Gondwana Research 24 (2013) 212–221

Contents lists available at SciVerse ScienceDirect

Gondwana Research

journal homepage: www.elsevier.com/locate/gr

The Capitanian (Permian) minimum of $^{87}Sr/^{86}Sr$ ratio in the mid-Panthalassan paleo-atoll carbonates and its demise by the deglaciation and continental doming

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ARTICLE INFO

Article history:
Received 29 March 2012
Received in revised form 16 August 2012
Accepted 26 August 2012
Available online 4 October 2012

Keywords:
Permian
Sr isotope
Seamount
Limestone
Panthalassa

ABSTRACT

The Capitanian minimum in the Permian represents one of the most significant features in the Phanerozoic seawater $^{87}Sr/^{86}Sr$ history. In order to establish the detailed Sr chemostratigraphy around the Guadalupian minimum, $^{87}Sr/^{86}Sr$ ratios were measured for the Capitanian (upper Middle Permian) paleo-atoll limestones at Akasaka in Japan. The limestone was primarily deposited on a paleo-seamount in the low-latitude mid-Panthalassa, and was secondarily accreted to Japan (South China block) margin in the Jurassic. As being free from local continental influences, the Akasaka limestone recorded well-mixed seawater isotope composition of the Permian low-latitude mid-superocean. We detected extremely low $^{87}Sr/^{86}Sr$ ratios (ca. 0.7068–0.7069) in the 70 m-thick Capitanian interval, immediately below the Guadalupian–Lopingian (Middle-Late Permian) boundary (G–LB), of the Akasaka limestone. This Sr isotopic profile at Akasaka suggests that the global seawater was least affected by radiogenic continental flux throughout the Capitanian. As these values correspond to the lowest in the Paleozoic, this interval with low $^{87}Sr/^{86}Sr$ ratios, lasted for at least some milllion years, represents the Capitanian minimum, which marks the significant turning point from the Late Paleozoic decrease to Early Mesozoic increase in seawater $^{87}Sr/^{86}Sr$ ratio. The geological lines of evidence indicate that the Capitanian minimum was caused likely by the mid-Permian cooling that may have driven extensive ice-cover over continental crusts to suppress continental flux enriched in radiogenic Sr into the superocean. The rapid increase in $^{87}Sr/^{86}Sr$ values after the minimum can be explained either by the deglaciation or by the Pangean rifting.

1. Introduction

As Sr isotopic composition ($^{87}Sr/^{86}Sr$) of seawater has changed over geologic time, the high-resolution Sr isotope curve appears useful in chemostratigraphic correlation/dating for the Phanerozoic. Significant changes in global balance between the radiogenic continental flux and the less radiogenic mantle flux have left several remarkable Sr events in the Phanerozoic. One of such outstanding features is the "Capitanian minimum" that occurred during the Middle-Late Guadalupian (Middle Permian) to mark the lowest $^{87}Sr/^{86}Sr$ ratio, ca. 0.7068, in the Phanerozoic (Fig. 1; e.g., Veizer et al., 1999; McArthur and Howarth, 2004). Ever since the Cambrian, although with minor fluctuations, the long-term decrease of seawater Sr isotope ratio continued basically throughout the Paleozoic until the Capitanian minimum. In turn, immediately after the Capitanian minimum, $^{87}Sr/^{86}Sr$ ratio started to rise abruptly, in the most rapid rate in the Phanerozoic (Korte et al., 2006). The cause of this long-term trend change has not yet been identified, although some possible causal links were proposed, such as changes in global tectonics, sea-level, climate, weathering rate, and diagenetic processes (e.g., Veizer, 1989; Derry and France-Lanord, 1997; Korte et al., 2003; Banner, 2004).

