Nano/microstructure of polymer-derived SiOC ceramics

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The formation of nanodomains in a carbon-rich SiOC ceramic was investigated depending on annealing temperature. The high carbon content of the pure SiCO system was achieved by utilizing divinyl benzene as an intrinsic cross-linking agent. The incorporation of carbon- and silica-rich regions within the amorphous matrix implies the questions about domain size and thermal stability of such local domains. The nanostructure of the carbon-rich material was studied in detail upon pyrolysis at 1000 °C and after additional thermal anneal at 1450 °C. High-resolution and energy-filtered TEM as well as electron energy-loss spectroscopy were employed to gain an understanding of the intrinsic micro/nanostructure of such polymer-derived ceramics. Although a progressive structural rearrangement within the SiOC matrix was confirmed with increasing temperature, the sample heat treated at 1450 °C remained predominantly amorphous. Based on the experimental observations, a structural model is presented, which is consistent with the high-temperature mechanical response.

Fe-Ni-O-S phase relations during serpentinization (MAR 15°N)

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The strongly reduced nature of the vent fluids in ultramafic-hosted hydrothermal systems is due to the production of hydrogen by hydrolysis of ferrous iron in the host rock. The specific fluid-rock reactions and phase relations involved, however, are incompletely understood. To further our understanding of hydrogen production during serpentinization, we investigate the composition and phase relations of oxides, sulfides, native metals, hydrous silicates, and hydroxides in serpentinites. These phases are not only indicative of redox conditions, temperature and fluid flux during serpentinization, some of them are also important surface catalysts for organic synthesis reactions.

On thin section scale, opaque phases, except for Cr-spinel, are generally not randomly distributed. They are developed either in mesh rims or associated with serpentine and serpentine-magnetite veins. Primary opaque phases are Cr-spinel (Cr# ca. 0.5) and cobaltian pentlandite. While Cr-spinel shows only incipient alteration to magnetite, pentlandite is invariably desulfurized and altered to secondary Fe and Ni phases. The phase relations change systematically with increasing extent of serpentinization. In samples where relict olivine is present, pentlandite is replaced by an iron-nickel metal alloy, awaruite (Ni_3Fe), and/or heazlewoodite (Ni_3S_2) along with magnetite indicating very low oxygen and sulfur fugacities. In contrast, millerite is the dominant Ni-sulfide in completely serpentinized rocks. It is usually accompanied by pyrite(+/- polydymite), and the assemblage represents increased oxygen and sulfur fugacities, which develop when the reducing capacity of the rock is exhausted. These observations indicate that phase relations in the system Fe-Ni-O-S are sensitive indicators of the evolution of hydrogen and sulfur fugacity during serpentinization, as predicted by Frost (1985). Using geochemical modeling and concentration-fugacity relations, we were able to compare our observations with H_2S and H_2 concentrations determined in vent fluids from ultramafic-hosted systems. In the Rainbow and Logatchev field, those are consistent with metastable equilibria between pentlandite, awaruite, heazlewoodite and magnetite. Our calculations for the Lost City field yielded similar results, despite apparent environmental differences between these systems.

The abundance of talc in rocks with pyrite-millerite+/- polydymite assemblages indicate that high activities of aqueous silica and increased sulfur and oxygen fugacities are related. These relationships are explored in a companion paper presented in session S92.

Reference

Frost B. R. (1985), *J. Petrol.* **26**, 31–36.