

Peculiarities of the Oxygen Isotope Ratio in Precious Opals

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Abstract—This paper presents the results of the $\delta^{18}\text{O}$ study of the precious opals from Primor'e (Raduzhnoe deposit), Australia, and Ethiopia and the modern opals from the hydrotherms of the Mendeleev Volcano (Kunashir Island, Kuril Islands).

It is established that the oxygen isotope ratio in opals may serve as a criterion for the estimation of their formation temperature. The low-temperature sedimentary opals are relatively enriched in the heavy oxygen isotope independently of the sedimentary or volcanic host rocks. Examples are the Australian and Slovakian opals of the A-type. The hydrothermal opals are enriched in the light oxygen isotope, which depends on the precipitation temperature. The higher the temperature, the lighter the oxygen isotope ratio of the precipitating opal is and the closer it is to that of the hydrothermal fluid.

Keywords: opal, oxygen isotopes, hydrogen isotopes, stable isotopes

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INTRODUCTION

The studies of the last decades have established that the deposits of precious opals include sedimentary and hydrothermal groups, which are mostly based on the characteristics of precious opals [4, 8, 11, 13, 14].

Sedimentary precious opals with spherical nanostructures are mainly composed of amorphous silica (A-type opals). Silica as cristobalite and tridymite (C- and CT-type opals) is dominant in hydrothermal opals with fibrous, tabular, lepispheric, and net nanostructures [1–3, 9]. Probably, such differences are related to the temperature of the opals formation, which may be estimated from the oxygen isotope ratio. For example, a CT-type opal from Mexican rhyolites is characterized by $\delta^{18}\text{O}$ of 13‰, which corresponds to high-temperature conditions, whereas $\delta^{18}\text{O}$ of ~31‰ in Australian (opal-A from argillites) and Slovakian (opal-A from andesites) opals indicate a formation temperature of less than 45°C [7, 12]. In New Zealand, the low (7.5–8.4‰) and high (26.6–26.9‰) $\delta^{18}\text{O}$ values are measured in cristobalite–tridymite opals and amorphous opals with microspherules from volcanic- and clay-based soils, respectively [16]. At the same time, opals from hydrothermally altered volcanic rocks of Japan and the United States are characterized by $\delta^{18}\text{O}$ values of 6.8–25.9‰ [10]. However, no systematic comparative studies of this have been conducted.

The given paper presents the results of the study of the $\delta^{18}\text{O}$ value in the precious opals from Primor'e (Raduzhnoe deposit), Australia, and Ethiopia, and the

modern opals from the hydrotherms of the Mendeleev Volcano (Kunashir Island, Kuril Islands).

ANALYTICAL METHODS

The isotopic analysis of the oxygen was carried out at the Far East Geological Institute of the Far East Branch of the Russian Academy of Sciences. As known, the oxygen in opal is present in various compounds. Its most part is incorporated in the structure of the Si–O tetrahedral; however, it also occurs in the crystallization and porous water that saturates opals. The water oxygen exchanges isotopes with the meteoric water after the opal's formation. This changes the primary oxygen isotopic composition of the opal water. To exclude the influence of the exchanged oxygen on the results of the isotopic analyses, the porous water was removed from the studied opals by laser heating up to the melting temperature in an argon atmosphere. Then, the oxygen was released from the molten samples using an IR laser (10.6 μm) in the presence of BrF_3 (~210 torr). After fluoridation, the extracted oxygen was cleaned on two cryogenic traps with liquid nitrogen and on an absorbent with KBr. The $^{18}\text{O}/^{16}\text{O}$ isotope ratios were measured on a MAT 253 mass spectrometer using a double injection system. The calibration of the method was carried out based on laboratory and international (NBS-28) standards. The reproducibility of the $\delta^{18}\text{O}$ measurements was no less than $\pm 0.2\text{‰}$. Such an approach allowed us to analyze the oxygen isotopic composition of the

Table 1. Oxygen isotopes in the opals from Primor'e, Australia, and Ethiopia

Nos.	Description	$\delta^{18}\text{O}_{\text{smow}}$
Primor'e (Raduzhnoe deposit, CT-type opal)		
1	Milky white precious opal	19.73
2	Black precious opal	19.33
3	Water-transparent precious opal	18.54
4	Milky white opal	22.13
5	Muddy green opal	23.10
6	Water-transparent opal	21.03
Australia (Coober Pedi, A-type opals)		
7	Milky white precious opal	33.43
8	Milky white precious opal	33.02
9	Milky white opal	32.84
Ethiopia (Wolo province, CT-type opals)		
10	Water-transparent precious opal	26.17
11	Muddy white sugar precious opal	27.36
12	Brown precious opal	27.21

Si–O tetrahedra, which corresponds to the temperature of the isotope equilibrium at the opal formation.

