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ORIGINAL PAPER

Positron annihilation in precious and common opals

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Abstract. The nano-porosity structure of several non-crystalline opal samples of different origin was investigated with positronium atoms. The obtained data show that the structure depends on both the kind of opal (precious, common or hyalite) as well as the place of its creation (sedimentary or volcanic rocks). The sizes of the pores "seen" by positronium atoms are relatively small, not greater than about 1 nm for all studied samples which may suggest that the pores are located inside the silica matter from which the samples are made. Moreover, the pores detected in the "sedimentary" precious opals are smaller and have less diverse sizes than those found in "sedimentary" common opals and "volcanic" precious opals.

Key words: opal-A • porosity • positron annihilation

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Introduction

Opals are natural hydrous silica ($SiO_2{\cdot}nH_2O$) with either amorphous (opal-A) or disorder cristobalite/tridymite structure (opal-C and -CT) [4, 6]. Opal-A is subdivided into two groups: (1) opal-AN (network) or "hyalite" being transparent and having a glass-like structure; and (2) opal-AG (gel) having a body colour and a structure consisting of packed silica spheres generally 100–500 nm in diameter. In the latter case one distinguishes two kinds of opals, precious opal showing diffraction of visible light called the play of colour and common opal not showing the play. In the precious opal the diffraction is observed because the silica particles are uniform in size and form three-dimensional superlattice with lattice translation parameters in the range ~150–350 nm. In common opal the spherical particles exhibit a range of sizes, are imperfectly shaped, are too large or too small to diffract the visible light, or are not well ordered. Thanks to its play-of-colour and/or attractive body colour opal-AG is valued in the gem trade.

Opal-AG occurs in sedimentary or volcanic host rocks, where it was deposited in cavities by concentration of an aqueous solution of silica, forming first a gel and finally spheres of silica. The structure of the spheres is still intensively studied as it is unlike for samples of different origin. The study show that there are opal spheres with and without concentric shell-like structure and the spheres can be solid or multishelled, with up to six shells. Moreover, the shells can be composed of silica particles with sizes of the order of 10 nm, although such particles are not always observed.

In this paper we present results of our positron annihilation study of silica matter forming opal-A in order to check if the nano-porosity structure of the matter observed with positronium atoms depends on the opal origin. The positron annihilation technique belongs to the suitable tools for such studies. Its usefulness for mineralogical sciences is known more than 20 years [7]. In case of opals, it has been already used a couple of times [1, 2, 9].

Experimental and results

The atomic-scale empty spaces in natural opal-A were observed with positronium probes by using positron annihilation lifetime spectroscopy (PALS). The positron lifetime spectra were measured at room temperature for seven samples of opals:

1) white common opal from Poland (Szklary) – "sedimentary";
2) honey common opal from Poland (Nasławice) – "sedimentary";
3) bluish precious opal from Australia – "sedimentary";
4) bluish precious opal from Australia – "sedimentary";
5) black precious opal from Australia – "sedimentary";
6) blue precious opal from Slovakia (Dubnik) – "volcanic";
7) transparent hyalite from Poland (Jordanów).

Some of the spectra are presented in Fig. 1. They were collected by using an ORTEC "fast-fast" spectrometer with full width at half maximum (FWHM) of the time resolution function being about 320 ps.

The obtained positron lifetime data were analyzed with the LT computer program [5], in terms of three-component model which assumes (1) the intensity ratio of annihilating *para*- and *ortho*-positronium of 1:3, (2) lifetime of annihilating *para*-positronium, τ_1, of 125 ps, (3) the presence of the log-normal distribution for both, the mean lifetimes τ_2, corresponding to the free annihilation of positrons and the mean life times τ_3 related to annihilation of *ortho*-positrons by "pick off". In the analyzed spectrum this corresponds to the components with mean value $<\tau_2>$ and dispersion value σ_2 as well as the mean value $<\tau_3>$ and dispersion value σ_3, respectively. The spectrum model consisted of the two components with dispersions because one could expect that (1) the natural materials under investigation are not homogeneous ones as well as (2) the atomic-scale empty spaces existing in them are of different sizes. The results of the analysis are presented in Table 1.

