# <sup>230</sup>Th/<sup>234</sup>U CHRONOLOGY OF MIRABILITE FROM CAPE BARNE IN ROSS ISLAND, ANTARCTICA

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**Abstract:** A <sup>230</sup>Th/<sup>234</sup>U method was applied for the dating of a mirabilite collected from Cape Barne in Ross Island, Antarctica. The age of the mirabilite was estimated to be 4700±900 y. The <sup>234</sup>U/<sup>238</sup>U activity ratio was 1.23±0.07, which is concordand with the sea water origin of this mineral. Mean uplifting rate of the ground level in the Cape Barne area was estimated to be 5±1 mm/y from the <sup>230</sup>Th/<sup>234</sup>U age and the altitude of the sampling point.

#### 1. Introduction

Many kinds of secondary minerals and evaporites are found in Antarctica, particularly in the Dry Valleys area of Southern Victoria Land, Antarctica (TORII and OSSAKA, 1965; TORII *et al.*, 1966; DORT and DORT, 1969; MORIKAWA *et al.*, 1975). These evaporites are considered to have been formed by rock weathering, by evaporation of water from the sea and glacial melt, and/or by air-borne salts. The formation age of these evaporites provides useful information for understanding the geochemical history of a localized area and/or climatic events in the past. The <sup>230</sup>Th/<sup>234</sup>U and <sup>14</sup>C chronology has been applied extensively to the dating of evaporites collected from the Dry Valleys area (HENDY, 1978, 1980; HENDY *et al.*, 1969, 1977, 1979), although some problems remain still unsolved in the <sup>14</sup>C chronology (OMOTO, 1983).

The <sup>230</sup>Th/<sup>234</sup>U chronology of mirabilite crystal ( $Na_2SO_4 \cdot 10H_2O$ ) has been applied to examine the usefulness of mirabilite as a reference material for dating glacial event because this mineral is considered to have been formed by evaporation of sea water and is found at various locations in the Dry Valleys area (NAKAI and KAMINUMA, 1976). The method of analysis and the result of <sup>230</sup>Th/<sup>234</sup>U chronology are reported in this paper.

#### 2. Sample and Method of Analysis

Large mirabilite crystals were found above the deposit containing marine fossils. Several hundred grams of mirabilite crystals were collected in the 1979/80 summer season at the edge of Deep Lake in Cape Barne of Ross Island, Antarctica (Fig. 1).



Fig. 1. Sampling location of mirabilite.

The height of the sampling point was not measured, but it is considered to be 24 m above sea level because our sampling point is identical with the description by DEBENHAM (1914) who found mirabilite at Cape Barne during the Terra Nova Expedition in 1910.

A mirabilite crystal of about 180 g was taken for the <sup>230</sup>Th/<sup>234</sup>U dating. After removing the contamination on the surface, the mirabilite was dissolved in distilled water and undissolved matter mainly of soil component was removed by filtration. Hydrochloric acid was added to the solution and then an aliquot of <sup>232</sup>U equilibrated with its daughter <sup>228</sup>Th was spiked as the yield tracers of uranium and thorium isotopes during chemical procedures. Uranium and thorium were then radiochemically separated and purified successively by co-precipitation with ferric hydroxide, anion exchange separation using Dowex-1X8, solvent extraction using ethyl acetate (uranium) and/or cation exchange separation using Dowex-50X8 (thorium). Finally  $\alpha$ -ray counting sources of uranium and thorium were prepared by electrodeposition on stainless steel discs of 25 mm in diameter.

The  $\alpha$ -spectrometry of each counting source was performed by using the surface

barrier type Si(Au) detector with 450 mm<sup>2</sup> of active area coupled with the 1024 channels pulse height analyzer.

### 3. Result and Discussion

Since the concentration of uranium and thorium isotopes in the mirabilite was extremely low, over 20 days of total counting time was required to obtain desirable counts for  $^{230}$ Th/ $^{234}$ U dating. Examples of  $\alpha$ -ray spectra are shown in Figs. 2a and 2b for the uranium and thorium fractions, respectively. As can be seen from Fig. 2a, activities of  $^{234}$ U and  $^{238}$ U are very low as compared with the  $^{232}$ U tracer, but each peak is well resolved in the spectrum. Many peaks due to the thorium series nuclides are attributed to the *in situ* growth of the short-lived daughter nuclides of  $^{232}$ U. On



Fig. 2. (a) Alpha-ray spectrum of uranium fraction. (b) Alpha-ray spectrum of thorium fraction.

