X-ray study of high pressure induced densification of lithium disilicate glass

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Lithium disilicate glass ($Li_2O.2SiO_2$) is a very interesting vitreous material, because, besides several important technological applications (e.g. biomaterial to produce prostheses and implants), shows a large difference between the Tg and Tc values. This is important for the investigation of the crystallization mechanism on vitreous phases, as it allows the independent study of the nucleation and growth stages. In this work, we have investigated the effect of high-pressure processing in the induction of structural changes in the amorphous phase. This can give place to polyamorphism and/or to the generation of possible seeds for a crystalline phase nucleation. Using toroidal type high-pressure chambers, glass samples were processed at 2.5 GPa, 4 GPa, 6 GPa and 7.7 GPa at room temperature. X-ray diffraction using synchrotron radiation was used to obtain the radial distribution functions in order to follow the structural changes at different ranges. Compared to a pristine sample, the main change observed for the samples processed up to 6 GPa was associated to the distortion of the SiO4 tetrahedra, as already observed in the literature. However, for the sample processed at 7.7 GPa, we have identified a drastic change in the RDF, which points for the production of a different amorphous phase with a local structure closer to that observed for the Li_2SiO_3 crystalline phase.

The ^{15}N and ^{18}O isotopic signature of abiotic reduction of nitrite by iron

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Evidence is mounting for the importance of interactions between reactive intermediates of multiple elemental cycles. For example, while previous studies have shown that oxidation of Fe(II) by nitrate (NO_3^-) and nitrite (NO_2^-) – a reactive intermediate of both reductive and oxidative N cycling processes - the controls on these reactions in the environment are poorly understood. Moreover, the N product of abiotic, anaerobic NO_2^- reduction by Fe(II) can include nitrous oxide, nitric oxide, ammonium or dinitrogen gas – yeilding a myriad of implications for the fate of N across all types of ecosystems. Furthermore, we posit that these types of reactions may represent an important control on the dual NO_3^- and NO_2^- isotopic composition in Fe-rich, reducing environments low in organic carbon (e.g., aquifers). To date, however, the kinetic isotope effects of these processes remain uncharacterized.

Here we present the first investigation of the dual isotope systematics of abiotic NO_2^- reduction by Fe(II) under a variety of environmentally relevant pH values and reactant concentrations. In our experiments, we observe a rapid decrease in NO_2^- postively correlated with Fe(II) concentrations, followed by a second phase of slower NO_2^- reduction, possibly implying the involvement of secondary Fe(II)/Fe(III) mineral phases. Samples were collected for NO_2^- N and O stable isotope analyses in order to determine the isotope effects associated with abiotic NO_2^- reduction by Fe(II). As many studies suggest a potential for anaerobic, abiotic nitrogen transformations coupled with iron cycling, the N and O isotope effects determined here will be helpful for using dual isotopes of nitrite (and nitrate) to decipher the biogeochemical fate of N in host of important environments including soils, sediments, wastewater treatment plants and aquifers.

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