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Trace Elements in Agate
from the Pavlodar Region, Kazakhstan

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In various geological processes, we often meet periodical precipitation of material. Diverse laminated formations are encountered in mineralogy. Chalcedony with a visible zonal, banded structure is called agate. Intricate patterns and color diversity of agates have attracted attention from ancient times. Nevertheless, no reliable genetic theory has been created for this splendid chalcedony variety until now. Analyzing causes of the formation of the rhythmic structure of agate, we must take into account that they can be both internal and external. The internal causes are related, for instance, to peculiarities of crystallization in a closed physicochemical system (internal rhythms), while the external causes are due to a pulselike (intermittent) introduction of the material. The concentration on a certain process can lead to a one-sided, oversimplified explanation of causes of the rhythmicity formation, since the natural specimens can be consequences of both these processes [1]. In recent years, numerous works were devoted to the investigation of the rhythmic zonality in agate, including observations of self-organizing structures in agates [2], mathematical modeling of agate-forming processes [3–5], qualitative analysis of dynamic models for obtaining plausible phase portraits [6–8], and, finally, calculation of statistical characteristics of the rhythmic agate zonality by means of correlative and fractal analyses [9–11]. It is obvious that variations in the structure or chemical composition of a mineral reflect conditions of the growth environment. However, the correlation between variation in trace element concentrations and local characteristics of their growth near the crystallization surface or the surrounding medium remains unclear. An important information on formation conditions can be derived from the data on trace elements and the interpretation of their distribution. For this purpose, we examined the trace element distribution across the zonality in agate from the Pavlodar region, Kazakhstan. The data were interpreted based on statistical methods for revealing periodic regularities and obtaining quantitative estimates of the heterogeneity. This was performed to reveal the role of internal factors of growth (relative to external ones) and compare statistical characteristics of the rhythmic zonality of the specimen under investigation to those of agate from Mongolia [9].

The ion microprobe analysis of the Fe, Sr, and Zn contents in the agate from Kazakhstan was performed at Guelf University, Ontario, Canada. It was conducted along two profiles denoted by letters (A and B, Fig. 1). In both cases, the beginning and end of arrow correspond to the first and last point of the analysis respectively. Profiles A and B include 2305 and 2189 points, respectively, the distance between them being constant (0.00781 mm). We do not present here detailed distributions of the trace elements along the profiles. Let us only note that concentration profiles from the central part of the agate to its external boundaries represent oscillating functions with several irregular peaks, the highest peaks being for Fe and Zn. This is explained by the fact that the studied specimen contains inclusions of individual Fe and Zn oxides. Average values of the trace elements, which were found to be of the same order for the two profiles, and standard deviations of their distribution, which suggest the presence of admixtures in the experimental data, are presented in Table 1. As opposed to data reported for agate from the Arts-Bogdo region in Mongolia [9], the specimen from Kazakhstan provides no evidence as for the strong accumulation of residual admixtures in the course of its formation, although a tendency of accumulation is suggested by negative values of the angular coefficient revealed by the regressive analysis (Table 1).

Assuming that the trace element distribution in agate represents a time series describing a stochastic process and containing on admixture that does not affect the principal results, all the available distributions were subjected to autocorrelation analysis [12] to reveal periodic regularities. On a preliminary averaging of the data over four points, autocorrelation functions $R(g)$ were obtained for the Fe and Sr distribution along the profile A (Fig. 2). The autocorrelation functions are bounded by two lines denoting a 95% reliability level for the correlation coefficient values.

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As is seen from Fig. 2, maximum values of the correlation coefficient correspond to the lag $g = 98$ for Fe and to the lags $g = 16$, 94, and 110 for Sr.

We do not present here the autocorrelation function for Zn; let us only specify numbers of the lags where it is maximum, namely, lags $g = 92$ and $g = 132$. Since the distance between the points where the analyses were made was equal to 0.00781 mm, the length of a single lag for the data averaged over four points is equal to 0.03124 mm. Therefore, it may be considered that the distribution of Fe, Sr, and Zn along the profile A manifests a reliable periodicity of about 3 mm and that the distribution of Sr additionally manifests a periodicity of ~0.5 mm. The data on Sr were filtered using the method of running averaging over two points; the data on Zn, over three points; and the data on Fe were not filtered.

