SPELEOTHEMS OF AEROSOL ORIGIN: REPLY

ALEXANDER B. KLIMCHOUK
Ukrainian Speleological Association, P.O.Box 224/8, Kiev-30, 252030 UKRAINE

VLADIMIR M. NASEDKIN
Ukrainian Speleological Association, P.O.Box 224/8, Kiev-30, 252030 UKRAINE

KIMBERLEY I. CUNNINGHAM
SubTerra Consulting, 1245 Lakeshore Drive, Boulder, CO 80302-9533 USA

We strongly disagree with the comments by Maltsev on our original article, and hope that our response clearly explains our disagreement.

We do not feel sufficiently qualified to discuss whether the Curie principle is so universal a tool for identifying a speleothem's origin. In real cases there may be many factors complicating this rule. It seems that Maltsev is wrong in saying that surface geometry does not affect the process of aerosol deposition. Based on the works of Hungarian researchers (Cser & Maucha, 1968; Cser & Gadoros, 1988; Gadoros, 1989) we emphasized that the behavior of charged aerosols must be determined to a certain extent by forces of electric interaction. Surface geometry may affect aerosol deposition through distribution of the electrostatic potential, which has been shown both experimentally and theoretically. In addition, the mechanisms of precipitation from aerosols are not very clear. We suggested that crystallization occurs when a supersaturated hydroaerosol droplet contacts the rock (crystal) surface, but we also hypothesized that microcrystals form in the aerosol droplet when it joins with other particles which can play the role of the crystallization nuclei. After "dry" aerosols precipitate, the speleothem so formed may be further recrystallized.

For a long time the main problem with the interpretation of aerosol effects was that previously suggested mechanisms of cave aerosol generation had limited applicability for the formation of speleothems. The central point of our article was in offering a new hypothesis of aerosol generation: high-energy alpha particles and recoil atoms may dislodge clusters out of a mineral crystal lattice and knock out mineral fragments, generating small-sized aerosol particles. Combining with hydroaerosols, or becoming condensation nuclei themselves, such particles dissolve in water provided that the hydroaerosols contain sufficient dissolved material which may be deposited under appropriate physiochemical conditions. Because elevated levels of radon and its daughters are a fundamental characteristic of the cave environment, the above mechanism can, most likely, be widely applied to explain aerosol effects in caves.

To disprove this hypothesis, Maltsev calculated unrealistic quantities of lead which would accumulate at the base of the radon decay chain as a result of aerosol generation driven by alpha-decay. These calculations (and accompanying speculations) are based on numerous faulty assumptions and misconceptions.

First, clusters may be dislodged out of a crystal lattice not only due to alpha-decay occurring outside of a rock, but also due to alpha-decay occurring within the rock (of course, the effective distance of alpha particles in a solid material is lower than in the air).

Second, not only can alpha-decay of radon produce the effect under discussion, but three radon daughters are alpha emitters as well.

Third, recoil atoms do have the same kinetic energy as alpha particles, although their initial speed is only 2% of the speed of alpha particles and the effective distance is much lower (approximately 0.1 cm) due to difference in mass and size (Serdjukova & Kapitanov, 1975). Recoil atoms can, however, contribute to the effect along with alpha-particles.

Fourth, the assumption about the "effective volume" is very far from reality. In fact, radon release from a mineral grain occurs not only into the cave space but also into porous and micro/macro fissure space. The combined volume is, most likely, much greater than the volume of the cave itself. The same applies to aerosol generation; however only those pores and fissures which are directly connected with the cave volume can supply aerosols. But even this "connected" space can be comparable to, or exceed, the volume of the cave. Moreover, the effective surface is not merely a formalized geometric figure of the cave but, in reality, has well developed relief and includes the surface of all loose rock fragments (for example, breakdown boulders). It is difficult to make realistic assumptions using the above parameters, but it is clear that Maltsev's 5% is an underestimated figure. The true figure is more likely between one to two orders of magnitude greater.

Fifth, we hypothesized that not only single ions can be knocked out from the solid phase but clusters of crystal lattices consisting of many atoms. It has been shown by Baranov et al. (1981; cited after Dubashinsky et al., 1988) that alpha-decay can cause detachment of small particles, containing approximately 10-1000 atoms, from a solid matrix. This further changes Maltsev's ratio between aerosol material and lead generation to one to three orders of magnitude greater.

Finally, it is not clear what the quantity of "aerosol" gypsum that Maltsev assumed in his calculations was. We would roughly evaluate this quantity for Optimisticheskaya Cave at around 2000 lbs. (one ton), which appears to be much less than

the figure used by Maltsev.

In general, we do not see much sense in pursuing such rough calculations when so many factors and parameters are involved where quantification is highly uncertain. However, it is quite clear that Maltsev's quantities of lead are truly unrealistic, not because our model is patently wrong, but due primarily to the wrong assumptions and methodology that form the basis of Maltsev's calculations.

Although it is not directly related to the aerosol topic, it is interesting (and possible) to make some rough calculation on the quantity of lead which could be produced under certain radon levels. Assuming a radon level of 20,000 Bq per cubic meter for Optimisticheskaya Cave that is in equilibrum for 400,000 years (the suspected duration of the vadose stage), we calculated that 1.3x10-e4 gm. of lead would be produced from 1 cubic meter of cave volume. This gives 6.5 kg of lead for the 500,000 cubic meters of the cave.

