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New aragonite $^{87}Sr/^{86}Sr$ records of Mesozoic ammonoids and approach to the problem of N, O, C and Sr isotope cycles in the evolution of the Earth

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ABSTRACT

New Sr isotope data from well-preserved aragonite ammonoid shell material from the Mesozoic are compared with that from a living *Nautilus* shell. The prominent negative Sr isotope excursions known from the Middle Permian, Jurassic and Cretaceous probably have their origins in intensive plate tectonic activity, followed by enhanced hydrothermal activity at the mid-ocean ridges (mantle volcanism) which supplied low radiogenic Sr to seawater. The maximum positive (radiogenic) shift in the lower Mesozoic Sr isotope curve (Lower Triassic peak) was likely caused by a significant expansion of dry land surfaces (Dabie-Sulu Triassic orogeny) and their intensive silicate weathering in conditions of extreme warming and aridity in the very end of the Smithian, followed by warm and humid conditions in the late Spathian, which apparently resulted in a significant oceanic input of radiogenic Sr through riverine flux. The comparatively high $^{87}Sr/^{86}Sr$ ratio obtained from the living *Nautilus* shell is probably a function of both the Alpine orogeny, which was accompanied by significant continental weathering and input of radiogenic Sr to the oceans, and the weakening of mantle volcanism.

1. Introduction

Over the past four decades vast data on Phanerozoic Sr-isotope stratigraphy have been compiled from calcitic and apatite fossil material and whole-rock samples (e.g., Veizer and Compston, 1974; Brass, 1976; Burke et al., 1982; Hess et al., 1986; Koepnick et al., 1990; Clements et al., 1993; McArthur et al., 1993, 2000, 2004, 2012, 2016; Denison et al., 1994, 2003; McArthur, 1994; Jones et al., 1994; Jenkyns et al., 1995, 2002; Martin and MacDougell, 1995; Veizer et al., 1999; Zachos et al., 1999; Jones and Jenkyns, 2001; Korte et al., 2003, 2004, 2006; Van Geldern et al., 2006; Wotte et al., 2007; Prokoph et al., 2008; Wierzbowski, 2013; Madhavaraju et al., 2015). However, only a few aragonite-preserved fossils, originating mostly from the Campanian and upper Maastrichtian of North America (e.g., Cochran et al., 2003, 2016) and the lower Albian of Madagascar (Zakharov et al., 2016) have been used for this purpose. The benefit of aragonitic fossils in isotope studies lies in their absence of significant diagenetic alteration.

This paper focuses on some Mesozoic Sr isotope oscillations, derived from the study of well-preserved, aragonitic cephalopod shells. We also present oxygen and carbon isotope data from ammonoids and other fossils, and some paleoenvironmental reconstructions.

2. Materials and methods

Material for Sr isotope investigation includes ammonoid shells from the lower and upper Olenekian and mid Anisian of Arctic Siberia, the lower Toarcian of Western Switzerland, the upper Callovian and lower Aptian of the Russian Platform, the upper Santonian and lower Campanian of North America, and finally a shell of living *Nautilus pompilius* Lenne from the Philippines (Fig. 1). Lower Toarcian mollusc shells from Western Switzerland, as well as some fossils from the lower Bathonian and lower Callovian of Central Switzerland, upper Hauterivian of Argentina, and lower Barremian of the Alps were also utilized for O and C isotope investigations.