The trace element concentration in the beginning points of the profile B exceeds the average concentration of the element over the profile by 10 times (by 100 times for Fe). In order to obtain more correct results, all the data were first averaged by four points and, then, smoothed by two points. The calculations were conducted for a shortened series that did not involve the above-specified peaks. Fourier analysis of the trace element distribution along the profile B also revealed the presence of significant periodical components in them. The lag numbers (g) corresponding to the first maximum values of the autocorrelation functions are approximately the same for all the trace elements (13 for Fe, 15 for Sr, and 15 for Zn); i.e., a periodicity of about 0.4 mm was manifested for all three trace element distributions.

On the profile A, only the Fe distribution exhibits a strong linear trend. On the profile B, in contrast, such a trend has been found for all the trace elements, particularly for Fe. This is probably related to the fact that the periodicity of about 3 mm in the autocorrelation functions of the trace element distributions (which is observed along the profile A) is missing from the profile B, although the Fourier spectra of Fe and Sr yield the maximum for the fourth harmonic, while the spectrum of Zn, yields the maximum for the fifth one.

In order to determine the degree of interrelation between different trace elements, we found cross-correlation functions, one of which is shown in Fig. 3. The correlation coefficient (value of the cross-correlation function at the lag $g = 0$) for various pairs of trace ele-

Fig. 1. Photo of the surface of the agate specimen from the Pavlodar region, Kazakhstan. The profile A is 18 mm long and the profile B is 17.1 mm long.

ments along the two profiles is presented in Table 2. Since the correlation coefficient square [11] means how much a change in one of the variables is responsible for the change in another variable, the data of Table 2 allow

Table 1. Statistical characteristics of the trace element distribution in agate

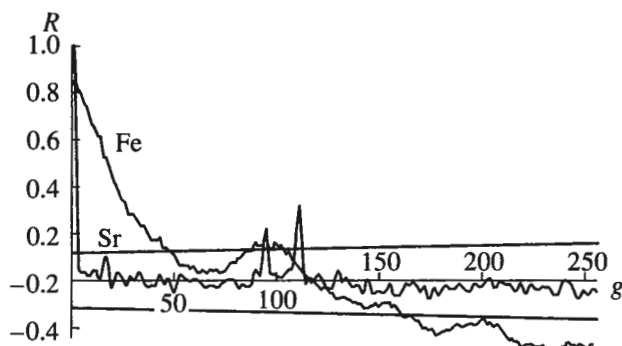| Parameter	Profile A			Profile B		
	Fe	Sr	Zn	Fe	Sr	Zn
Average, ppm	124.9	1.9	2.4	152.7	2	3.2
Standard deviation, ppm	145.8	5.4	3.8	225.6	2.9	3.9
Beginning value, ppm	134.	2.1	3.6	603.3	2.2	10.4
Angular coefficient	−0.117	−0.001	−0.005	−0.322	−0.0002	−0.005

Fig. 2. Autocorrelation functions of the Fe and Sr distribution along the profile A vs. the lag g. The solid lines are values of the correlation coefficient, corresponding to the 95% reliability level.
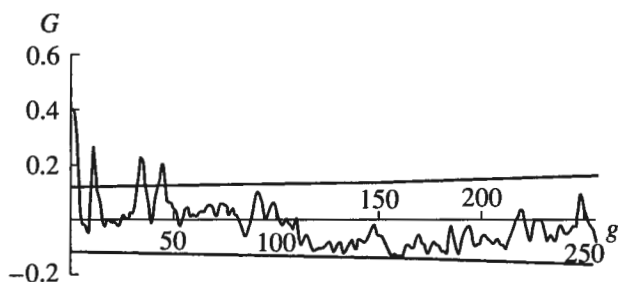

Fig. 3. Cross-correlation function between the distributions of Sr and Zn along the profile B; g is the lag number. The significance region of the correlation coefficients is bounded by the solid lines.

us to conclude that there exists a high correlation between the trace elements in each of the profiles (up to 20%, and even 80% between Fe and Sr in the profile A). Investigation of cross-correlation functions demonstrated that they reach the maximum values at $g = 0$.

