

Argon and water diffusion in water-poor silicate glasses

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Knowledge on volatile diffusion is crucial for understanding the degassing behaviour of silicate melts as well as for understanding corrosion of glasses. H₂O is commonly the most abundant volatile in magmatic systems but it plays an important role in glass manufacturing as well. Argon diffusion is of particular interest because the diffusivity of argon is similar to that of molecular CO₂. Comparison of argon and water diffusion gives insights into the diffusion mechanisms of volatiles in general. At low concentrations H₂O dissolves as OH groups in silicate melts/glasses while argon acts as an inert species.

Here we report new experimental studies on Ar and H₂O diffusion in silicate and aluminosilicate glasses. The major objective of the work was to evaluate compositional effects on diffusion. Experiments were performed in cold seal gas pressure vessel using argon as the pressure medium. Polished glass wafers of water-poor, air-melted glasses (typical size 4 x 3 x 2 mm) were wrapped into Au foil so that the samples were directly exposed to the pressure medium. Water is usually present as impurity in the gas at per mill concentration. Thus during the experiment both H₂O and Ar diffuse into the samples. After the experiment, a section was cut perpendicular to the polished surface. Ar profiles were measured on the polished section by electron microprobe, H₂O profiles were analyzed using IR microspectroscopy. Surface concentrations in aluminosilicate glass are typically 0.13 -0.20 wt% Ar and 0.1 - 0.2 wt% H₂O at 200 MPa. Ar profiles are always described well with an error function while some of the H₂O profiles show a slightly convex shape. Deviation from ideal diffusion profiles in case of H₂O may be due to temporary changes in water content in the pressure medium and/or to increasing water diffusivity with increasing water content.

In silica glasses Ar diffusivity (D_{Ar} in m²/s) decreases by a factor of 1.5 from water-rich Suprasil (450 ppmwt H₂O) to water-poor Infrasil (<10 ppmwt% H₂O) emphasizing the role of dissolved water on noble gas diffusion. In alkali aluminosilicate glasses Ar diffusion is typically faster than in silica glass, but the diffusivity depends strongly on Al/(Na + K) ratio (ASI). For example at 705°C, 200 MPa log D_{Ar} increases from -14.1 for ASI=0.5 over -13.5 for ASI=1.0 to -13.1 for ASI=1.5. Incorporation of alkaline earth elements in aluminosilicate glasses reduces strongly the mobility of argon. At 620°C, 200 MPa D_{Ar} is two orders of magnitude slower in an Ca,Mg bearing aluminosilicate (andesite) than in a pure alkali aluminosilicate (rhyolite). Water diffusion in alkali aluminosilicate glasses is one order of magnitude slower than argon diffusion at 500°C but due to lower activation energy only 0.2 log units slower at 800°C.

Fractionation between inorganic and organic carbon during the Lomagundi carbon isotope excursion

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The Lomagundi (2.22-2.1 Ga) positive carbon isotope excursion in seawater composition was argued to cause or be associated with the rise in atmospheric oxygen. The subsequent studies have shown that the former was preceded by the latter. The amount of oxygen released to the exosphere during the Lomagundi excursion depended on fractionation between inorganic and organic carbon, which is poorly known. Since seawater dissolved inorganic and organic carbon reservoirs were arguably larger at the time of lower solar luminosity and redox state of the exosphere, decoupling between these two variables might be expected.

We studied carbon isotope composition of carbonates and organic matter in carbonates and shales of the Silverton Formation, South Africa and the correlative Sengoma Argillite Formation just across the border in Botswana. These units were deposited along the margin of the Kaapvaal Craton in open-marine deltaic settings and experienced lower greenschist facies metamorphism. Their age is bracketed by the underlying 2.22 Ga volcanics and the intrusive contact with the 2.06 Ga Bushveld Complex. The pro-delta to offshore marine shales are overlain by the subtidal carbonate sequence. Carbonates are ¹³C-enriched with $\delta^{13}C$ values ranging between 8.3 and 11.2‰ consistent with their deposition during the Lomagundi excursion. Their total organic carbon (TOC) content ranges from 0.01 to 0.6% and $\delta^{13}C$ values are from -24.8 to -13.9‰. Thus, fractionation between organic and carbonate carbon was 30.3±2.8‰ (n=31) in the shallow-marine environment. The underlying shales have highly variable TOC content (0.14 to 21.94%) and $\delta^{13}C$ values (-33.7 to -20.8‰) with the average of -26.9±3.0‰ (n=48). Considering that the shales were deposited during the Lomagundi excursion and taking $\delta^{13}C$ values of the overlying carbonates as representative of dissolved inorganic carbon during shale deposition, fractionations as large as ~45‰ were in the deeper part of the Pretoria Basin during the Silverton time. These enhanced fractionations with respect to the shallow-water environments might reflect methane recycling or sulfide oxidation at the redoxcline, whereas euxinic conditions were indeed inferred for these shales based on independent evidence.