A thermodynamic and mass transfer analysis of organic/inorganic interactions during thermochemical sulfate reduction in carbonate reservoirs

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Thermochemical sulfate reduction (TSR) occurs in deep carbonate reservoirs at temperatures ranging between 100 and 180°C [1]. TSR involves the reaction of aqueous sulfate with hydrocarbons, which produces hydrogen sulfide (H_2S), organic sulfur compounds, elemental sulfur, carbon dioxide (CO_2), pyrobitumen, and other oxidized species of carbon [1, 2]. Water (H_2O) may be a reactant or product of TSR, depending on the H/C ratio of the reacting hydrocarbon phase.

Although the overall TSR process is irreversible under sedimentary basin conditions, many of the reactions involved in this process appear to proceed at or near equilibrium. For example, gas-phase concentrations of methanethiol (CH_3SH) in carbonate reservoirs from the Sichuan Basin [3] are consistent with metastable equilibrium involving CO_2 and H_2S at redox conditions close to the pyrite-pyrrhotite-magnetite buffer. These redox conditions are also consistent with the organic sulfur content of crude oils, which increases with increasing H_2S content of the gas phase. In contrast, the anhydrite-calcite-sulfur assemblage cannot be stable under these conditions in the presence of an aqueous phase. Accordingly, anhydrite should dissolve irreversibly unless protected by secondary calcite [4].

Based on these observations, mass transfer calculations have been carried out at 150°C and 500 bar to quantify the relative importances of anhydrite dissolution, hydrocarbon destruction, CO_2 and H_2S generation, petroleum sulfurization, and calcite, sulfur and pyrobitumen precipitation during thermochemical sulfate reduction.

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Coexistence of abyssal and ultra–depleted SSZ type mantle peridotites from the Muğla area, SW Turkey

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Mantle peridotites of the Muğla area, south-western Turkey are classified as cpx-harzburgite, depleted harzburgite, and dunite, on the basis of their modal mineralogy, geochemical features, and mineral chemistry. Cpx-harzburgites are characterized by their higher average CaO (2.27 wt.%; $\sigma = 0.22$), Al_2O_3 (2.07 wt.%; $\sigma = 0.18$), REE (53 ppb; $\sigma = 13.3$), and initial Os isotopic composition (0.12715; $\sigma = 0.0021$), and contain Al-rich pyroxene with lower Cr content of coexisting spinel (Cr# = 17.7; $\sigma = 1.98$). In contrast, depleted harzburgites and dunites are represented with their lower average CaO (0.58 wt.%; $\sigma = 0.29$), Al_2O_3 (0.42 wt.%; $\sigma = 0.20$), REE (1.24 ppb; $\sigma = 2.9$), and initial Os isotopic composition (0.12113; $\sigma = 0.0072$), and contain Al-poor pyroxene with higher Cr content of coexisting spinel (Cr# = 57.4; $\sigma = 6.50$). Mineral chemistries and whole-rock geochemistry indicate that the depleted harzburgites and dunites experienced higher degree partial melting than those of cpx-harzburgite, which is consistent to be the residua of extraction of MORB type melt (5-15% partial melting) during the sea-floor spreading. Calculated low temperature of equilibration, positive correlation between the Cr# of spinel and oxygen fugacity values, and LREE enrichment against their ultra-depleted nature of harzburgites and dunites, support the idea that cpx-harzburgites have subsequently been modified in a suprasubduction environment by percolation with boninitic melt, produced from high degree partial melting (up to ~35%) of already depleted cpx-harzburgite. Dunites around the chromite deposits are considered to be the product of melt-peridotite interaction.