ISOTOPIC RATIOS OF SULFUR (^{32}S, ^{33}S, ^{34}S, ^{36}S) IN ARCHAEAN ROCKS OF KARELIA − EVIDENCE OF MICROBIAL LIFE AND OXYGEN-FREE ATMOSPHERE

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SUPPLEMENTARY MATERIAL

Table presents sulfur isotope values for the samples of sulfides from the rocks of the Sumozersk-Kenozersk and Kostomuksha greenstone belts, Karelia. These data and the previously published sulfide isotope signatures of these rocks [Vysotsky et al., 2022; 2023] were interpreted here as evidence of microbial activity in the Mesoarchaean ocean and the absence of free molecular oxygen in the atmosphere during the formation of the Karelian deposits ~2.9-2.7 billion years ago.

Table. Sulfur isotope analysis of sulfides in rocks of the greenstone belts of Karelia.

Sample number	Mineral	δ^{34}S (‰)	Δ^{33}S (‰)	Δ^{36}S (‰)	References
Sumozersk-Kenozersk greenstone belt					
Zolotye Porogi					
C-604-82.8; 2	pyrite	-2.5	-0.95	1.0	This research
C-604-82.8; 6	pyrite	-1.7	-0.63	0.8	—//—
C-604-82.8; 7	pyrite	0.9	-0.79	0.9	—//—
C-604-82.8; 8	pyrite	2.8	-1.05	1.2	—//—
C-604-82.8; 9	pyrite	1.7	-1.11	1.2	—//—
C-604-82.8; 10	pyrite	2.4	-1.41	1.2	—//—
C-604-82.8; 11A	pyrite	1.3	-0.71	1.0	—//—
C-604-82.8; 12	pyrite	1.2	-1.25	1.3	—//—
C-604-82.8; 13 B	pyrite	1.2	-0.96	0.9	—//—
C-604-82.8; 14	pyrite	1.7	-0.76	0.5	—//—
C-604-82.8; 15A	pyrite	1.7	-0.72	0.7	—//—
C-604-82.8; 17	pyrite	2.9	-0.28	0.5	—//—
C-604-82.8; 1z	pyrite	1.7	-1.17	1.0	—//—
C-604-82.8; 2z	pyrite	1.5	-1.24	1.3	—//—
C-604-82.8; 3z	pyrite	-1.9	-1.01	0.9	—//—
C-604-82.8; 13z A	pyrite	-1.9	-1.15	1.3	—//—
C-604-82.8; 4z	pyrite	1.6	-1.08	1.0	—//—
C-604-82.8; 5z	pyrite	2.0	-0.99	0.7	—//—
C-604-82.8; 6z	pyrite	1.6	-0.93	0.8	—//—
C-604-82.8; 7z	pyrite	3.1	-1.19	1.2	—//—
C-604-82.8; 8z	pyrite	1.3	-1.45	1.6	—//—
C-604-82.8; 9z	pyrite	2.4	-0.67	0.5	—//—
C-604-82.8; 10z	pyrite	1.4	-0.81	1.1	—//—
C-604-82.8; 11z	pyrite	1.3	-0.31	0.4	—//—
C-604-82.8; 12z	pyrite	1.2	-0.57	0.6	—//—
C-604-82.8; 13z	pyrite	1.4	-0.95	0.7	—//—
C-604-82.8; 14z	pyrite	1.3	-0.84	0.5	—//—
C-604-82.8; 16z	pyrite	2.7	-0.37	0.2	—//—
C-604-82.8; 18z	pyrite	2.3	-0.27	0.3	—//—
C-604-82.8; 20z	pyrite	2.0	-0.16	0.2	—//—
C-604-82.8, 6-7 A	pyrite	-2.2	-0.73	0.5	—//—
C-604-82.8, 6-7 B	pyrite	-1.6	-0.84	0.9	—//—
C-604-82.8, 6-7 C	pyrite	0.6	-0.74	0.6	—//—
Central Vozhma					
C39-303,9б	pyrite	-1.0	-0.32	0.3	This research
C39-303,9б	pyrite	-0.7	-0.29	0.5	—//—
C39-303,9б	pyrite	-0.2	-0.29	0.6	—//—
C39-303,9б	pyrite	-0.2	-0.35	0.6	—//—
C39-303,9б	pyrite	-2.6	-0.38	0.8	—//—