RESULTS

The results of the studies are shown in Table 1. Three groups of opals are distinguished.

1. The precious opals from the Raduzhnoe deposit have shown the lightest $\delta^{18}\text{O}$ values ($19.2 \pm 0.6\text{‰}$, on average). The common opals (free of iridescence) from the deposit are more enriched in the heavy oxygen isotope with an average $\delta^{18}\text{O}$ of $22.1 \pm 1.1\text{‰}$.

2. The noble opals from Ethiopia are intermediate. The average $\delta^{18}\text{O}$ value is $26.9 \pm 0.7\text{‰}$.

3. The Australian opals from the Coober Pedi deposit contain the maximum amount of the heavy oxygen isotope. The average $\delta^{18}\text{O}$ is $33.1 \pm 0.3\text{‰}$.

It should be noted that the $\delta^{18}\text{O}$ dispersion in the Australian sedimentary opals is almost less than the determination error in contrast to the significantly wider variations in the $\delta^{18}\text{O}$ value in the hydrothermal opals from Primor'e and Ethiopia. This indicates the

different formation conditions of the hydrothermal opals even within one deposit.

The fluids and opals were sampled from the modern hydrotherms of the Mendeleev Volcano on Kunashir Island (Kuril Islands) to determine the influence of the temperature and water oxygen composition on the oxygen isotopic composition of the opals. The results are shown in Table 2. As seen from the table, the $\delta^{18}\text{O}$ values of the water sampled from three hydrothermal vents are insignificantly distinct. The $\delta^{18}\text{O}$ values agree well with the results previously published for this region [5]. The temperature of the hydrothermal waters, however, strongly varies, as well as the oxygen isotopic composition of the crystallizing minerals.

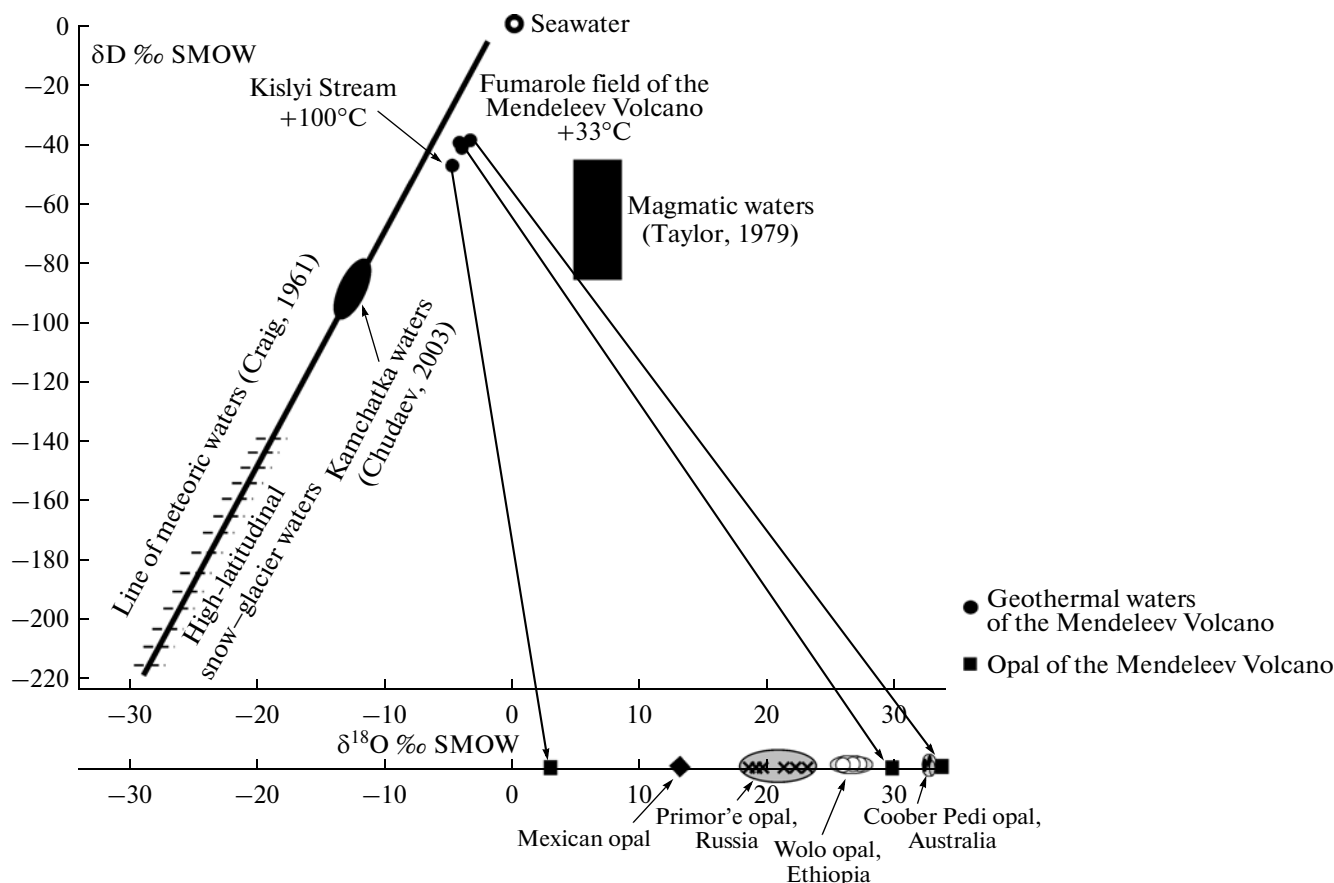
In the warm mineral springs with a temperature somewhat higher than 30°C , the crystallized silicates are significantly enriched in the heavy oxygen isotope in comparison with the water. In the hot springs with a surface temperature of 100°C , the fractionation of the oxygen isotopes between the minerals and the fluid was considerably lower. According to the isotope ratio, the high-temperature opal approaches the composition of the parental hydrothermal fluid.

