American Mineralogist, Volume 94, pages 600–608, 2009

Effective radii of noble gas atoms in silicates from first-principles molecular simulation

Liqun Zhang,[1,2] James A. Van Orman,[1,*] and Daniel J. Lacks[2]

[1]Department of Geological Sciences, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.
[2]Department of Chemical Engineering, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

Abstract

An understanding of how noble gas atoms are dissolved in mantle minerals and melts is necessary to infer geological information from the constraints provided by noble gas geochemistry. For this purpose, first-principles molecular simulations are carried out on liquid and crystalline (stishovite) silica systems with dissolved noble gas atoms (He, Ne, Ar, Kr, and Xe). The first principles nature of the simulations, which do not involve empirical force field parameters, enables the determination of the effective radii and structural environments of the noble gas atoms. The noble gas atoms are shown to be highly compressible, so that their effective radii depend strongly on the molar volume of the system (which in turn depends on pressure). Due to the continuous nature of interatomic forces, the effective radii also depend on the extent to which the surrounding atoms can relax in response to the presence of the noble gas atom. In this regard, different definitions of effective radii are relevant in different situations: "equilibrium radii" that correspond to the optimal interatomic distances at the molar volume of the system, and "repulsive wall" radii that correspond to the interatomic distances where the interatomic potentials of mean force change from attractive to repulsive at that molar volume. The equilibrium radii determine the interatomic distances in a melt, and the repulsive wall radii determine the interatomic distances for interstitial sites in a crystal. Based on these effective radii, the structural environment surrounding the noble gas atoms at high pressure is shown to correspond to a close packing of O atoms around the central noble gas atom. Compression of the noble gas atoms is shown to correspond closely to the compression of the porosity within the silicate melt structure.

Keywords: Silicate melt, ionic radius, molecular dynamics simulation, density functional theory