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Interactive comment on "In vitro formation of Ca-oxalates and the mineral glushinskite by fungal interaction with carbonate substrates and seawater" *by* K. Kolo and Ph. Claeys

K. Kolo and Ph. Claeys

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Authors reply to Referee #1

The referee's comments are in *Italic.*

We tried to answer all points listed in the comments and the issues raised by Referee #1.

General comments

We agree with the referee that "*the restriction of fungal-rock interactions to rock surfaces suggests that the processes do not contribute significantly to the diagenesis of thick sequences of sedimentary strata" w*hen compared to other sedimentary diagenetic processes. First, we visualize the significance of these interactions as microscopic processes that modify carbonate substrates and are capable of leaving a clear and observable signature on the substrates. Secondly, we see these interactions and the role of fungi as diagenetic factors, weathering agents, metal recyclers and carbonate precipitators. Some authors have seen the role of fungi as major players in the calcium carbonate accumulation in paleosoles and enrichment of terrestrial sediments with $CaCO_3$ throughout geological time (Verrecchia et al., 2003).

Specific comments

Here the referee raised several profound issues of discussion. Here again, we agree with the referee regarding his statement that "*These questions have implications for recognizing the products of fungal interaction in ancient strata and in rocks from other planets.*" This was one of the issues that motivated our experiments.

The Referee raised the question "*To what depth in a rock surface are fungal interactions apt to occur? Is this strictly a surface phenomenon, not even penetrating through a 30 micron thick thin section, or are the effects of such processes in naturally exposed rock surfaces apt to penetrate to somewhat deeper depths?*"

Fungi dwelling on exposed rock surface do not seem to penetrate deeply in the rock strata. The common depths encountered are within few mm to a few centimeters. Usually the fungi form a millimetric crust on the attacked surface, especially as a mycobiont of lichen; field cases fall within these penetration depths (e.g. Russ et al., 1996; Verrecchia, 2000; Arocena et al., 2003). High rock porosity, fractures and nutrient availability could enhance the penetration of fungal hyphae within the rock system to deeper depths. Gorbushina et al. (2000) considered the microflora living within a rock can reach a depth of 20cm. As to the experimental work, the 30 micron thick thin section was totally removed in most of the trials within 15days, which demonstrate the "efficiency" of the process. The above interactions, although basically a surface phenomenon, have in fact a depth factor. When repeated generations of fungi (or lichens) inhabit the same rock surface and cause repeated weathering of the rock surfaces (exfoliations, pitting, chipping, and disintegration: Sterflinger, 2000). Formation of calcretes illustrates fungal interactions that go beyond surface interactions and take part in the diagenetic process (Verrecchia, 2000).

In ancient strata, the fungal interaction products have been cited. In the calcretes of the Lower Carboniferous (Visèan, northern France) rich fungal communities were recognized (Kolo et al., 2001; Kolo et al., 2002; Preat et al., 2003). Under SEM dolomite crystals appeared arranged along the fungal filaments, many times dichotomous. Irrespective of how this filamentous dolomite had formed in such environment, its close relationship to fungal filaments is evident. In our experimental work, minerals composed of Mg, Ca, C and O were formed during a fungal-dolomite substrate interaction. Whether these newly formed minerals are double-metal oxalates or true dolomite is currently being evaluated but their presence raises the question of dolomite precursor and of the recycling of sedimentary dolomite in natural environments by fungi.

Another point of the reviewer is:

"How likely are Ca-oxalates and glushinskite to survive for extended periods of time on natural surfaces? Are these minerals thermodynamically stable at Earth surface conditions, or are they apt to be dissolved and/or replaced by more stable mineral forms?"

Both forms of Ca-oxalates (weddellite and whewellite) are considered unstable over extended periods of time on natural surfaces, especially when oxidized by bacteria. It is now well accepted that the Ca-oxalates enter the carbonates cycle and end up forming $CaCO_3$ (Gadd, 1999; Verrecchia, 2000; Verrecchia 2003). The question is: how long do these two minerals remain stable? Actually no direct measurements are available. In a study by Russ et al. (1996) on the origin of whewellite rich rock crust, they produced C^{14}dating of 5570 years B.P. Manning (2000) presented examples where the Ca-oxalates entered the geological cycle and were precipitated with other minerals in sediments ranging from Carboniferous to Paleocene. He also showed that Ca-oxalates are stable under 160°C; this practically means that the Ca-oxalates would be stable under normal geological conditions. Compared to Ca-oxalates, glushinskite is a relatively new mineral and its natural occurrences are rare. No data is available on the stability of glushinskite in the natural environment. Experimental data on thermally treated and Raman tested glushinskite was produced by Frost et al. (2003). The results of this treatment suggested the possibility of transitional formation of magnesium carbonate. Here again glushinskite as a mineral is invoked as a possible precursor to dolomite formation. Unfortunately the evidence supporting this hypothesis is not complete.

"Regarding the discussion of concentric Ca-oxalate crystals and potential diagenetic pathways in lines 29-30 on page 464, I disagree with their comparison to sedimentary ooids."

These concentric crystal forms with a nucleus and produced through fungal interaction with the substrates are reported here for the first time. We agree with the referee on his remark concerning the size of these concentric crystals but the available growth time and mechanism differ from the marine environment. So here we were going a step further in considering a situation where these concentric crystals are introduced into real sedimentary environment. We speculated that the time and growth would be in favor of formation of real ooids. We found that such possible scenario is worth mentioning. Fungal ooids have been reported in natural environments of microbial mats (Krumbein et al., 2003).

"There is a morphological similarity between your spindle-shaped glushkinite and dumbbell-shaped dolomite grown in a liquid medium by Vasconcelos et al. (2005) Geology, v. 33, p. 317-320. Perhaps there are some comparisons to be drawn."

Unfortunately we could not relate our spindle-shaped glushinskite to the dumbbell-shaped dolomite. But we have observed from our experimental work that some of our EDX analyses of fungally produced biominerals, gave signatures very similar to the signature of the dolomite produced experimentally by Vasconcelos and his colleagues.

We wish to conclude this reply by thanking anonymous Referee #1 for his time and comments.

Authors

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