The following criteria were used to determine diagenetic alteration: (1) hand-sample visual indications; (2) percentage of aragonite in mollusc shells, which were originally represented by 100% aragonite; (3) presence or lack of diagenetic admixture, determined by X-ray diffraction analysis; (4) the degree of integrity of shell microstructure,

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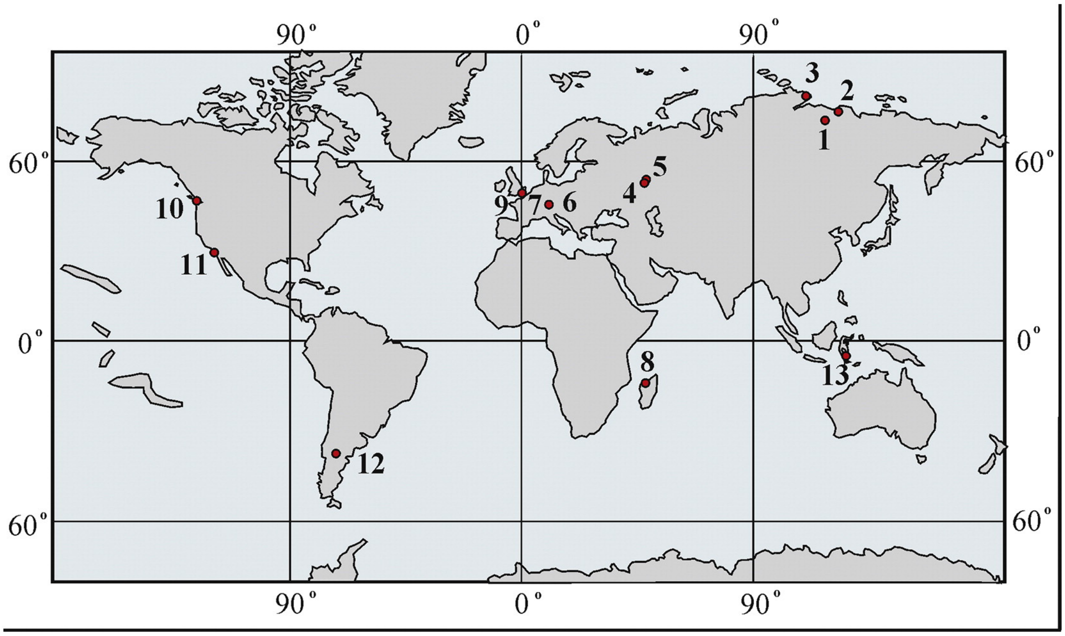

Fig. 1. Location of investigated areas: 1, Buur River, Arctic Siberia (Induan–Olenekian boundary beds; 2, Mengilyakh Creek, Olenek River (uppermost Olenekian); 3, Keshin Creek, Taimyr (mid Anisian); 4, Ryazan area, Russian Platform (upper Callovian); 5, Ulyanovsk area, Russian Platform (lower Aptian); 6, Teysachaux mountain, Western Switzerland (lower Toarcian); 7, the village of Anwill, Northern Switzerland (Bathonian–Callovian boundary); 8, Madagascar (lower Albian); 9. Dorset, South West Englang (uppermost Berriassian); 10, Vancouver Island, British Columbia (upper Santonian); 11, Butte Creek, California (lower Campanian); 12, Patagonia (upper Hauterivian); 13, Bohol Island area, Philippines (living *Nautilus pompilius* Linne).

determined under a scanning electron microscope (SEM). We have recognized four stages of diagenetic alteration in aragonitic mollusc shells (Zakharov et al., 1975, 2016).

X-ray powder analyses were carried out at the Analytical Centre (FEGI) in Vladivostok using a desktop X-ray diffractometer MiniFlex II (Rigaku Firm). SEM and X-ray studies of selected Mesozoic fossils suggest that most of them retain their original shell microstructure, and thus their original Sr, C and O isotope compositions. X-ray diffraction analysis reveals the lack of secondary admixtures, including α-SiO_2, in most samples from this area, and 75–100% aragonitic composition of most of our selected ammonoids, and some bivalve shells.

O and C isotope measurements at the Stable Isotope Laboratory (*FEGI FEB RAN*, *Vladivostok*). Oxygen and carbon isotope measurements were carried out using a Finnigan MAT-252 (Analytical Centre, FEGI, Vladivostok). The laboratory gas standard used in the O and C isotope measurements was calibrated relatively to NBS-19 $\delta^{13}C = 1.93‰$ and $\delta^{18}O = -2.20‰$ (Coplen et al., 1983). Reproducibility of replicate standards was always better than 0.1‰.

