Mineral composition of iron sulphide framboids from Neogene sediments and dump materials (East Maritsa Coal Basin, Bulgaria) – preliminary results

Минерален състав на железни сулфидни фрамбоиди от неогенски седименти и насипищни материали (Източномаришки басейн) – предварителни резултати

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Introduction

Most of the modern sediments and ancient sedimentary rocks contain authigenic iron sulphides (often pyrite) as heavy minerals because of the nature of the environment required for their formation – fine sediments buried in anoxic sulphate-reducing sedimentary environments. Framboids are the dominant form of these sulphides, more typical for pyrite framboids formed via monosulphide precursors mackinawite and greigite.

There are not any studies on iron sulphides in East Maritsa Basin (EMB) sediments, except of some mineralogical data on the sulphides in the EMB coals. Pyrite was reported as main iron sulphide mineral and a lack of marcasite was outlined (Kostova, 2005). Here we present our first data on the study of mineral composition and spatial relationships between the phases found in the iron sulphide framboids separated from the sediments and dump materials from East Maritsa Basin.

Geological background

EMB is a part of a graben formed as an extensional structure during the final stages of continental collision along the southern margin of the Alpine orogene. The basin is a complex structure built of pre-Paleogene basement, pre-Miocene Paleogene basement and Miocene-Pliocene cover. The Miocene-Pliocene cover is divided into 3 formations: Marishka fm. (coal bearing sediments presented by gray-black clays and sands and three coal seams); overcoal Gledachevska fm. (freshwater lacustrine clays mainly, sands, sandstones and limestones); formation of fine dispersed clays. Characteristic are the active faults that framed the basin (e. g. Sokolishki, Sazliyski), the neotectonic processes, the mud volcanoes and the ancient and modern, natural and technogenous landslides (Nedjalkov, Rachev, 1990).

Material and Methods

Framboids in rock pieces and heavy fractions separated from core sediments and surface and core dump materials were studied. The main characteristics as form, texture and appearance were determined under stereomicroscope. The morphology, size, chemical content and relationships of the framboids' microcrystals were studied in epoxy resin cemented samples on SEM JEOL Superprobe 733. Single Raman spectrometer LabRAM HR Visible equipped with an Olympus optical microscope with various objectives and Peltier cooled CCD detector was applied for collection of Raman spectra using a 633 nm He-Ne laser. Powder Xray data were obtained on a TUR M62 diffractometer using Fe filtered CoKα radiation.

Results and Discussion

The Neogene clayey sediments enriched in sand and organic matter contain single disseminated and/or lenses of sulphide framboids ca. 1–5 wt.%. The other sediments along the core log contain disseminated single framboids ca. <1 wt.%. Sulphide pseudomorphoses of organic phyto- remnants were observed elsewhere. Sulphides' content in the dump materials was very irregularly distributed and did not show any relationship to depth or type of material. Single iron sulphide crystals and aggregates were found in all the fractions studied, but in very different quantities – from single crystals to nearly 100% of the heavy fraction. As a rule, in a same sample the richer in sulphides were the finer fractions, e.g. 0.032–0.063 mm.

Iron sulphide framboids are more often spherical to sub-spherical, irregular nonspherical aggregates of (poly)framboids. In reflected light most of them were fully recrystallised to cubic crystals or radial laths replacement; some were recrystallised on periphery only, and the other were not recrystallysed. SEM study revealed the complicated structure of the (poly)framboids and their polymineral and polystage formation.

The mineral composition of the fully recrystallised ones is presented by cubic pyrite crystals and massive aggregates of cubic and octahedral microcystals. The texture and mineral composition of the partly recrystallised framboids were characterised by core with surrounding radial crystals (sunflower form). In some cases, pentagon crystal-like framboids or pentagon crystals with framboids in the core were observed with microcystals of 0.58–0.73 µm. Micro-Raman study determined pyrite core overgrown with radiating, blade-shaped crystals of marcasite and pyrite in variable amounts. Both minerals' presence was confirmed by the XRD patterns too.

The mineral composition of the "fresh" (poly) framboids usually finer than 20 µm was difficult to determine unambiguously. SEM study reveal typical polyframboid textures built of equal or different in size framboids. The individual framboids contain often octahedral microcrystals, and more rarely – cubic (0.18–0.83 µm to maximum 1.68 µm) determined as pyrite by Raman spectroscopy. Some of the framboids are closely packed in the polyframboid, others connect to each other via tiny neomorphed microcrystals (0.3 µm). The mineral composition of the sulphide neomorphed microcrystals was not determined unambiguously. Attempts to obtain clear XRD patterns failed – the peaks were clear, but with low intensity, probably because of the crystals' size. Some clear picks of pyrite only were identified. The Raman spectra obtained are clear and of marcasite. About same problems reported Kostova (2005) when trying to identify by TEM "melnikovite, mackinawite, pyrrothite and greigite(?)". Very probably the nature of the neomorphed microcrystals is polyphase and polystage.

Problems concerning pyrite formation in sediments, as well as its stability in dump materials have been recently studied very actively. What is interesting in the case studied is how pyrite crystals have survived the oxidation processes in surface dump materials, whereas processes of acid mine drainage in the dumps of Middle German coal district were so active that 1–2 years after heaping pyrite was not identified in the surface dump materials (Cesnovar, Pentinghaus, 2000). Probable answers are to be searched for in the recrystallisation of pyrite to marcasite above described, geochemical indexes of organic matter pointed to redox rather oxidative processes (Markova et al., 2011) and active tectonic processes in the region.

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