Kurze Originalmitteilungen

Für die Kurzen Originalmitteilungen sind ausschließlich die Verfasser verantwortlich

Pre-Ceramics?

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Puddles formed on loess soil are known to fissure up on drying [1]. The irregular, dish-like, concave pieces thus formed may reach a 100 cm^2 area and are from 1 mm to 1 cm thick (Fig. 1 a). They are formed by sedimentation; their upper fine layer contracts more quickly than the rest and the pieces break away from the soil beneath.

I took some such fragile, soft crumbs and burned them under small bonfires, about $^1/_2$ m high and 70 cm Ø which were fed wood for about 4 hours. We obtained hard, dish-like crumbs which could be broken by hand only with difficulty. These crumbs have a Mohr hardness between 3 and 5, a water-absorbing capacity between 8 and 25%, and a modulus of rupture between 30 and 60 kg/cm^2. Modern data on burned fire clay range from 50 to 220 kg/cm^2.

I propose that dish-like pieces burned accidentally in bonfires may have given to prehistoric man the idea that ceramic dishes can be made by moulding certain clays by hand and burning them. He may have sometime accidentally obtained his plate together with his steak and proceeded to obtain it on purpose. The hypothesis is difficult to prove. Nevertheless there seems to be a way of distinguishing between accidental "pre-ceramics" and sherds of deliberately formed, man-made pottery. The outer surface of man-made pottery is always smooth, as is its inner face. The outer surface of naturally formed soil crusts, not having been smoothed, is very often course: it is the breakaway surface from the subsoil. Its inner face is always smooth because of its having been formed by fractional sedimentation and subsequent contraction. If archeologists were to find "ceramic" pieces course on their outer surfaces, this could be the proof that they were not made by man. Were they found in places indicating human habitation, it would be probable that man made use of them.

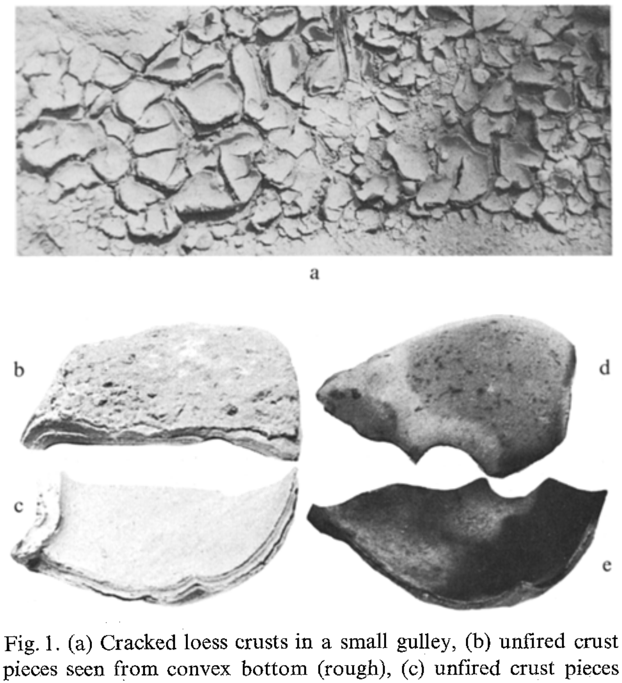

Fig. 1. (a) Cracked loess crusts in a small gulley, (b) unfired crust pieces seen from convex bottom (rough), (c) unfired crust pieces seen from concave top (smooth), (d) fired crust pieces seen from convex bottom (rough), (e) fired crust pieces from concave top (smooth)

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Two Mechanisms of Microbial Carbonate Precipitation

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Although various aspects of microbial activity have been correlated with the precipitation of carbonates, relatively little information is available on the actual biogeochemical process of carbonate precipitation. Two new mechanisms of microbial carbonate precipitation were investigated in laboratory experiments: a redox reaction and a process involving carbon dioxide production.

Microbiological activities leading to the formation of new minerals, especially those processes that lead to the precipitation of carbonates, are of considerable interest to mineralogists. However, most of the research in this field has been carried out by microbiologists. The growing interest of geologists in such geomicrobiological phenomena arose mainly from carbonate sedimentologists working with Recent sediments [1, 2]. The importance and ubiquity of microbial activity in the topmost centimeters of sediments is being increasingly realized, and calls for an interdisciplinary approach [3].

Apart from the deposition of carbonate minerals inside cell membranes, the deposition of carbonates outside the microbial cell through the metabolic activity of certain microbes is considered. Precipitation outside the microorganism will induce a mechanical function of the carbonate as a "submarine cement". Microbial activities are related to the deposition of $CaCO_3$, which includes production of ammonia, nitrate reduction, oxidation of organic calcium complexes, and withdrawal of carbon dioxide [4]. Bacterial sulfate reduction also contributes to the formation of $CaCO_3$; early investigators thought that the reaction took place in the following manner:

$$2\,C + CaSO_4 + H_2O \rightarrow CaCO_3 + CO_2 + H_2S \text{ [5]},$$

or:

$$CaSO_4 + CH_3COOH \rightarrow CaCO_3 + H_2S + H_2O + CO_2 \text{ [6]}.$$

However, both of these theoretical reactions produce CO_2 and H_2S – compounds that tend to solubilize calcium carbonate.