The following equation was used for palaeotemperature calculation (Grossman and Ku, 1986): $T\ (C) = 20.6–4.34\ (\delta^{18}O_{aragonite} - \delta w)$.

In this equation T (C) is the ambient temperature; $\delta^{18}O_{aragonite}$ is the measured oxygen-isotope value of aragonite (versus VPDB), and δw (‰) is the ambient water isotope ratio (versus VSMOW). A δw of $-1.0‰$ is often assumed to be appropriate for an ice-free world (e.g., Shackleton and Kennet, 1975; Hudson and Anderson, 1989; Huber et al., 2002; Pirrie and Marshall, 1990; Price and Hart, 2002; Lukeneder et al., 2010). It is known that there are definitely ice and ice-free times during Mesozoic (Price and Passey, 2013; Veizer and Prokoph, 2015), but intervals investigated in this study correspond to ice-free times. However, the isotopic composition of Cretaceous seawater may have varied considerably due to freshwater input and/or evaporation.

Sr isotope measurements at the Laboratory of Isotope Geochemistry (*IG SB RAS*, *Irkutsk*). Laboratory methods for the Sr isotope analysis followed instrumental and operating specifications as discussed in Degryse and Schneider (2008). Material for our Sr isotope investigation, taken from well preserved cephalopod shells that still exist in their original aragonitic mineralogy, was obtained by chemical preparation of straight Sr fractions, using ion-exchange polymers BioRad AG 50W*8, 200–400 mesh and BioRad AG 50*12, 200–400 mesh (Collective Enjoyment Center of Isotope Geochemical Investigation, Institute of Geochemistry of Russian Academy of Sciences, Siberian Branch, Irkutsk).

>50 ng (nanogram) of each sample were loaded onto rhenium filaments (cathode) and analyzed for $^{87}Sr/^{86}Sr$ on a Finnigan MAT-262 seven-collector (Collective Joint Center of Geodynamic and Geochronology, Institute of Earth Core, Russian Academy of Sciences, Siberian Branch, Irkutsk) using the multi-dynamic routines that include a correction for isobaric interference from ^{87}Rb ($^{87}Rb/^{85}Rb = 0.386$). The rhenium cathode was previously covered by an activator, prepared on the basis of Ta_2O_5. The ^{88}Sr ion current was usually been equal to $2–3 * 10^{(-11)}$ A. Data have been normalized to a value of 8.37521 for $^{88}Sr/^{86}Sr$.

$^{87}Sr/^{86}Sr$ measurements were made using the following most common standards: (1) NBS-987 (known earlier as SRM987); and (2) BCR-2. The $^{87}Sr/^{86}Sr$ values for these standards are (1) 0.710249 ± 8 (2 SD, $n = 12$); and (2) 0.705011 ± 14 (2 SD, $n = 7$) respectively, where SD is standard deviation and n is number of measurements. External precision (2σ) is typically in the range of ± 0.00001 to ± 0.00003 (Banner, 2004).

3. $^{87}Sr/^{86}Sr$, $\delta^{18}O$ and $\delta^{13}C$ records

3.1. Cretaceous

Previously, Sr isotope data for the Cretaceous has been obtained from aragonite-preserved lower Albian *Eotetragonites*, *Desmoceras*, *Cleoniceras*, and *Douvilleiceras* shells from Madagascar ($^{87}Sr/^{86}Sr = 0.707241–0.707276$; Zakharov et al., 2016) and upper Maastrichtian *Sphenodiscus*, *Hoploscaphites* and *Discoscaphites* shells from North America ($^{87}Sr/^{86}Sr = 0.707699–0.707795$; Cochran et al., 2003). We now add to this data with material from the Russian Platform and from North America.