

## The stability of carbonate melt in eclogite rocks with respect to oxygen fugacity

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The redox relationship between carbon and iron species in eclogitic rocks is important for the earth's internal carbon cycle and the formation of diamond. Using a sliding Fe-Fe redox sensor the oxygen fugacity at which carbonate melts are reduced to either graphite or diamond was measured in eclogitic rock compositions. Multianvil experiments were performed between 3 and 6 GPa and temperatures between 1000-1300°C. The oxygen fugacity corresponding to the equilibrium between graphite/diamond and carbonate melt was determined. Oxygen fugacities normalized to the FMQ buffer were found to decrease with temperature, most likely as a result of dilution of the carbonate liquid with silicate as temperatures increase. In contrast to previous arguments, the carbonate melt stability field was found to extend to lower oxygen fugacity in eclogitic rocks compared to peridotite rocks.

The same set of carbonated eclogite experiments also contained monomineralic layers of clinopyroxene and garnet that allowed the ferric Fe contents of these minerals to be measured using Mössbauer spectroscopy. A relatively simple model was derived for determining the oxygen fugacity of eclogitic rocks from the compositions of garnet and clinopyroxene coupled with determinations of the garnet ferric Fe content. The model was able to reproduce the experimental data to within 0.5 log units. The equilibrium was used to estimate the oxygen fugacity of eclogitic xenoliths from the Siberian and Kaapvaal cratons. These rocks were found to record ranges of oxygen fugacity that are very similar to those recorded by peridotite xenoliths from the same localities. By assuming a typical bulk ferric Fe content of oceanic crust, we calculate that subducting eclogitic rocks would remain in the carbonate stability field until depths of at least 300 km. Ferric iron contents of cratonic eclogites appear to be lower than would be expected if they are sections of subducted oceanic crust.

## Rate dependence of <sup>44</sup>Ca/<sup>40</sup>Ca fractionation during inorganic aragonite precipitation from seawater

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In order to examine the relationship of Ca isotope fractionation and precipitation rate for inorganic aragonite formation a set of lab experiments were conducted. Therefore the CO<sub>2</sub> diffusion rate technique was applied (1) using natural seawater (sw). The range of precipitation rates (R = 40-4700 μmol·h<sup>-1</sup>) was achieved using different initial carbonate ion concentrations (130-1080 μmol/kg sw) at temperatures of 15, 25 and 30°C.

We measured δ<sup>44/40</sup>Ca of sw and the inorganic aragonite on a TIMS (TRITON, ThermoFisher) using the <sup>43</sup>Ca/<sup>48</sup>Ca double spike method (2). In accordance with results for inorganic aragonite in diluted aqueous solutions (3) our data show that <sup>44</sup>Ca/<sup>40</sup>Ca fractionation in aragonite is positively correlated to precipitation rates. Thus no significant difference in <sup>44</sup>Ca/<sup>40</sup>Ca fractionation due to different salinities is observed.

The impact of precipitation rate on Ca isotope fractionation during aragonite formation is similar to observations in calcite by (4), but opposite to experimental studies and modelling results for calcite by (5) (6). Possible mechanisms for the discrepant behaviour of Ca isotope fractionation in calcite and in aragonite are discussed.

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