Most of the previous studies on the Permian record of $^{87}Sr/^{86}Sr$ ratios were performed for biostratigraphically well-constrained shallow marine carbonates and/or well-preserved brachiopod shells from western North America (Denison et al., 1994; Denison and Koepnick, 1995) and the Tethyan domain (Korte et al., 2006). On the other hand, mid-oceanic carbonates in general may have good advantage in recording the world average Sr isotope ratio of well-mixed seawater due to the absence of local influences from continents. Nishioka et al. (1991) first reported the Early-Middle Permian Sr-isotope record of the superocean Panthalassa from the paleo-atoll carbonates at Akiyoshi in Japan. With more intense focus on the Middle-Late Permian (Guadalupian–Lopingian) boundary (G–LB; 260 Ma), Kani et al. (2008) detected the Capitanian minimum for the first time in the Middle-Upper Permian paleo-atoll carbonates at Kamura, Japan. Brand et al. (2009) also added more data from the Lower to lower Middle Permian paleo-atoll carbonates in Japan. These paleo-atoll data confirmed the Capitanian minimum in the low-latitude mid-superocean. This major chemostratigraphic signal of global context is significant as it might be related with the contemporary G–LB extinction (e.g., Isozaki, 2009a, 2009b). Nonetheless, the onset timing and total duration of the Capitanian minimum were not yet strictly

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http://dx.doi.org/10.1016/j.gr.2012.08.025

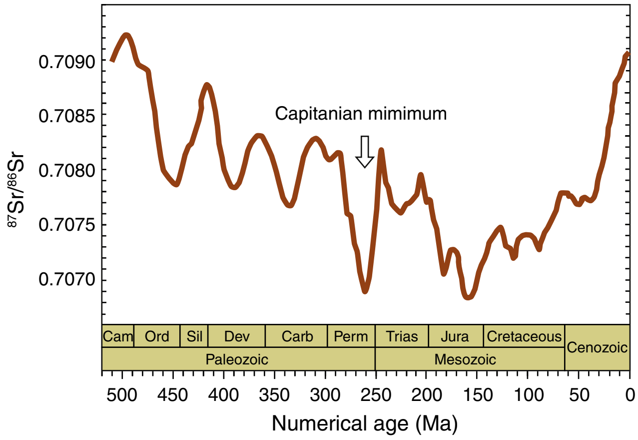

Fig. 1. The Phanerozoic secular change of Sr isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) and the Capitanian minimum (modified from McArthur and Howarth, 2004).

constrained. In a continuous section without any missing interval, therefore, we need to identify precise horizons of the onset and end of the Capitanian minimum.

In order to check the unique Sr event in mid-Panthalassa, this study analyzed a continuous single section of the Guadalupian–Lopingian carbonates of the Akasaka limestone in central Japan. This limestone body was deposited likewise as a paleo-atoll complex in mid-Panthalassa but was formed on a separate paleo-seamount from those of Akiyoshi and Kamura mentioned above. This article reports the high-resolution Sr isotope chemostratigraphy of the continuous Guadalupian–Lopingian rocks at Akasaka and discusses their geological significance.

2. Geologic setting

Numerous blocks/lenses of Permian limestone occur as allochthonous units in the Jurassic accretionary complex in SW Japan, including the ones at Akasaka and Kamura (Fig. 2A). These limestones were primarily deposited as paleo-atoll complexes developed on the top of Permian seamounts in low-latitude domains of the superocean Panthalassa (Fig. 2B, C; Sano and Kanmera, 1988; Sano and Nakashima, 1997; Isozaki, 1997; Ota and Isozaki, 2006; Kasuya et al., 2012). During the Triassic and the earlier half of the Jurassic, these paleo-atoll limestones were transported horizontally across Panthalassa to the subduction zone along the Mesozoic Asian margin. Through the subduction/accretion processes at trench, these rocks were eventually dismembered into numerous fragments, large and small, to be incorporated into the Middle Jurassic accretionary complex in Japan.

The Middle-Late Permian limestone at Akasaka forms an exotic block of the size no less than 3 km × 2 km (Fig. 3). By virtue of well-preserved various megafossils (e.g., mollusks, rugose corals, and large-tested fusuline), its bio- and litho-stratigraphy have been clarified in detail (e.g., Akasaka Research Group, 1956; Ozawa and Nishiwaki, 1992; Zaw Win, 1999; Ota and Isozaki, 2006). This limestone is composed of the lower, middle, and upper members of the Akasaka Limestone Formation plus the Ichihashi Formation in ascending order (Zaw Win, 1999; Ota and Isozaki, 2006). The limestone generally strikes NNE–SSW and dips 45–65° westward. The total stratigraphic thickness of the limestone is estimated to be over 250 m. The Middle Permian is composed of almost pure shallow marine limestones, whereas the Upper Permian contains dolomitic limestone and dolomite (Zaw Win, 1999; Ota and Isozaki, 2006).

