



Internally consistent database for oxygen isotope fractionation in minerals: theory and application to high-pressure metamorphic rocks (Sesia Zone, Italy)

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Stable isotopes are important tools for a wide range of applications in Earth sciences as the oxygen isotopic signature of minerals records the physical and chemical conditions of equilibration. Oxygen isotope fractionation between minerals has often been used for thermometry, but also to investigate samples that experienced fluid-rock interactions. The petrological interpretation of oxygen isotope data requires the knowledge of equilibrium fractionation between two phases and its evolution with temperature. A few well-documented compilations of fractionation factors are available in the literature, but they are either restricted to small chemical systems or based on different methods making the data not consistent with each other. In this study, we report the first internally consistent database for oxygen fractionation that includes fractionation factors for most major and accessory phases and a pure H₂O fluid phase. This database has been derived simultaneously using a least square regression technique based on a large dataset of experimental, theoretical and natural data from the literature. All the constraints for a given phase contributed to the refinement of its fractionation properties making the final database internally consistent.

This database can be applied in a general thermodynamic framework to model the evolution of $\delta^{18}\text{O}$ in minerals through their metamorphic history. For a given a bulk rock composition, the mineral assemblage, modes and compositions can be predicted along any P-T path using Gibbs free energy minimizations. If the $\delta^{18}\text{O}$ of one phase or phase zone is known, it is possible to recalculate the $\delta^{18}\text{O}$ of the other phases of the equilibrium assemblage as well as the bulk $\delta^{18}\text{O}$. In situ oxygen isotopes analysis performed by ion microprobe allows the isotopic composition of mineral zones to be resolved and to be related to mineral textures reconcilable with typical growth zoning, but also resorption, replacement or any other fluid-driven process.

This strategy was applied to investigate metamorphic and metasomatic evolution of high-pressure (HP) rocks from the Sesia Zone in the Western Alps. This succession of accreted continental fragments consists of poly-metamorphic and mono-metamorphic lithologies such as metagranitoids, metasediments, and mafic and felsic boudins, that record different pre-Alpine histories and different P-T-t path during Alpine orogenic cycle. Several lines of evidence support the presence of fluid at HP and the modelling of its $\delta^{18}\text{O}$ is critical to reconstruct fluid sources and pathways through the crust during subduction. Different metasediments from the Eclogitic Micaschist Complex, contain relics of pre-Alpine garnet that shows systematically higher $\delta^{18}\text{O}$ values with respect to Alpine rims. However, fluid replacement textures do not necessarily imply a change in $\delta^{18}\text{O}$ values, as observed in garnet from the Ivozio mafic complex. This suggests that the metasediments experienced significant input of external fluids changing the $\delta^{18}\text{O}$ bulk composition between the Permian high temperature stage and the HP evolution, while the fluid-related textures in Ivozio must be related to no change in fluid isotopic composition.