C39-303,9б	pyrite	-2.9	-0.32	0.5	—//—
C39-303,9б	pyrite	-2.8	-0.37	0.6	—//—
C39-303,9б	pyrite	-0.7	-0.45	0.5	—//—
C39-303,9б	pyrite	-0.3	-0.37	0.4	—//—
Leksa					
C1/75	pyrite	3.7	1.76	-1.3	
C1/75	pyrite	2.8	1.57	-2.0	
C1/75	pyrite	3.8	1.93	-2.4	
C1/75	pyrite	3.8	1.85	-2.5	
Kostomuksha greenstone belt					
2-2/4-1	pyrite	-0.1	0.46	-1.0	This research
2-2/4-1	pyrite	-0.1	0.47	-1.2	-//-
2-2/4-1	sphalerite	-2.1	0.52	-0.8	-//-
2-2/4-1	pyrite	-0.2	0.49	-0.5	-//-
2-2/4-1	pyrite	-0.4	0.47	-0.6	-//-
17/3b	pyrite	-3.4	0.29	n.d.	Vysotskiy et al., 2023
17/3b	pyrite	-3.0	0.33	n.d.	Vysotskiy et al., 2023
17/4a	pyrite	-1.7	0.89	n.d.	Vysotskiy et al., 2023
174a	pyrite	-1.9	0.89	n.d.	Vysotskiy et al., 2023
1-4/3	pyrite	-7.7	0.57	-1.1	This research
1-4/3	pyrite	-7.8	0.63	-1.1	-//-
1-4/3	pyrite	-7.5	0.60	-1.1	-//-
669,5	pyrrhotite	1.7	-0.03	n.d.	Vysotskiy et al., 2023
669,5	pyrrhotite	2.2	-0.06	n.d.	Vysotskiy et al., 2023
669,5	pyrite	-4.8	0.72	n.d.	Vysotskiy et al., 2023

* n.d. – the value was not determined.

Models of $\delta^{34}S$ sulfate and $\delta^{34}S$ sulfide evolution during Rayleigh distillation for precipitation of pyrite from sulfate in a system closed to external sulfate sources

Pyrites with high positive $\delta^{34}S$ values up to +32.8‰ were found in the volcanogenic-sedimentary sulfide ore deposit Lexa (Fennoscandinavian Shield). It is ~15‰ higher compared to the available literature data for sedimentary pyrites of Mesoarchaean age [Farquhar et al., 2000; Ono et al., 2006; Guy et al., 2012]. The easiest way to explain the observed ^{34}S enrichment in pyrite is to relate it to bacterial sulfate reduction in a closed system of pore water. Sulfate-reducing bacteria prefer to consume predominantly light sulfur isotope, which leads to the formation of isotopically light pyrite. In our case, values down to -10‰ were recorded. Formation of isotopically heavy pyrite occurs due to depletion of light sulfur isotope by bacteria in a closed system, and thus enrichment of the remaining sulfate fraction with heavy sulfur isotope. We recorded the sulfur isotopic composition of pyrite up to +33‰. However, the question arises: whether it is correct to assign such isotope fractionations only to Rayleigh distillation and whether such a value can be achieved due to bacterial sulfate reduction alone in a closed system.

To meet the challenge, we employed the Rayleigh distillation model (Fig. 1a), showing the sulfur isotopic composition of the remaining sulfate fraction during precipitation of pyrite from sulfate. We adopted the following assumptions in our model: (1) the initial sulfur isotope composition of marine sulfate was assumed to be 0‰ [Canfield, 2004], which is within the range of alternative estimates from -5 to +6‰ [Ono et al., 2003; Ueno et al., 2008; Roerdink et al, 2012]; (2) the sulfate concentration in the Archean ocean is 200 µmol [Habicht et al., 2002], although it could be lower than ≈80 µmol [Jamieson et al., 2013]; (3) sulfur isotope fractionation between sulfate and pyrite $\delta^{34}S_{sulfate}$ - $\delta^{34}S_{sulfide}$ is ≈10‰. It should be mentioned that the magnitude of sulfur isotope fractionation in bacterial processes depends on many factors, including sulfate concentration and availability of organic substrate [Leavitt et al., 2013]. The lower sulfate concentration, the lower sulfur isotope partition coefficient between sulfate and sulfide in bacterial sulfate reduction processes. Today in ocean the magnitude of sulfur isotope effects can

