Sulfide assemblages in the alkaline silicate rocks and associated carbonatites of the Kaiserstuhl volcanic complex, SW Germany

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The Miocene Kaiserstuhl volcanic complex is situated in the Upper Rhine Graben in southwest Germany and consists of a variety of alkaline silicate rocks, carbonatites and ultramafic diatremes. The main sulfide assemblage in carbonatites consists of pyrrhotite, chalcopyrite, pyrite and galena with minor amounts of sphalerite, alabandite, pentlandite and cubanite. Sulfide formation in the carbonatites can be subdivided in three distinct phases: (1) early formation of an immiscible sulfide melt, now present as pyrrhotite I and chalcopyrite aggregates, (2) magmatic crystallisation of pyrrhotite II, galena and sphalerite and (3) hydrothermal alteration which redeposits and overgrows sulfide assemblages (1) and (2) forming substantial amounts of pyrite. In silicate rocks, stage (1) and (2) formation of pyrrhotite and chalcopyrite is similar to the carbonatites, while magmatic formation of galena and sphalerite was not observed. Stage (3) hydrothermal processes are analogous to the carbonatite rocks.

There is an indication of redistribution of metals during emplacement of the complex, as chalcophile elements like Ni seem to migrate from ultramafic rocks into carbonatitic melts resulting in relatively Ni-rich pyrrhotite and pyrite in such samples. Likewise, variable redistribution processes during subsequent cooling and hydrothermal overprint are evident: For example, the trace element composition of pyrite (e.g., Co and Bi content) allows for distinguishing several populations, probably related to precursor sulfide (e.g., pyrrhotite, galena) replacement.

We compare these findings to variably evolved alkaline and peralkaline rocks from Greenland, Morocco, and Canada, which have a very similar sulfide inventory with distinctively different minor and trace element contents though. Elevated contents of Ni and Co were observed together with mafic and ultramafic rocks, while sulfides in the highly evolved peralkaline rocks only contain very small amounts of minor elements. Further, pyrrhotite \((\text{Fe}_{1-x}\text{S})\) stoichiometry in some of these rocks seems to be connected to oxygen fugacity and approaches stoichiometric \(\text{FeS}\) (troilite) in some of the most reduced rocks. This observation will be further elaborated by comparing these data with new results from the highly oxidized rocks of the Kaiserstuhl complex.