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Synthesis and Photocatalytic Properties of Nanocrystalline Hematite Films: Comparison to Natural Hematite Crystals

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Amino acids composition in kerogen of shungite rocks (Karelia, Russia)

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Significant accumulation of autochthonous organic carbon in Palaeoproterozoic rocks is rare. One of the largest and most remarkable occurrences is the Karelian deposit in Russia [1]. The age of the rocks is 2.15 – 2.00 Ma. The organic substance of shungite rocks consists mostly of carbon (90–95%), and there are also smaller amounts of H (~1%), N (~0.8%), S (~0.4%), and O (~2.4%). Study of amino acids proves probable biogenic origin of Karelian Precambrian shungite primary organic substance [2].

The differences in the group and individual content of amino acids in shungites reflect not only the ways of shungite rock formation (sedimentary, migrated, redeposited) but also a different ratio of carbon and mineral components in the studied samples. To prove the hypothesis presented, kerogens from type-I shungite of Shunga and type-III shungite of Zazhogino were used. It was found out that after mineral matrix is deleted from the samples, the content of amino acids in them decreases threefold. Thus, in higher anthraxolite kerogen, the amount of amino acids decreased from 48 to 19 µg/g of the sample, and in type-III shungite – from 80 to 29 µg/g.

The concentration of most amino acids (alanine, threonine, valine, glycine, leucine, phenylalanine, and glutamic acid) in kerogen, extracted from higher anthraxolite, was 1.5–3 times lower. The same tendency is observed in case of type-III shungite, except alanine, the concentration of which compared to the initial samples, was four times lower. In both cases, the concentration of isoleucine and proline decreased especially sharply.

The results of kerogen study show that in Karelian shungite rocks, amino acids are connected both with the shungite substance itself and its mineral component (quartz and almosilicates). Alanine, glycine, valine, leucine, threonine, phenylalanine, and glutamic acid are directly connected with shungite substance, but aliphatic amino acid, having the simplest composition, prevail. In shungite rock mineral matrix, all the amino acids mentioned above and also isoleucine, serine, proline, and aspartic acid are present.

Only some amino acids in the structure of shungite carbon (alanine, glycine, valine, leucine, and glutamic acid) can be referred to original, connected directly with the primary organic substance of shungite rocks.

- [1] Melezhik (2004) *Ore Geology Reviews* **24**, 135-154.
[2] Shanina (2007) Goldschmidt Conference Abstracts, A291.

Synthesis and photocatalytic properties of nanocrystalline hematite films: Comparison to natural hematite crystals

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Metal oxide semiconductors have long been recognized as photocatalysts whose properties give insight into both natural and technological systems. Hematite in particular has been the subject of much recent study, and its photocatalytic properties may play a role in photochemical oxidation of organic molecules, photochemical processes on the early Earth, and possibly in photocatalytic water loss from Mars. In a solar energy context, hematite has been studied for many years as a photocatalyst for water splitting; light is absorbed by the oxide, and photogenerated “holes” oxidize water to oxygen. Hematite is particularly attractive for this role because it absorbs a significant amount of light in the visible portion of the spectrum, is nontoxic, stable, and – most appealingly – inexpensive.

An obstacle to economical water splitting by hematite (with the intent of coupling it to either proton or bicarbonate reduction via a second semiconductor system) is the relative photocatalytic inefficiency of hematite. Here, we compare the properties of synthetic nanocrystalline hematite films with those of natural hematite crystals. For example, crystals have been used to show that photocurrent generation by water splitting is 5 to 10 times more efficient when illuminating crystal edges instead of (001) crystal faces, probably because of better conductivity and thus better charge separation in direction perpendicular to [001].

Hematite is also thought to harbor an “intragap” electronic state that mediates recombination of photogenerated electron-hole pairs. One possibility is that ambient water is incorporated into the hematite structure during deposition, leading to goethite-like impurities. We have conducted experiments to test this hypothesis by growing n-type doped hematite nanocrystalline films, using simple Atmospheric Pressure Chemical Vapor Deposition (AP CVD). While some results are consistent with the hypothesis that water impurities reduce photocurrents, reproducibility is complicated by the role of water in the doping process.