reach 60-70‰ with a sulfate concentration of 28 mmol. Meanwhile, in the Archean low-sulfate ocean, this value is expected to be much lower. The maximum ^{34}S depletion in the pyrite samples in our work was no more than 10‰ and, therefore, it was used in the calculations for our model.
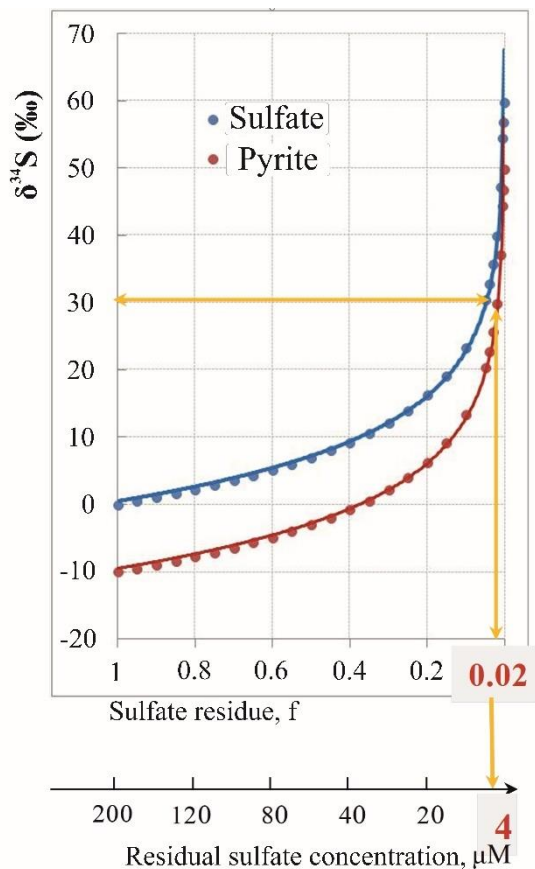

Figure 1a. Simulation δ^{34}S variations of sulfate and sulfide during Rayleigh distillation for pyrite precipitation from sulfate (initial δ^{34}S = 0‰) in a system closed to external fluids or other sulfur sources. The blue curve shows the progressive sulfate enrichment of heavy sulfur isotope when its residue is brought to infinitesimal value during the pyrite formation in the closed system, and the red curve shows the enrichment of the precipitated pyrite, respectively. The yellow arrow points to the state when the δ^{34}S value of the sulfide reaches +30‰.

The calculation shows that the δ^{34}S value in pyrite can reach 30‰ if 98% of sulfate is exhausted by bacteria (Fig.1a). This corresponds to a sulfate sulfur concentration of 4 micromoles, given an initial seawater sulfate content of 200 μmol. However, bacteria barely can cause such depletion, since the threshold value where bacteria are still alive and active is 20 μmol [Ingvorsen et al., 1984]. Thus, the progressive enrichment of pyrite (as well as its formation) should have stopped at δ^{34}S level of about +10‰.

Therefore, simple distillation process does not provide an explanation for the high δ^{34}S values found in the pyrite samples. Nevertheless, there are two possibilities to resolve this issue. The first one is to assume the initial isotope composition of marine sulfate to be at least 20‰, not 0‰. But there is no geologic, geochemical, or isotopic evidence for that. On the contrary, all available evidence supports zero isotope composition of sulfate in the Archean Ocean. The alternative is a localized increase in sulfate concentrations. It means there should be some source of sulphate, and isotopically heavy sulphate. The role of the sulfate producer can be assigned to the processes of disproportionation of elementary sulfur into hydrogen sulfide and sulfate, that occur only with the bacteria participation.

This generates isotopically heavy sulfate, where the isotopic effect of δ^{34}S can exceed 30‰ (Fig. 2a). In the presence of sulfate-reducing bacteria, isotopically heavy sulfate produced by bacterial disproportionation of elemental sulfur is reduced to pyrite (Fig.3a). Progressive disproportionation-reduction accompanied by Rayleigh depletion increases the ^{34}S enrichment in pyrite. Thus, the detection of isotopically heavy pyrite (δ^{34}S up to +33‰) in Mesoarchaean sedimentary rocks can be considered as evidence of the early elemental sulfur-disproportionating bacteria coexisting with sulfate-reducing bacteria.
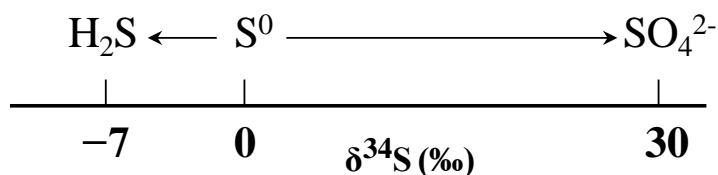