We studied mainly on the Capitanian interval in the northern part of the limestone body (35°25′N, 136°35′E) near Ichihashi (Fig. 3). On the east-facing quarry surface, the Upper Member and the overlying Ichihashi Formation are widely exposed. The Upper Member consists mainly of muddy black limestone, bearing the Capitanian (Late Guadalupian) fusulines, such as *Yabeina igoi* Morikawa and Suzuki, *Y. katoi* (Ozawa), *Y. globosa* (Yabe), *Neoschwagerina minoensis* Deprat, and *N. margaritae* Deprat (Ozawa and Nishiwaki, 1992; Zaw Win, 1999). The Ichihashi Formation consists mainly of gray to white dolomitic limestone, characterized by the Wuchiapingian fusulines of the *Codonofusiella kueichowensis–Reichelina changhsingensis* assemblage (Sakagami, 1980). Refer to Zaw Win (1999) and Ota and Isozaki (2006) for more details.

We collected samples for geochemical analyses from 2 sections; i.e. Sections 1 and 2 (Fig. 3). Section 1 is a newly excavated quarry surface of Kawai Lime Ltd., whereas Section 2 is an old abandoned surface located ca. 200 m to the north of Section 1. Section 1 exposes the main part of the Capitanian interval (i.e., the *Yabeina globosa* Zone and the barren interval of the Upper Member). Section 2, previously described by Ota and Isozaki (2006), displays the transitional interval from the Upper Member to the Ichihashi Formation across the G–LB.

3. Methods

3.1. Material

Fine-grained micritic limestone (or lime mudstone) is suitable for measuring primary $^{87}\text{Sr}/^{86}\text{Sr}$ signature rather than sparitic bioclastic limestones, as demonstrated in a good agreement among the coeval conodonts, brachiopods, and limestones of the Permian age (Popp et al., 1986; Denison et al., 1994; Denison and Koepnick, 1995; Martin and Macdougall, 1995). Owing to the facies-related scarcity of brachiopods and conodonts in the Permian limestone of Akasaka, we specifically chose fine-grained limestone (micritic part composed of pure carbonates with scarce terrigenous components) for analysis.

Out of over 50 samples of fine-grained limestone collected from the above-described two sections in Akasaka (Sections 1 and 2), 29 samples of vein-free fresh limestone were analyzed for Sr-isotope ratio. At Section 1, we newly collected 23 samples from the *Yabeina* Zone and the barren interval. The sample numbers from the barren interval of Section 2 are common with those used in Ota and Isozaki (2006). The stratigraphic horizons of these are shown in Fig. 4.

3.2. Sr isotope analysis

For Sr-isotope measurements, 40–50 mg of handpicked specimens from each sample was dissolved in 5 ml of 1 M suprapure acetic acid. Sr was extracted in 1 ml micro-columns filled with 100 μl Sr Spec resin (ElChrom Industries). The column was rinsed with 3 ml of 3 M HNO_3, and Sr was eluted with 1 ml of H_2O. Separated Sr was loaded on single W filaments with Ta activator. Samples were analyzed by thermal ionization mass spectrometer (TIMS; Finnigan MAT 262) at the Faculty of Science, Kumamoto University, with a reproducibility of 1×10^{-5}. All data were corrected for internal mass bias using $^{87}\text{Sr}/^{86}\text{Sr} = 0.1194$. Recent average value of standard NIST SRM 987 are $^{87}\text{Sr}/^{86}\text{Sr} = 0.710267 \pm 14$ (2SD; $n = 24$). Our laboratory blanks were <500 pg.

In the Carboniferous and Permian carbonates in Japan, strontium concentrations are varied from 300 to 3400 ppm, and Rb/Sr ratios are always very low (<0.01) (e.g., Fujinuki, 1968). The very low Rb/Sr ratios make the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of carbonates close to the initial ratios of Permian with negligible age effect.

4. Results

Table 1 shows the measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the 29 carbonate samples collected from two studied sections at Akasaka. Fig. 4 displays their stratigraphic change. The $^{87}\text{Sr}/^{86}\text{Sr}$ values from the Upper Member range in 0.7068 to 0.7072. The residence time of Sr in seawater is estimated ca. 3 m.y. in modern oceans. When we discuss past records on the resolution of several tens of million years,