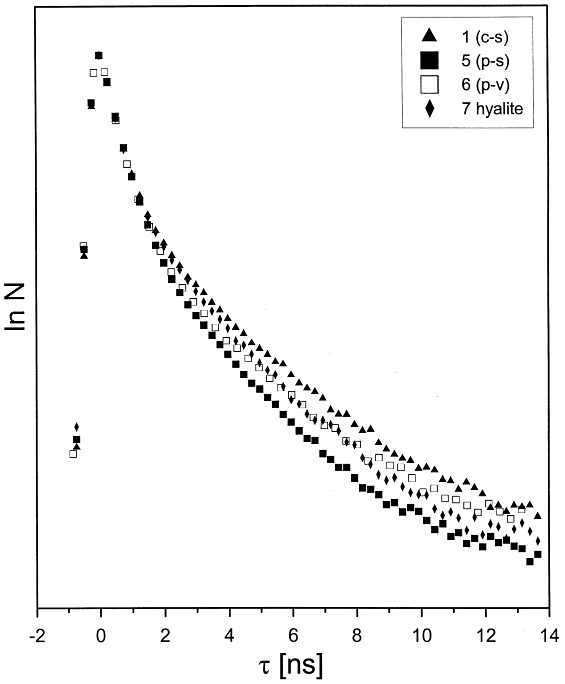

Fig. 1. Positron lifetime spectra normalized to the same height for samples of opal; no. 1 – "sedimentary" common opal (triangles), no. 5 – "sedimentary" precious opal (full squares), no. 6 – "volcanic" precious opal (open squares) and no. 7 – hyalite (rhombuses).

Taking into account the relationship between the lifetime τ_3 of an *ortho*-positronium atom and the radius R of the spherical empty space trapping the atom before its decay [3, 8], the findings show that the "sedimentary" common opal and "volcanic" precious opal have more open structure than "sedimentary" precious opal and hyalite. The relationship mentioned above is given by the following formula:

$$\tau_3[\text{ns}] = \frac{1}{2}\left[1-\frac{R}{R_0}+\frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \tag{1}$$

Table 1. Some of the best-fit parameters of the positron lifetime spectrum model and resulting from them mean radius of the spherical empty space trapping the *ortho*-positronium atom before its decay

No.	Sample	$<\tau_2>$ (ns)	σ_2 (ns)	$<\tau_3>$ (ns)	σ_3 (ns)	$I_1 + I_3$ (%)	$<R>$ (nm)
1	White common opal from Poland (Szklary) – "sedimentary"	0.4089(75)	0.120(15)	1.946(70)	0.760(74)	41.0(1.1)	0.280(7)
2	Honey common opal from Poland (Nasławice) – "sedimentary"	0.4017(16)	0.1273(23)	1.926(14)	0.829(17)	35.67(15)	0.278(1)
3	Bluish precious opal from Australia – "sedimentary"	0.4101(49)	0.063(16)	1.553(44)	0.426(43)	35.97(99)	0.240(5)
4	Bluish precious opal from Australia – "sedimentary"	0.4092(38)	0.068(11)	1.573(41)	0.434(41)	31.39(81)	0.242(5)
5	Black precious opal from Australia – "sedimentary"	0.4161(34)	0.055(12)	1.544(45)	0.504(42)	29.33(84)	0.239(5)
6	Blue precious opal from Slovakia (Dubnik) – "volcanic"	0.4108(96)	0.158(20)	1.967(73)	0.692(69)	26.8(1.1)	0.282(7)
7	Transparent hyalite from Poland (Jordanów)	0.3937(67)	0.098(16)	1.686(47)	0.422(50)	39.3(1.0)	0.254(5)

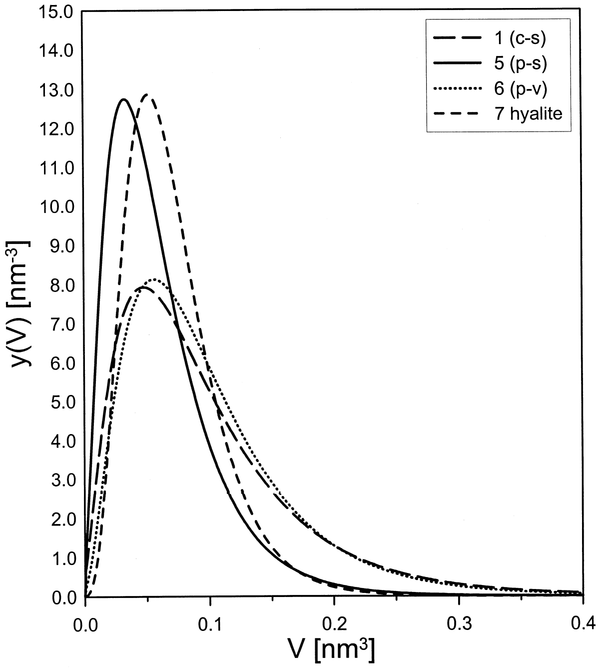

Fig. 2. Normalized size distributions of empty spaces in chosen samples of opal-A: no. 1 – "sedimentary" common opal, no. 5 – "sedimentary" precious opal, no. 6 – "volcanic" precious opal and no. 7 – hyalite.

where $R_0 = R + \Delta R$, and $\Delta R = 0.1656$ nm. The $<R>$ values computed for the determined $<\tau_3>$ ones with formula (1) are given in Table 1. The formula was used also to calculate the normalized distribution $y(V)$ of volume of the empty spaces "seen" by positronium atoms in the studied materials. It was done on the basis of the log-normal distribution of τ_3 values described by the model $<\tau_3>$ and σ_3 parameters. Results of the calculation are presented in Figs. 2–4 where the area under each distribution $y(V)$ is the same and equal to