The extrapolation of the data on the dependence of the oxygen isotope of the modern opals from the fluid temperature allows the estimation of the crystallization temperature of the ancient opals (figure). A crystallization temperatures of $30\text{--}33^\circ\text{C}$ may be inferred for opals from the Coober Pedi deposit. The Ethiopian opals are more high-temperature ($35\text{--}40^\circ\text{C}$). The highest temperatures ($50\text{--}70^\circ\text{C}$) are typical of the Primor'e opals. The precious opals crystallized from higher temperature fluids relative to the common opals.

The latter is in accordance with the previously published results on opals' nanostructure [2, 3]. In the precious opals from the Raduzhnoe deposit, the thermal effects led to the formation of two-dimensional photon zones created by nets, the cells of which resulted from the thermal effects according to the principle of Bénard cells. The decrease in the temperature prevents the formation of these cells and, correspondingly, cellular photon zones and the opalescence effect.

Table 2. Oxygen and hydrogen isotopes in the mineralized waters and the precipitating minerals in the Mendeleev Volcano on Kunashir Island

Number	Location	Water temperature	Mineral	$\delta^{18}\text{O}_{\text{smow}}$ of the mineral	$\delta^{18}\text{O}_{\text{smow}}$ H_2O	$\delta\text{D}_{\text{smow}}$ H_2O
1	Fumarole field	$t = 31.1^\circ\text{C}$	Opal–chalcedony	+33.5 ‰	–3.2	–40.6
2	of the Mendeleev Volcano	$t = 33.1^\circ\text{C}$	C-type opal	+28.4 ‰	–3.2	–42.7
3	Kislyi Stream	$t = 100^\circ\text{C}$	T-type opal	+3.0 ‰	–4.5	–47.4



Isotope ratios in the geothermal waters and opals. The compositions of the fluids from the Mendeleev Volcano on Kunashir Island (Kuril Islands) and the precipitating opals are connected by the arrows. The temperature of the geothermal waters on the surface is shown by the numerals. The fields of the meteoric and magmatic waters are given after [6, 15].

CONCLUSIONS

Thus, the oxygen isotope ratio in the opals may serve as a criterion of the estimation of the temperature of their formation. The low-temperature exogenic opals are relatively enriched in the heavy oxygen isotope independently of their host (sedimentary or volcanic) rocks. The examples are the Australian and Slovakian opals. On the contrary, the endogenic opals are enriched in the light oxygen isotope, the value of which depends on the temperature of the precipitation from the fluid. The higher the temperature of the fluid, the lighter the $\delta^{18}\text{O}$ values of the precipitating opal and the closer its oxygen isotopic composition to that of the hydrothermal fluid.

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