



## **Biomineralization of greigite and pyrrhotite in gas hydrate-bearing marine sediments; results from ODP Leg 204 (southern Hydrate Ridge)**

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We present a mineral magnetic study of gas hydrate-bearing marine sediments drilled at southern Hydrate Ridge (SHR) during ODP Leg 204 (Cascadia Margin, offshore Oregon). We used hysteresis results, FORC analyses, and SEM observations to characterize the magnetic mineralogy of a set of 33 representative samples. A comparison of these results with bulk magnetic properties of the same samples allowed us to use IRM/k ratios of 560 additional samples to screen the studied sediments for the presence of greigite and pyrrhotite. Our results indicate that these two minerals are formed authigenically as a result of microbial activity at variable depths within the gas hydrate stability zone (GHSZ). Greigite occurs both in shallow (<10 m) and deep (between 20 mbsf and the base of the GHSZ) sediments (at Sites 1244 to 1250, and 1252), whereas pyrrhotite is found only in deep sediments (at Sites 1244, 1245, and 1248 to 1250). Authigenic greigite is produced in shallow sediments during early diagenetic degradation of organic matter (in low methane flux settings) and during anaerobic oxidation of methane (in high methane flux settings). Authigenic greigite and pyrrhotite in deep sediments appear always growing over iron-bearing minerals such as detrital sheet silicates, pyrite and siderite. This suggests that greigite and pyrrhotite formed by the interaction of dissolved sulphide with highly reactive iron on the surface of iron-bearing minerals. Preferential conditions for the formation of greigite and pyrrhotite in deep sediments are the occurrence of high concentrations of methane in the vicinity

of gas hydrates. Since deep sediments are located well below the sulphidic zone ( $>10$  m), other sources of sulphide are required to form greigite and pyrrhotite. In SHR, the most likely source for this sulphide is the anoxic oxidation of pyrite. Limited amounts of sulphate released by this process are likely to react with methane. This might fuel anaerobic methane oxidation in deep sediments, in such a way that the resulting sulphide can diffuse and react with iron on the surface of iron-bearing minerals to form greigite and pyrrhotite. The results presented here bear two important implications. First, the co-occurrence of greigite and pyrrhotite might indicate the past presence gas hydrates in ancient sediments, since they can be preserved through geological time as opposed to gas hydrates, which eventually dissociate as sedimentation continues. And second, formation of authigenic greigite and pyrrhotite at different depths implies variable timed magnetizations, which are likely to compromise paleomagnetic results of greigite- and pyrrhotite bearing sediments.