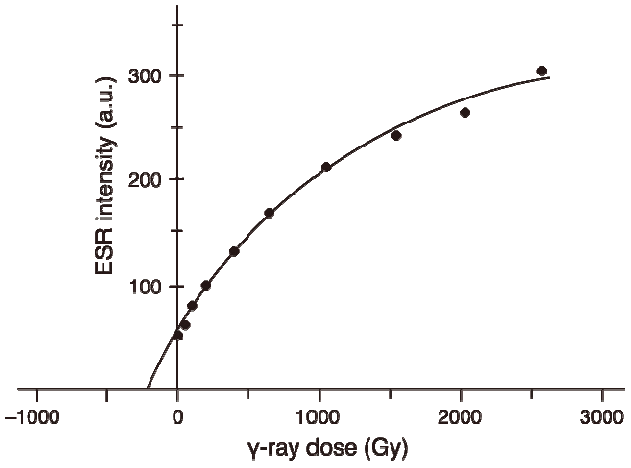

Fig. 3. *Dose response curve of the SO_3^- signal fitted to a saturating exponential function for marine barite in chimney 903-R7-2.*

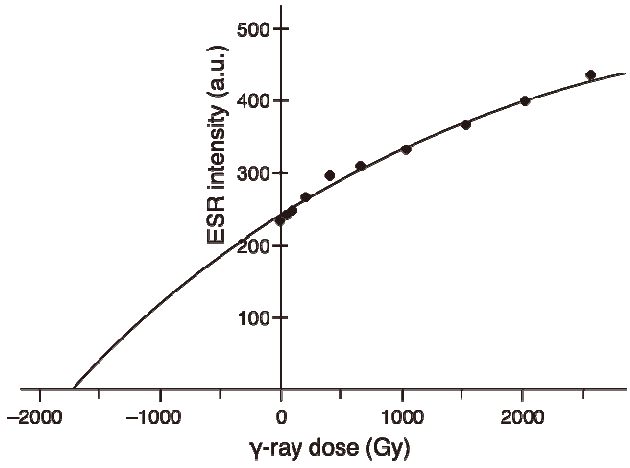

Fig. 4. *Dose response curve of the SO_3^- signal fitted to a saturating exponential function for marine barite in chimney 220-E.*

was calculated to be approx. 7.2 μm. The internal alpha-dose was calculated to be 0.8 times the value for infinite media where the attenuation factor was obtained from the Fig. A-1 of Grün (1989) after correcting for the difference in density; the density of barite is 4.5 g/cm^3 while that of quartz is 2.7 g/cm^3. The internal beta dose in barite was estimated to be 5% of the value for infinite media, according to Grün (1987) estimation for hydroxyapatite (density: 2.95 g/cm^3) in a layer. The external β ray dose was estimated to be reduced by 5% where the external β ray dose was calculated from the Ra concentration averaged over the whole sample. In order to evaluate the effect of gamma dose within the chimney, we estimated the amount of gamma dose contribution to the central portion of sample. The γ ray dose exponentially decreases with distance. The half-thickness for the absorption of γ ray was estimated from that in aluminum (Firestone and Shirley, 1996), which is 2.2 cm after correcting for the difference in density. It is necessary to estimate the missing contribution of γ ray which come from the outside more than 7 cm to the sample in central 2 cm hewed out from the core of the chimney ~14 cm in diameter. After integrating the exponential function, we calculated this contribution to be 11%. Therefore, the gamma ray dose was estimated to be 89% of value for infinite media. The cosmic ray dose was assumed to be negligible because of sample on the sea floor at a depth ~3000 m under water. The doses from Th and K were also negligible and hence not considered. As results, the natural dose rates were calculated to be 493 mGy/y for chimney 903-R7-2 and 305 mGy/y for chimney 220-E (**Table 1**). In this estimation, the conversion factors proposed by Adamiec and Aitken (1998) were used after subtracting the contribution from ^{238}U to ^{230}Th. The efficiency of the defect formation by alpha particles was assumed to be 0.1 (Aitken, 1998) which is the case for luminescence in quartz to be 0.25 (Nagar *et al*., in press) which is the case for the ESR signal in gypsum.

ESR ages

ESR ages of hydrothermal chimney 903-R7-2 and 220-E are listed in **Table 1**. The age of chimney 903-R7-2 from Archaean site, South Mariana Trough was computed to be 300-470 years. This is to be contrasted with an estimate of 31.1±1.5 years before 2005, using ^{210}Pb/^{226}Ra disequilibrium method (Noguchi, 2007). ESR age is approx. 10-15 times older. For the chimney 220-E from the Hakurei site, Izena caldron, ages of 3620-5670 years old were calculated from ESR dating. However, Noguchi (2007) reported that the ^{210}Pb/^{226}Ra age ranges from 24 to 33 years before 2005. ESR age is approx. 100-200 times older than that by the ^{210}Pb/^{226}Ra disequilibrium method. The results presented in the current study show that ESR ages of chimney are systematically, orders of magnitude older than those obtained by ^{210}Pb/^{226}Ra method.

