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Sulfur isotopes constraints and thermodynamic modelling of Mendez Gwen (MAR) chimney mineralization

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The Menez Gwen hydrothermal field (37º50,8'N, 31º31,8'W) lies on a volcanic segment (KP-5) of the Mid-Atlantic Ridge, near the Azores, at water depths of 840-870 m. It covers 200m^2 where both diffuse and focused venting are observed, releasing fluids with temperatures up to 281ºC. Chimneys are mainly composed of anhydrite, showing minor sulfide mineralization. This study uses thermodynamic models to simulate mineral precipitation and predict S isotope fractionation during formation of a Menez Gwen chimney. Detailed optical-microscope and SEM investigation reveal that the chimney is composed mostly of chalcopyrite-pyrite in the inner walls and silica-barite-sphalerite-galena in the outer parts. Thermodynamic modelling of hydrothermal fluids/seawater interactions, using compositions and temperature from the MARHYS database (Diehl et al. 2020) both for hydrothermal fluids and seawater, allowed reconstruction of the mineral precipitation process across chimneys. The simulations revealed a sequence of mineral precipitation along with increasing mixing processes of seawater/fluid (1/1000 to 4/1 and T: 400 to 50 °C): anhydrite (~390°C, disappeared at ~220 °C) - chalcopyrite (~370°C, disappeared at ~260 °C) - pyrite (~370°C) - quartz (~290°C) - sphalerite (~270°C) - bornite (~260°C) -galena (~220°C) - barite (~90°C). These results are consistent with the mineralogy observed from the inner to outer walls of the chimneys. Modeling results also showed that as compared to the inner walls, outer walls were formed at lower temperatures and higher f_{O2} and sulfate/sulfide ratios. In-situ S isotopes composition (determined by LA-MC-ICPMS) of pyrite and chalcopyrite pairs along the chimney, revealed that $\delta^{34}S$ values increases from the outer to the inner walls (pyrite: 1.7‰ to 3.5‰; chalcopyrite: 0.86‰ to 3.0‰). Such variation is possibly caused by 1) input of lighter S isotopes to sulfides of outer wall by higher extent of equilibrium fractionation between sulfide and sulfate at lower T and higher f_{O2} and/or contribution of biogenic H_2S from seawater, 2) rapid and quantitative reduction of seawater sulfate to sulfide in the inner conduit. These results will be discussed in light of the fluid evolution processes and $\delta^{34}S$ behavior along the chimney growth.

(335/350 words)