Another obvious misconception in Maltsev's comments is his statement that any lead produced must be precipitated at the points of aerosol precipitation. Aerosols, radon, radon daughters, and lead itself—all have different migration properties and mechanisms of accumulation, so there is no expected spatial relation between areas of aerosol precipitation and lead accumulation.

We stress that the hypothesis of aerosol generation driven by alpha-decay is based not only on our speculations. After publishing the Russian version of our article (1993) we found some other publications in the physical sciences supporting the hypothesized mechanism. In addition to the above mentioned work of Baranov and others, Dubashinsky et al. (1988) have estimated that for particles < 0.1 mkm, the adhesion energy of any bond is as high as several 0.1 Mev, and that the same order of energy is required to split particles of 0.1 mkm or to separate such particles from the massive sample. The experimental work of the same authors has demonstrated that above a radioactive soil surface the concentration of large aerosol particles (<1.1 mkm) is 2.5-10 times greater than that observed in a control (nonradioactive) situation; the difference in concentration increases considerably with time. These references had been used in our English publication, but were ignored by Maltsev.

Maltsev also questions our data on radon levels reported in detail in Klimchouk and Nasedkin (1992). From Maltsev's text it could be understood that in Maltsev et al. (1995) data on radon measurements in Kugitang caves are compared from other sources and from Maltsev's own measurements. In reality, there was no other radon measurements made in these caves except ours. However, it follows from the units that appeared in the text that he actually meant gamma radiation. Our reported gamma-radiometry data range from 17-149 mkr/h while Maltsev indicates 5-70 mkr/h: it is not a striking difference if one considers that the measurements were made in different places. However, it is absolutely incorrect to compare measurements of gamma radiation with radon measurements made in different points and at different times, primarily due to the high spatial variability of both parameters and the temporal variability of radon concentrations. As to the methodology of our radon studies, we are quite sure that it was correct: it was used during the two year program that encompassed many caves in various regions, including 15-months monitoring in Marble Cave, Crimea, repeatedly controlled and published in detail along with the results (Klimchouk & Nasedkin, 1992).

As far as speleothems are concerned, Maltsev repeated conventional views on their origin giving no additional solid arguments in favor. In our article we certainly suggested alternative explanations based on the newly hypothesized mechanism of aerosol generation. Occam's razor is fully justified in cases where existing models are strongly supported by solid theoretical and experimental data, but that cannot be said about many fields of cave mineralogy. We assert that at the present stage of the study of speleothems concerned, conventional models are "proved and workable" no more then our suggested explanations. The appearance of new data on the physical characteristics of the cave environment, and of new hypotheses on the processes evolved, are strong enough reasons for suggesting new explanations for the origin of some speleothems.

Maltsev, referencing his article in the *NSS Bulletin* (Maltsev, 1990), states that the model for gypsum "snow" is well known. In this article he suggested that the growth of gypsum frostwork in Dzhurinskaya Cave, Western Ukraine, and the fall of crystals and their accumulation on the floor in form of "gypsum snow", are evaporation-condensation phenomena related to a seasonal reverse of airflow and subsequent change of relative humidity between 70-100%. The model has many controversial points, commented on in Klimchouk and Nasedkin (1984), but here it is enough to note that Maltsev's basic assumptions about microclimate of the cave, on which his speculations are based, are completely wrong. Our detailed 18-month monitoring of microclimate in this cave (Klimchouk et al., 1990) showed that the zone of notable seasonal variations of temperature and humidity encompasses only a limited part of the cave close to the entrance. But 5-10 m deep into the cave the relative humidity is nearly constant throughout the seasons (close to 100%). One of us has worked in the cave hundreds of hours in all seasons and has noticed nothing like Maltsev's "findings" that were made during his single visit to the cave. In other giant maze caves of the Western Ukraine, gypsum frostwork and snow is widespread, but not in conjunction, in the deep internal parts of the caves where there is no measurable seasonal variations of temperature and humidity.

Another reference made by Maltsev in his Comment is to the same article, and concerns hollow stalagmites from the Cupp-Coutunn Cave: "their genesis is also known and described". In fact, the only mention of these speleothems in his article is as follows: "Stalagmites present are hollow and may be up to 3 m in diameter. Their walls are 1-30 cm in thickness and consist of recrystallized frostwork" (p. 101). In the present Comment Maltsev speculates on condensation-evaporation and seasonal humidity cycles, though in another publication (Maltsev, 1994), he asserted that there is a biogenic

component in the mechanism of formation of these hollow stalagmites, and that they "are not hollow but have aggressive to gypsum biogenic substance inside" (p.96). The question arises then, what particular genesis is described and known from Maltsev's publications?

In publishing our article we realized that the suggested mechanisms were speculative to a considerable extent and required further theoretical and experimental justification. Some of the aspects of the topic extend beyond the limits of our direct competence. One of the main goals in writing this paper was to stimulate further discussion and studies of the physical properties of the cave environment and aerosol effects in caves. Regrettably, Maltsev's comments give no constructive contribution to the problem and obviously have more of a scandalous agenda. The only positive result of this discussion may be that it will draw the attention of serious investigators to the topic.

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