Recent experimental investigation of the biogeochemical activity of sulfate-reducing bacteria in carbonate sediments has revealed that the mechanism takes place as a redox reaction. At pH 7 to 8 of the medium (seawater), and below $E_0 \pm 250$ to 300 mV, the bicarbonate ion combines with the hydrogen ions to form methane gas:

$$3\,Ca^{2+} + 4\,HCO_3^- + 6\,H^+ + 8\,e^- \rightarrow CH_4 + 3\,CaCO_3 + 3\,H_2O \text{ [7]}.$$

Laboratory experiments demonstrated the precipitation of calcium carbonate (aragonite) through the activity of sulfate reducers (Fig. 1). Sterile tests failed to show any precipitation phenomena. Sulfate reduction can be considered almost universal in soils and sediments, and may thus be of importance in the submarine cementation processes of Recent sediments.

A second type of microbial activity capable of mobilizing and reprecipitating considerable quantities of carbonate material is found in the metabolism of (marine) yeasts. The production of CO_2 during respiration, or even fermentation, of yeasts in a carbonate sediment increases the bicarbonate concentration and thereby dissolves carbonate. However, upon the escape CO_2 at the liquid/air, or sediment/liquid, interface the dissolved ions reprecipitate as carbonates. Laboratory experiments showed that the formation of relatively large quantities of $CaCO_3$ is the result of microbial mobilization by yeasts influencing the bicarbonate balance of the medium. Sterile controls failed to show any solubilization/reprecipitation phenomena when the same glucose medium was used. The use of both stereo scanning electron microscopy (Fig. 1) and light microscopy resulted in the demonstration of a definite relation between crystal morphology and microbial activity. Sulfate reduction creates spherulitic aggregates of aragonite with a multitude of rod-shaped, carbonate-encrusted bacteria (Fig. 1). Mobilization by yeasts appears to have taken place at such a quick rate that numerous yeast cells were incorporated into the newly formed carbonate crystals.

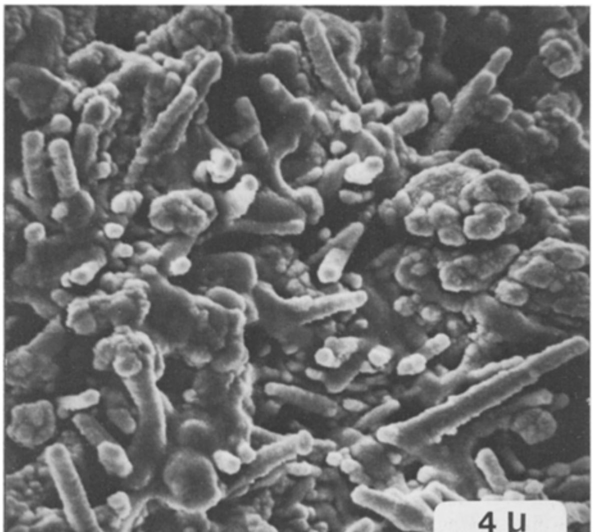

Fig. 1. Stereo scanning electron photomicrograph of the outer surface of a spherulitic aragonite crystal aggregate, showing a multitude of rod-shaped, carbonate-encrusted bacteria

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Orthorhombic Strontium Alumogermanate $Sr[Al_2Ge_2O_8]$

A New Variant of the Feldspar Structure

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When crystallizing melts of $SrAl_2Ge_2O_8$-composition single crystals of the new compound suitable for X-ray work can be obtained. Its *d*-spacings are close to those of the disordered triclinic feldspar $Sr[Al_2Ge_2O_8]$. Indexing based on the setting of this structure, however, leads to a primitive monoclinic cell. The powder pattern omits all feldspar reflections for l = odd. The infrared spectrum of the new compound cannot be distinguished from that of the disordered SrAlGe-feldspar thus indicating that both Al and Ge are tetrahedrally coordinated and most probably randomly distributed, too.

Single crystal X-ray photographs reveal orthorhombic symmetry and the space group *Fddd*. Precession photographs of a^*b^* layers for l = even show a feldspar pattern with its characteristic intensity distribution. For l = odd, however, the resulting pattern is strikingly different: superstructure reflections lead to a doubling of the *b*-axis.

Exactly this structural variant has been predicted by Laves [1] based upon his observations of synthetic and lunar feldspar samples. His prediction states the formation of orthorhombic nuclei displaying the S.G. *Fddd* and the lattice parameters:

$$a_{\text{orh.}} \sim \sqrt{3}\, a_{\text{feldsp.}};\ b_{\text{orh.}} \sim 2\, b_{\text{feldsp.}};\ c_{\text{orh.}} \sim c_{\text{feldsp.}}$$

The compiled lattice parameters of the new compound and the corresponding disordered feldspar demonstrate excellently how Laves' prediction is fulfilled.

The structure determination, its refinement, and a detailed discussion of the structural variant will be published in Z. Krist. by Kroll, Pentinghaus and Laves.