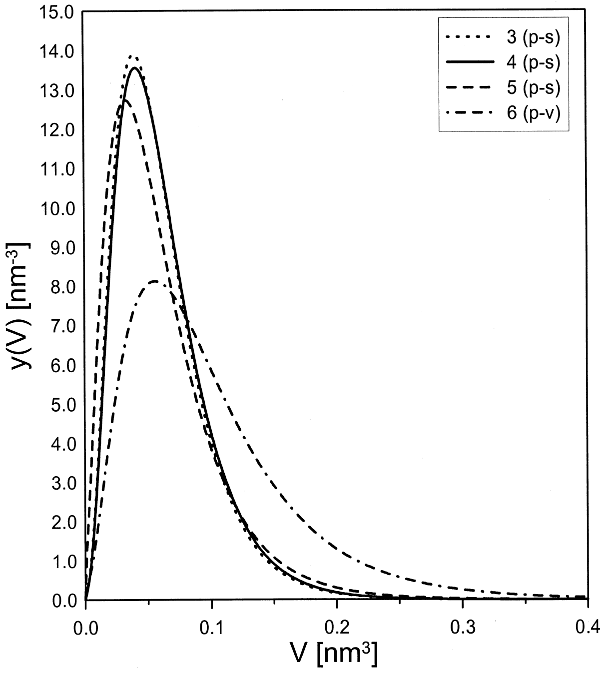

Fig. 3. Normalized size distributions of empty spaces in all studied samples of precious opals: no. 3, 4 and 5 – "sedimentary" opal, no. 6 – "volcanic" opal.

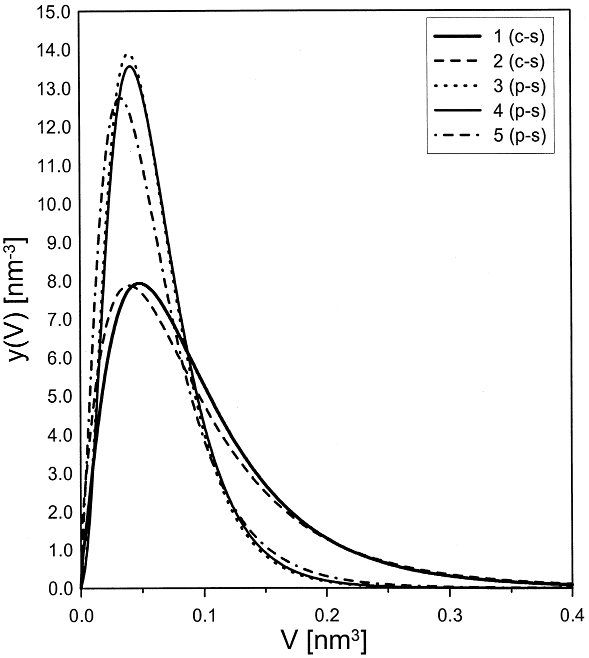

Fig. 4. Normalized size distributions of empty spaces in all studied samples of "sedimentary" opals: no. 1 and 2 – common opal, no. 3, 4 and 5 – precious opal.

1\. Figure 2 shows the volume distributions resulting from the positron lifetime spectra displayed in Fig. 1, whereas in Figs. 3 and 4 there are the distributions for all studied precious opals and all studied "sedimentary" opals, respectively.

As one can see, there are differences in the shapes of the distributions. Generally speaking, we observed two groups of the distributions: (1) narrower for hyalite and "sedimentary" precious opals, and (2) wider for "volcanic" precious and "sedimentary" common opals. In other words the shape depends on both the kind and the origin of studied opals.

Conclusions

The obtained data speak in favour of the suggestion that:

1. Positronium atoms are able to distinguish between precious and common opals deposited in sedimentary rocks – the sizes of the positronium traps as well as diverse of the sizes are smaller in the "sedimentary" precious opals; the differences in the corresponding parameters are at least 20%.
2. Positronium atoms are able to distinguish between "sedimentary" precious opals and "volcanic" precious opals – the sizes of the positronium traps as well as diverse of the sizes are smaller in the "sedimentary" precious opals; the differences in the corresponding parameters are at least 20%.
3. The sizes of the empty spaces trapping positronium atoms before their decay are relatively small, smaller than about 1 nm for all studied materials including hyalite, which suggests that the vacuities are located in the silica body of the materials, i.e. inside the silica spheres in case of opal-AG.

The differences in the intensity of the positronium component observed for positron lifetime spectra measured for unlike samples of opal-A can be explained by their different degree of crystallinity or different content of non-crystalline phase, which is the main place where the positronium traps are located.

As the results were obtained for several samples only, all the conclusions should be treated with appropriate caution.

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