Figure 2a. Elemental sulfur (S^0) bacteria disproportionation scheme, where the products are reduced (H_2S) and oxidized (SO_4) forms of sulfur. The δ^{34}S isotope effects associated with this process are also shown [Canfield et al., 1994, 1998; Böttcher et al., 2005; Johnston et al., 2005].

PYRITE FORMATION VIA BACTERIA-CATALYZED PROCESSES

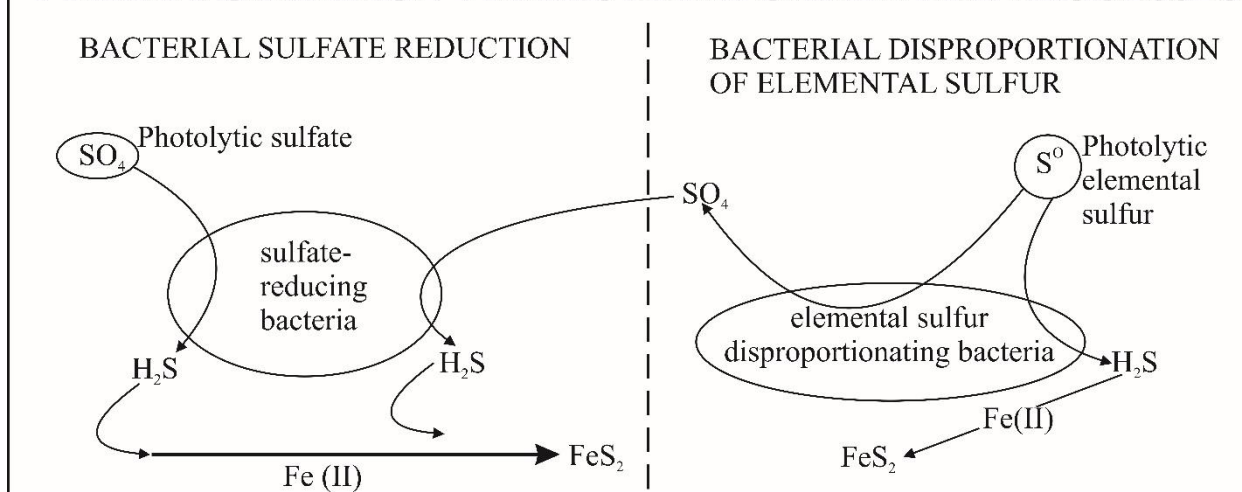**BACTERIAL SULFATE REDUCTION** | **BACTERIAL DISPROPORTIONATION OF ELEMENTAL SULFUR**

Figure 3a. Graphic representation of pyrite formation in bacterially mediated processes.

The pyrite formation during the Archean time may have been caused by (1) bacterial sulfate reduction, when atmospheric sulfate of photolytic origin dissolved in sea water is reduced to H_2S or (2) bacterial elemental sulfur disproportionation, when elemental sulfur of photolytic nature is disproportionated to H_2S and SO_4. When the two bacterial pathways occur simultaneously in pore waters, additional sulfate becomes available for bacterial sulfate reduction, resulting in the conversion of additional H_2S to FeS_2. Such a community of sulfur metabolizing bacteria of different types explains the wide range of sulfur isotope fractionation and high positive $\delta^{34}S$ values recorded in the sulfides of the Lexa deposit. Compilation of $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ data presented in our work confirms the functioning of different groups of organisms during sulfide ore formation at the Lexa deposit. When bacterial sulfate reduction was of minor importance, pyrite formed predominantly from H_2S, produced by elemental sulfur- disproportionating bacteria. This pyrite is characterized by a narrow range of sulfur isotopic fractionation and negative $\delta^{34}S$ values (see Fig. 2a). Comparative analysis of $\delta^{34}S$ and $\Delta^{33}S$ in sulfides from banded iron formation of Kostomuksha deposit, presented in the paper, indicates a significant role of bacterial disproportionation during the formation of these rocks.

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