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Noble gas solubility in $MgSiO_3$ perovskite and the terrestrial noble gas signature

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The atmospheres of Earth and Mars are strongly depleted in xenon relative to argon and krypton if compared to a “chondritic” noble gas pattern. This depletion cannot result from hydrodynamic escape alone, which would affect argon and krypton more than the heavier xenon. Despite a number of attempts to find the “missing” xenon somewhere in the Earth, the cause for the observed depletion is purely understood.
Numerous studies on noble gas solubility and noble gas partitioning involving upper mantle minerals demonstrated that noble gases are extremely incompatible. However, at higher pressure the behavior of noble gases could be different. We have therefore considered $MgSiO_3$ perovskite, the main constituent of the lower mantle as a potential reservoir of noble gases and studied the solubility of Ar, Kr and Xe in perovskite.
In order to synthesize Ar, Kr and Xe-saturated $MgSiO_3$-perovskites, glasses with variable Si/Mg ratio and Al content were loaded together with 40–80 bars of noble gases into platinum capsules and were converted first to denser crystalline phases (enstatite or ringwoodite + stishovite) in a 1200t multianvil press at 1200°C and 10-18 GPa. Recovered capsules were re-run without opening in a 5000t multianvil press at 1600-1800°C and 23-24 GPa for 1h. Numerous empty cavities indicating saturation of the samples with Ar, Kr or Xe were observed in the respective run products.
The Ar content of perovskites was measured by electron microprobe. No Ar was found (detection limit 120-150 wt.ppm) in all stoichiometric perovskites (Si/Mg=1) or in other high-pressure minerals (e.g. ringwoodite, akimotoite, stishovite, periclase, majorite). Electron microprobe analyses of recovered non-stoichiometric perovskites (Si/Mg<1) show that 0.1-1.1 wt.% of Ar is dissolved in perovskite.
Kr and Xe content of perovskites was measured by LA-ICP-MS (limit of detection 17-43wt.ppm for Kr and 3-5wt.ppm for Xe). Up to 0.3 wt.% of Kr was found in perovskite. Xenon solubility in perovskite, however, is an order of magnitude lower (300wt.ppm Xe) than that of Ar and Kr.
Scanning and transmission electron microscopy observations of the perovskite samples did not reveal any impurities or foreign phases, such as gas bubbles, that may account for the observed noble gas contents. We therefore conclude that the argon and krypton must enter the crystal lattice of the perovskite. It is consistent with preliminary single-crystal X-ray diffraction data. Some extra reflections in the X-ray diffraction pattern of Ar-bearing perovskite as well as systematic differences in reflection intensity and broadening of the reflections relative to Ar-free perovskite indicate internal strain caused by argon incorporation. Moreover, in some samples, high argon contents appear to correlate with low Si/Mg ratios. Therefore, noble gas atoms probably occupy oxygen vacancy sites in the structure, which are necessary for the reasons of charge balance and which are well documented for magnesium silicate perovskite. Thus, difference in solubilities of Ar, Kr and Xe is due to the size mismatch between noble gas atoms and the oxygen vacancies. While Ar and Kr atomic radii are relatively close to the size of an oxygen vacancy (1.26-1.4Å), xenon with an atomic radius of 1.96 Å is likely too large to fit into this site. Our K-bearing experiments, where up to 0.5 wt % Ar was found in phase X (simplified formula []KMg2Si2O7H, with [] = K vacancy) indicate that at high pressure noble gases can enter any crystal structure, containing vacancies of the appropriate size. Accordingly, the dependence of noble gas solubility on the size of the noble gas atom can be well described by a lattice strain model which predicts that helium and particularly neon should also be highly soluble in perovskite.
We therefore suggest that crystallization of $MgSiO_3$-perovskite from a magma ocean concentrated argon and krypton, but not xenon, in the lower mantle. The observed noble gas pattern of the Earth’s atmosphere probably results from a combination of hydrodynamic escape from the Hadean atmosphere and later outgassing of a lower mantle noble gas component selectively depleted in xenon.