Table 2. Paired correlation coefficients for different trace element distributions

Profile	Pairs of trace elements		
	Fe–Sr	Fe–Zn	Sr–Zn
A	0.42	0.96	0.37
B	0.36	0.32	0.32

Table 3. Values of the Hurst index H, calculated for the profiles A and B: (I) by the standard deviation method and (II) by the Fourier method

	Profile A			Profile B		
	Fe	Sr	Zn	Fe	Sr	Zn
I. $\log(l)$	0.5–2.1	0.3–2.5	0.5–1	0.3–2	0.6–2	0.6–2.1
H	0.24	0.15	0.19	0.48	0.1	0.3
II. H	0.13	0.41	0.31	0.38	0.23	0.22

This suggests that the variation in concentration of all the trace elements along profiles occurred synchronically and all the trace elements were similar in behavior during the agate formation. As is seen from Fig. 3, reliable positive values of the correlation coefficient between Sr and Zn along the profile B have been manifested not only at the lag $g = 0$, but at $g = 15$, 35, and 46 as well. This fact confirms once again the presence of periodical components in the distributions of Sr and Zn, revealed by the autocorrelation analysis.

As is shown in [10, 13, 14], quantitative estimates of rhythmic mineral zonality can be obtained using methods of fractal geometry. A record of measurements represents a curve of a fractal dimension D, if its standard deviation $w(l)$ on the interval l can be represented by the power dependence

$$w(l) \approx l^H,$$

where H is the Hurst index related to the fractal dimension by the relationship

$$D = 2 - H, \quad 0 < H < 1.$$

In addition, if the power spectrum $S(k)$ of a time series can be approximated by a relationship of the form

$$S(k) = k^{-B},$$

then the index B will be related to the fractal dimension D of the series by the relationship

$$B = 5 - 2D,$$

and with the Hurst index H, by the relationship

$$B = 1 + 2H.$$

The case H = 0.5 corresponds to ordinary Brownian motion. A persistent (long-standing) behavior is observed for $0.5 < H < 1$, when the data set is characterized by a positive correlation between the preceding events and the subsequent ones; i.e., when there exists a clearly pronounced tendency to variation with a relatively low admixture. If $0 < H < 0.5$, the data set is characterized by antipersistency (i.e., by a negative correlation between the preceding and subsequent events) and the data themselves look very contaminated [15].

The dependence of $\log(w)$ on $\log(l)$ for Fe, Sr, and Zn on the profile B are shown in Fig. 4. Values of the Hurst index H, obtained using the method of standard deviation (I) for intervals with a constant slope of the function $\log(w)$, and the Fourier method (II), are presented in Table 3. The Hurst index values obtained suggest that the fractal dependence is exhibited by all the trace element distributions but on different intervals. The largest interval for which the fractal dependence has been revealed belongs to the distribution of Sr along the profile A and is equal to 2.6 mm, which comprises 1/7 of the whole profile length. The shortest interval where the fractal dependence exists was obtained for the Zn distribution along the same profile A and is equal to 0.08 mm. As is seen from Table 3, the
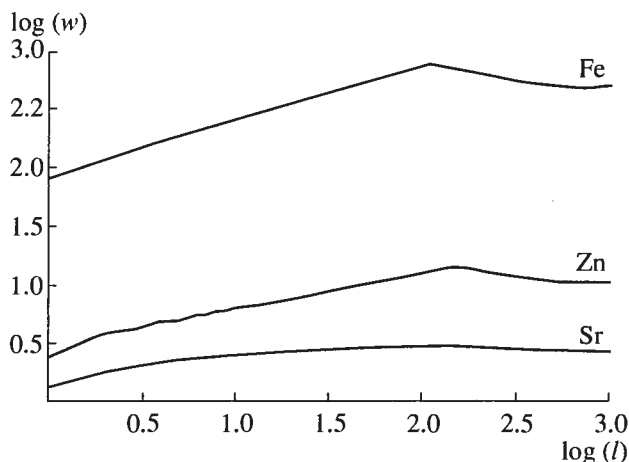
Fig. 4. Standard deviation $w(l)$ of the Fe, Sr, and Zn concentrations within an interval l for the profile B. Double logarithmic scale.

Hurst index values obtained by the two methods correspond, as in [9], to the antipersistent (H < 0.5) behavior of all the trace element distributions along the two profiles.

CONCLUSIONS

Results of the quantitative processing of ion microprobe data on the trace element content of agate from the Pavlodar region, Kazakhstan, can be summarized as follows: (1) distributions of Fe, Sr, and Zn oscillate along two profiles across the mineral zonality and contain periodical components; (2) a sufficiently strong interrelationship was found between different trace elements; and (3) the Hurst index values for all the distributions correspond to the antipersistent behavior (H < 0.5) and are restricted to the interval from 0.1 to 0.48. All the above observations evidence a predominant influence of the internal factor of growth in the closed system, as compared to the external one. Hence, the syngenetic rhythmic zonality in the agate from Kazakhstan has been found to be of the same type as that in the agate from Mongolia.

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