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Carbon and oxygen isotopes in the Frasnian–Famennian section of the Kuznetsk basin (*southern West Siberia*)

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Abstract

The first detailed isotope-geochemical study of carbonate deposits has been performed in the Lower Famennian stratotype section of the northwestern Kuznetsk Basin (Kosoy Utyos), which was localized in the middle latitudes of the Northern Hemisphere in the Late Devonian. The $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, and $\delta^{18}O$ variation curves were constructed for the section deposits. Geochemical and petrographic studies of carbonates allowed allocation of samples that underwent postsedimentation alteration and exclude them from further interpretation. Compared with coeval sections in the other world's regions, the Kosoy Utyos section is characterized by higher $\delta^{13}C_{carb}$ values, up to 5.4‰, whereas the maximum value in subequatorial area sections is 4‰. The isotope shift amplitude of the studied section reaches 4.6‰, which is 1.5‰ higher than those in other regions. The $\delta^{18}O$ values are 3‰ lower than the ones of the world's coeval sections. The results obtained show that $\delta^{13}C$ and $\delta^{18}O$ variation trends differ from those of coeval subequatorial sections. The high shift amplitude and maximum $\delta^{13}C_{carb}$ values in the Kosoy Utyos section are due to the shallow-water carbonate sedimentation environments on the Siberian continental shelf and, probably, the lower temperatures of waters in the middle latitudes as compared with the subequatorial areas.

Keywords: isotopes; carbon; oxygen; carbonates; Famennian Stage; Upper Devonian; northwestern Kuznetsk Basin

Introduction

Study of variations in the isotopic compositions of carbon and oxygen in ancient oceans is one of the main lines in the isotopic geochemistry of sedimentary rocks. Variations in the carbon isotope composition are most widely used for the subdivision and correlation of Precambrian deposits (Khabarov and Ponomarchuk, 2005; Knoll et al., 1986; Kuznetsov et al., 2006; Melezhik et al., 2001, 2008; Pokrovskii et al., 2006; Semikhatov et al., 2004).

Isotope-geochemical data are used to study the periods of the evolution of the Earth's sedimentary cover when biotic crises occurred. There were five global biotic events of the first rank in the Phanerozoic history of the Earth. They took place at the Ordovician–Silurian (O–S), Frasnian–Famennian (Upper Devonian) (F–F(D_3)), Permian–Triassic (P–T), Triassic–Jurassic (T–J), and Cretaceous–Paleogene (K–₽) boundaries (McLaren, 1970; Veimarn and Korneeva, 2007). The causes of these events are elucidated mainly by paleontological and sedimentological data and often by results of isotope-geochemical studies (Holser, 1997; Phipps et al., 2004; Zakharov et al., 2001). Isotopic data are invoked because the drastic excursions on the time trend of the carbon isotope composition, reflecting changes in the global carbon cycle, correspond to rapid large-scaled environmental changes (Scholle and Arthur, 1980). These changes are related to variations in the intensity of weathering, circulation of global oceanic streams, sea level, temperature, climate and to the periods of intense accumulation of organic matter, mass volcanism, etc. (Hayes et al., 1999; Kaufman and Knoll, 1995; Knoll et al., 1986; Kump and Arthut, 1999; Veizer et al., 1980).

In the Late Devonian, one of the five greatest Phanerozoic mass extinctions took place. This event was most significant in low-latitude tropical shallow-water ecosystems, whereas high-altitude and ground ecosystems were negligibly subjected to this process (Alekseev, 2000). In general, during the

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Frasnian–Famennian mass extinction, about 15% of families and 50% of genera of sea fauna died out, and reefs almost completely disappeared (Alekseev, 2000). The reasons for this biospheric crisis are widely discussed in literature (Joachimski and Buggisch, 1993; McGhee, 2001; Murphy et al., 2000; Ormiston and Oglesby, 1995; Racki, 1998).

Ubiquitously, this biotic event took place synchronously with the black-shale deposition, which reflects the conditions favoring the accumulation and conservation of organic matter in sedimentary basin (Alekseev, 2000; Riquier et al., 2006; Walliser, 1996). These horizons are known as the Kellwasser Horizons (Eder et al., 1977; Schindler, 1990). With their appearance, the carbon isotope composition of carbonates became heavier. The maximum $\delta^{13}C_{carb}$ values reach +4‰ in the McWhae Ridge and Casey Fall's (Australia), Devil's Gate (Nevada), and Budesheimer Bach (Germany) sections and +3 to +3.5‰ in the Fuhe and Baisha sections (South China) (Chen et al., 2005; Joachimski et al., 2002). The amplitude of these variations is 1.5–2‰. As the inorganic-carbon isotope composition becomes heavier, the $\delta^{13}C_{org}$ value in carbonates increases. The excursions on the carbon isotope curves for carbon and organic material are interpreted using the models elaborated by Kump and Arthur (1999). According to the models, the influence of various factors (the increasing supply of feeding materials with river runoff and the amount of volcanic emanations and the decreasing rate of silicate weathering) on the system ocean–atmosphere leads to changes in CO_2 contents and, hence, a carbon isotope shifts in both carbonate and organic matter. The only difference is that in some cases these shifts are synchronous and in others, with a slight delay either on the $\delta^{13}C_{org}$ or the $\delta^{13}C_{carb}$ curve (Kump and Arthur, 1999).

