Acta Mineralogica–Petrographica, Szeged, XLI, Supplementum B, 2000

GREIGITE FROM ROCKS: BIOGENIC OR NON-BIOGENIC?

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Iron sulfides that commonly occur in rocks include pyrrhotite ($Fe_{1-x}S$) of magmatic or metamorphic origin, pyrite and marcasite (both FeS_2), and greigite (Fe_3S_4). Pyrite and marcasite are paramagnetic, i.e., they contribute only to the magnetic susceptibility. Monoclinic pyrrhotite and greigite have ferrimagnetic properties; thus, they may also contribute to the remanence. When greigite was discovered and identified in rocks, it was first considered to be rare. However, greigite and pyrrhotite as carriers of the natural remanent magnetization in sediments have been increasingly reported over the last decade, and magnetic methods to screen rocks for the presence of ferrimagnetic iron minerals and for their identification have been developed.

Iron sulfides in sediments can be of either inorganic or biogenic origin. Biologically-induced mineralization (BIM) is known to produce greigite as an intermediate in a reaction sequence that starts with precipitated amorphous iron sulfide and terminates with pyrite (MORSE et al., 1987). Greigite is also produced by biologically-controlled mineralization (BCM) in magnetotactic bacteria (HEYWOOD et al., 1990). Except for a study that described presumably BCM greigite from soil (STANJEK et al., 1994), we have no information about the potential contribution of bacterial greigite to the magnetic signal of sediments or rocks.

In the Pannonian basin and its surroundings there are several occurrences of dark grey clay and marl that have been studied in the last three years primarily for obtaining paleomagnetic directions of tectonic value or for magnetostratigraphy; these rocks display magnetic properties characteristic of magnetic iron sulfides. We selected half a dozen samples from the above outcrops in which greigite was the likely carrier of the remanence, and studied them using analytical transmission electron microscopy (ATEM).

Electron diffraction and energy-dispersive X-ray spectra confirmed the presence of greigite and pyrite in two samples, a marl that deposited in a brackish environment (Laki, Poland), and a salty marl that formed in a hypersaline basin (Mihalovce, Slovakia). In the Laki specimen greigite crystals occurred in clusters, attached to the surfaces of clay minerals. The crystals typically showed non-uniform, blotchy contrast in the TEM (Fig. 1b). Similar spotty contrast was observed in BCM greigite from magnetotactic bacteria (Fig. 1a), and interpreted as resulting from a partially completed solid-state transformation of a precursor sulfide (mackinawite) into greigite (PÓSFAI et al., 1998). Greigite grains in the Mihalovce sample looked different from those in the Laki rock; they occurred in large clusters together with pyrite, and showed uniform black contrast (Fig. 1c).

A knowledge of the crystal size distribution (CSD) of a population of crystals is useful for assessing possible growth mechanisms (EBERL et al., 1998). We compared the CSDs of three populations of iron sulfide crystals, including bacterial (BCM) greigite and greigite from two rock specimens (Fig. 2). The CSD of bacterial greigite shows an almost perfect bell-shaped or normal distribution (Fig. 2a), in contrast to CSDs of BCM magnetite crystals that are asymmetric (DEVOUARD et al., 1998). The CSD of greigite from the Laki sample (Fig. 2b) is similar to that of bacterial greigite; however, the maximum of the curve is at 120 nm, indicating that greigite crystals in this rock are about twice as large as those from the MMP. The CSD for the Mihalovce sample differs significantly from both the bacterial and the Laki greigite CSDs: it has an asymmetric "tail" extending to large crystal sizes, and a maximum of the frequency at 400 nm (Fig. 2c).

The CSD for the Mihalovce sample can result from surface-controlled growth in an open system (EBERL et al., 1998), and both the CSD and the peak value are consistent with a framboidal (BIM) origin (WILKIN et al., 1998). On the other hand, the CSD and typical contrast features of greigite crystals in the Laki sample make it very likely that these grains are of BCM origin, even though they are larger than greigite crystals produced by contemporary magnetotactic bacteria.

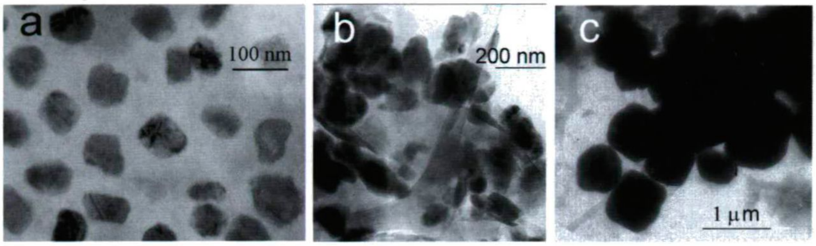

Figure 1. Bright-field electron micrographs of clusters of greigite crystals from (a) a multicellular magnetotactic prokaryote (MMP), and from rock specimens from (b) Laki, and (c) Mihalovce. Note that in (a) and (b) greigite crystals show uneven, spotty contrast in the TEM, whereas in (c) the rounded and relatively thick crystals produce uniform and dark contrast.

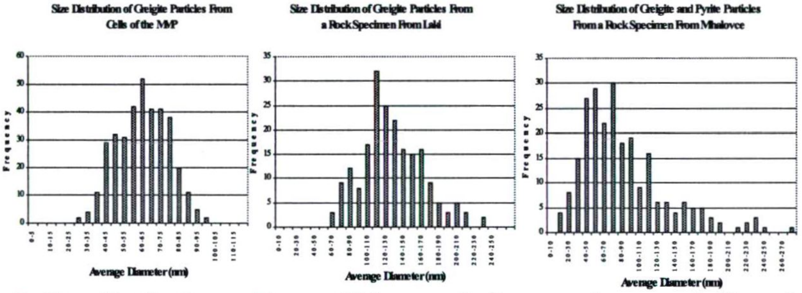

Figure 2. Size distributions of iron sulfide crystals from specimens as indicated on top of the figures

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This study was financially supported by Hungarian Scientific Research Fund (OTKA) project No. T029805 and a grant from the Hungarian Academy of Sciences (AKP #98-94 2.5).