Uranium content	$3.53 \pm 0.20$	(ppb)
Thorium content	<0.1	(ppb)
<sup>234</sup> U/ <sup>238</sup> U activity ratio	$1.23 \pm 0.07$	(dpm/dpm)
<sup>230</sup> Th/ <sup>234</sup> U activity ratio	$0.052 \pm 0.010$	(dpm/dpm)
Estimated age	4700±900	(y)
Crustal uplift	5±1	(mm/y)
Crustal uplift	$5\pm1$	(mm/y)

Table 1. Results of U and Th isotope analysis and 230Th/234U age for the mirabilite from CapeBarne in Ross Island, Antarctica.

the other hand, in the thorium spectrum shown in Fig. 2b, Th activity is much lower than that of the <sup>228</sup>Th tracer, and any appreciable peaks were not observed in the energy region of <sup>232</sup>Th. The results of  $\alpha$ -spectrometry are given in Table 1, in which errors are given by  $1\sigma$  of statistical error of counting. As known from Table 1, the uranium and thorium contents in the mirabilite crystal are measured to be only 3.53 ppb and less than 0.1 ppb, respectively, indicating that these elements were highly discriminated at the time of mirabilite formation.

Mirabilite found at various locations in Antarctica is considered to have been formed by the concentration of sea water under a frigid condition (THOMSPON and NELSON, 1956). NAKAI and MIZUTANI (1977) have also confirmed the sea water origin of this mineral by the measurement of the <sup>34</sup>S/<sup>32</sup>S isotopic ratio of the mirabilite collected from Cape Barne, Black Island, Hobbs Glacier and Miers Valley. If uranium in the mirabilite is trapped by the concentration of sea water, the <sup>234</sup>U/<sup>238</sup>U activity ratio must be concordant with the commonly accepted sea water value of  $1.15\pm$ 0.02 (THURBER, 1962). The <sup>234</sup>U/<sup>238</sup>U activity ratio was measured to be  $1.23\pm0.07$ , which is slightly higher but lies within the range of the sea water value. The uranium data also supports the sea water origin of the mirabilite.

It is well known that the <sup>230</sup>Th activity in sea water is far below the equilibrium value with parent <sup>234</sup>U. According to the compiled data by CHERRY and SHANNON (1974), the <sup>230</sup>Th content spreads in a wide range, but 'typical' level of this isotope is  $2 \times 10^{-14}$  g/l for oceanic water and  $20 \times 10^{-14}$  g/l for coastal water, which correspond to the <sup>230</sup>Th/<sup>234</sup>U activity ratios of  $4 \times 10^{-4}$  and  $4 \times 10^{-3}$ , respectively. Therefore, if we assume that the mirabilite is formed by the concentration of trapped sea water and that the discrimination factors for uranium and thorium isotopes were the same at the time of mirabilite formation, the initial <sup>230</sup>Th/<sup>234</sup>U activity ratio is expected to be less than  $4 \times 10^{-3}$ . This is very favorable for the <sup>230</sup>Th/<sup>234</sup>U chronology since the correction for the initial <sup>230</sup>Th activity in the sample is not required.

In the application of  ${}^{230}$ Th/ ${}^{234}$ U dating, it must be assumed also that the formation interval of mirabilite crystal should be reasonably short as compared with the age of this mineral. If these assumptions are satisfied for mirabilite, the formation age can be calculated to be  $4700 \pm 900$  y.

Since the sea water origin of this mineral seems reasonable from the evidences described above, we can estimate the crustal uplifting rate from the <sup>230</sup>Th/<sup>234</sup>U age and the altitude of mirabilite occurrence. The mean uplifting rate is roughly estimated to be  $5\pm1$  mm/y if the assumption of *in situ* formation of mirabilite is valid. This value is slightly higher but comparable to the value of around 3 mm/y estimated

for the Sôya Coast (YOSHIDA, 1983). HENDY *et al.* (1969) have measured the <sup>14</sup>C age of marine fossils collected from the deposit at 30 m above sea level in Cape Barne near our sampling point. They estimated the change of sea level of 200 m within the last 30000 y to 35000 y. From these values, the mean uplifting rate becomes 5 to 7 mm/y, which agrees well with the value of 5 mm/y estimated by the <sup>230</sup>Th/<sup>234</sup>U chronology. In the recent study by BRADY (1982), nonmarine diatoms were found from the deposit 31 m above sea level in Cape Barne. This suggests that the *in situ* formation of the deposit is incorrect. If Brady's suggestion is valid, the assumption of *in situ* formation of the mirabilite found on the marine deposit may be incorrect. Further study must be made to make clear the history of this area.

The mirabilite is considered to be a very suitable material for the <sup>230</sup>Th/<sup>234</sup>U chronology not only because this mineral can be obtained in a sufficiently pure form and the radiochemical separation of uranium and thorium is rather easy compared with other minerals but also because this mineral can be collected from various parts of the Dry Valleys area. The altitude of mirabilite occurrence in the Dry Valleys area ranges from 60 to 85 m above sea level (NAKAI and KAMINUMA, 1976), and the origin of the mineral is considered to be the same. Therefore, the <sup>230</sup>Th/<sup>234</sup>U chronology of mirabilite is believed to be very useful for the investigation of the advance and withdrawal of glaciation caused by the climatic changes in the past.

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