There could by several reasons for the discrepancy, especially those relating to dose rate estimation. The estimation of dose rates for α, β and γ in this study is based on model considering the grain size of actual barite in chimney core as plate-like crystal grain of 20 μm thickness. As our preliminary results for ^{230}Th/^{234}U in sulfide minerals indicate, the age of chimney 903-R7 to be in the range of 2000-3000 years. If this result is right, we still raise an additional issue of whether the ^{210}Pb/^{226}Ra disequilibrium system works for marine barite. Dating of marine barite leaves therefore an open issue to be investigated by every possible dating method.

The present results, first practical application of ESR dating method to barite, showed that the ESR signal, electronic SO_3^- centre, in marine barite could be used to deduce the age of hydrothermal deposit on the sea floor. However, in order to conduct practical ESR dating, further work is needed to pursuit how to calculate dose rate for α, β and γ rays in hydrothermal chimney. The efficiency of the defect formation by alpha particles in barite is another factor to be estimated by experimental He ion

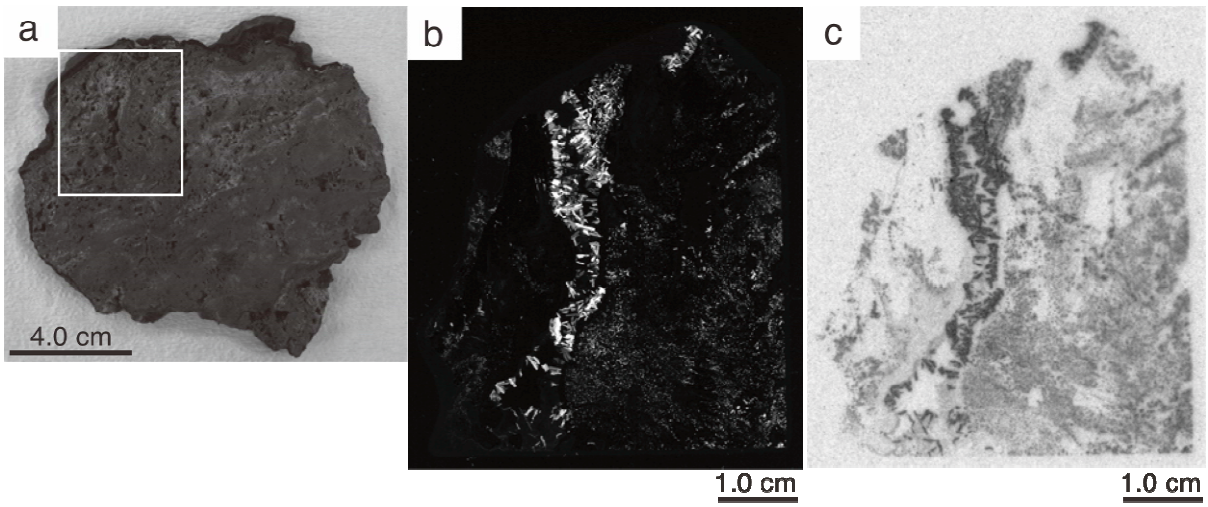

Fig. 5. *Images taken for chimney 903-R7-2. (a) Photograph of the whole cross section. Grains and crystals representing white are barite and those of black are spharelite and pyrite. (b) Polarized microscope of optical microphotograph. (c) Distribution of natural radioactivity of polished thin section of area outlined in cross-section photograph of chimney obtained by an imaging plate and Fuji BAS 1800II, a red-out device. The dark areas correspond to areas with relatively high content of radioactivity.*

Table 1. *Results of the present analysis of ESR dating.*

Sample No	Ra Concentration* (Bq/g)	Equivalent Dose D_e (Gy)	Dose rate (mGy/y)				Age (1)	Age (2)
			$D_\alpha(1)$	$D_\alpha(2)$	D_β	D_γ		
903-R7-2	7.72	231^{+33}_{-29}	186	465	123	184	470 ±60	300 ±40
220-E	4.77	1730^{+320}_{-240}	15	288	76	114	5670^{+1060}_{-770}	3620^{+680}_{-490}

*Bulk Ra concentration
The alpha efficiency is assumed to be (1) 0.1 and (2) 0.25.

implantation test. In addition, inhomogeneity of dose rate, the accumulated dose within a chimney sample could also affect the dose rate estimation. Internal consistency check, with several pieces from a same chimney sample would also be desirable.

5. CONCLUSIONS

In order to evaluate the date for the evolution of a hydrothermal system in the sea floor, the preliminary study of ESR dating using marine barite from chimney deposited from hydrothermal vent in the sea floor was carried out. ESR signal attributed to an electronic SO_3^- centre was observed in marine barite from the Archaean site in South Mariana spreading centre and at Hakurei site in the Izena caldron. The signal intensities in both samples was enhanced up to 2600 Gy with gamma ray dose. The ESR age of was tentatively estimated to be 300-470 years old for barite from the Archaean site and 3620-5670 years old for the Hakurei site. However, the ESR ages differed substantially from the $^{210}Pb/^{226}Ra$ disequilibrium ages previously reported. Further basic studies are needed to establish the ESR dating method for barite formed by hydrothermal activity.

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