Note that all studies of the isotopic compositions of carbon and oxygen were carried out for the sections that were localized in the subequatorial areas in the Late Devonian. The Late Devonian mid-latitude deposits, in particular, those that formed on the shelf of the Siberian continent, remained almost unstudied. Therefore, we performed isotope-geochemical studies of carbonate deposits in the northern Kuznetsk Basin (Fig. 1) in order to reconstruct the evolution trends of the isotopic compositions of inorganic and organic carbon and oxygen in the Late Devonian mid-latitude basin, study the changes in $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, and $\delta^{18}O$ values, and compare the obtained data with the results on Late Devonian subequatorial basins.

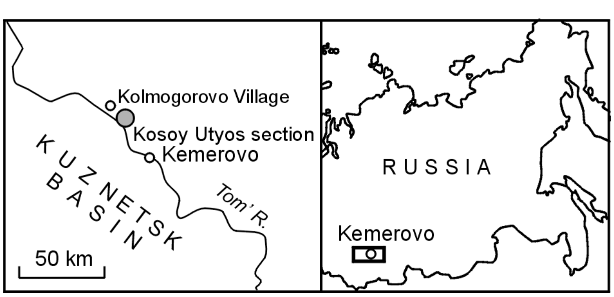

Fig. 1. Geographic map of Russia with the depicted locality of the study area (Kuznetsk Basin).

Methods

The carbon and oxygen isotope compositions of carbonates are usually studied using brachiopod and foraminifer shells and micritic carbonates. The results of the research into micritic carbonates drilled out of the samples are presented below. Petrographic studies and chemical-composition (Ca, Mg, Fe, Mn, and Sr) investigation of the carbonate were performed. They are highly effective for the allocation of diagenetically altered samples, which were excluded from the further interpretation of the obtained data.

The contents of Ca, Mg, Fe, Mn, and Sr in the soluble part of carbonate rocks were determined on an SP9 PI UNICAM atomic-absorption spectrometer. The determination error was no more than 10%. All analyses were carried out at the Analytical Center of the Sobolev Institute of Geology and Mineralogy, Novosibirsk.

To analyze the isotopic compositions of oxygen and carbon in carbonate and organic matter, a mass-spectrometric complex including a Finnigan MAT-253 mass spectrometer and Gas Bench II and Conflo + Flash ES-1112 sample preparation lines was used.

The isotopic composition of carbon dioxide was measured by mass spectrometry in a continuous helium flow.

For the measurements we used pure CO_2 produced by the decomposition of carbonate (limestone) powder in orthophosphoric acid for 2 h at 60 °C and by the combustion of organic matter in the presence of oxygen at 900 °C. Organic matter was extracted from limestones by dissolution of carbonates in 1 N HCl.

The accuracy of carbon and oxygen determination in carbonates was controlled by analysis of international (NBS19 $\delta^{13}C$ = +1.9‰, $\delta^{18}O$ = –2.2‰) and Russian (DVGI $\delta^{13}C$ = +1.2‰, $\delta^{18}O$ = +1.8‰) standard samples and was 0.1‰ for both $\delta^{13}C$ and $\delta^{18}O$. For organic matter, the determination accuracy was controlled by analysis of the international NBS 22 standard sample ($\delta^{13}C$ = –30.03‰). The error of isotope analysis was 0.5‰. All $\delta^{13}C$ and $\delta^{18}O$ values are given per mil relative to the PDB standard sample.

The paleogeography and stratigraphic sequence of the Upper Devonian strata in the Kuznetsk Basin

In the northwestern Kuznetsk Basin, numerous Late Devonian carbonate sections that formed on the shelf of the Siberian continent are cropped out (Dubatolov and Krasnov, 2000a,b; Yolkin et al., 2003). According to paleogeographic reconstructions (Dubatolov and Krasnov, 2000a,b; van Geldern et al., 2006; Joachimski et al., 2002), the Siberian continent was localized in the middle latitudes of the Northern Hemisphere (Fig. 2). During the Devonian, various sedimen-