



# New constraints on Xe incorporation mechanisms in olivine from first-principles calculations

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## Abstract

Storage of Xe at depth in silicate minerals has recently been proposed to explain the low Xe abundance in the Earth's and Mars' atmospheres compared to other noble gases (the so-called 'Missing Xenon' issue). Evidences for incorporation, and thus reactivity of Xe in olivine at high pressure and high temperature are based on variations in cell parameters and the appearance of a new Raman band. To constrain the, so far only hypothetical, Xe incorporation mechanism in olivine, we theoretically investigated models of Xe-bearing olivine using density functional theory. Three types of incorporation mechanisms are tested: Xe for Si and Xe for Mg substitutions, and interstitial Xe. Xe for Si substitution, implying an oxidation of Xe, is found to be the only mechanism consistent with experimental observations, leading to an increase of cell parameter *a* and the appearance of a new Raman band around 720–750 cm<sup>-1</sup> associated with Xe–O stretching vibrations. Raman spectroscopy makes it possible to identify Xe incorporation site, even at low Xe content, due to high Xe polarizability. An estimation of Xe content in olivine, based on present work and previous *in situ* experimental results, shows that up to 0.4 at.% Xe could be stored in olivine at depth.

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## 1. INTRODUCTION

Noble gases, highly volatile and poorly reactive elements, are of particular interest in Earth and planetary sciences to study and date the formation of the atmosphere (Avice and Marty, 2014) or to trace magmatic sources and degassing processes. Xenon, the heaviest of the noble gases,

with nine stable isotopes (<sup>124,126,128,129,130,131,132,134,136</sup>Xe), is at the heart of a long-standing question, the so-called 'Missing Xenon' issue. Elemental Xe, compared to other noble gases, is missing in the atmospheres of the Earth and Mars relative to chondritic abundances (Anders and Owen, 1977). According to Ozima and Podosek (1999), around 90% of Earth's primordial Xe is missing from the atmosphere. In addition, the atmospheres of Earth and Mars present a strong deficit in Xe light isotopes (<sup>124,126,128</sup>Xe) (Krummenacher et al., 1962 et al., 1962). Some Archean rocks present a Xe isotopic composition falling in between primitive chondritic and present-Earth

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atmospheric values, with an enrichment of the light non-radiogenic Xe isotopes relative to the present-Earth atmosphere of  $2.1 (\pm 0.3)\% \text{amu}^{-1}$  for a 3.5 Gy barite (Pujol et al., 2013), and  $1 (\pm 0.5)\% \text{amu}^{-1}$  for a 3.0 ( $\pm 0.2$ ) Gy quartz (Pujol et al., 2011). These findings indicate a storage and fractionation of Xe throughout the Archean (Avice and Marty, 2014) which could continue nowadays through subduction processes (Holland and Ballentine, 2006). Recently, a number of studies have supported storage of Xe in silicates at depth. Xe oxides have been synthesized:  $\text{XeO}_2$  at ambient pressure and temperature (Brock and Schrobilgen, 2010), and  $\text{Xe}_3\text{O}_2$  and  $\text{Xe}_2\text{O}_5$  at respectively 97 GPa and 83 GPa, and at around 2000 K (Dewaele et al., 2016); as well as a Xe-bearing perovskite (Britvin et al., 2015) at ambient pressure. Furthermore, experiments brought evidence of Xe-incorporation in  $\text{SiO}_2$  phases (Sanloup et al., 2002, 2005) and olivine (Sanloup et al., 2011) at crustal and upper mantle P-T conditions. If the presence of pure Xe oxides in the Earth is unlikely, storage in silicates as a trace element may be a significant phenomenon in Xe retention at depth. Furthermore, a granite from the Sudbury impact structure (Kuroda et al., 1977) as well as siliceous sediments (Matsubara et al., 1988; Matsuda and Matsubara, 1989) have been found to be enriched in Xe by 2–3 orders of magnitude.

A detailed understanding of incorporation mechanisms of Xe, and reliable values of Xe solubility in minerals are presently needed to quantify the role of Xe incorporation in minerals in the context of the ‘Missing Xenon’ issue at the Earth’s scale. Reliable partition coefficients are also needed to understand the fate of Xe in melting and crystallizing processes (from the magma ocean era to the current day magmatic processes). All available data on Xe-solubility in minerals are based on *ex situ* analyses of Xe-saturated samples, synthesized at high temperatures and, in some cases, at high pressures. Measured Xe solubility in olivine varies from 6.5 ppb down to 0.67 ppt (Hiyagon and Ozima, 1986; Broadhurst et al., 1992; Heber et al., 2007). Similarly, olivine melt partition coefficient varies from 90 to  $6 \cdot 10^{-4}$  (Hiyagon and Ozima, 1986; Broadhurst et al., 1992; Heber et al., 2007) and the compatibility (or not) of Xe in minerals remains controversial. In samples recovered from high pressure and temperature experiments, Xe is at least partly located in gas bubbles, and inconsistencies in Xe solubility and partition coefficient mainly stem from whether or not bubbles are analyzed, keeping in mind that their sizes range from the nm to the mm scale, and that part or all of these bubbles may form upon quenching to room conditions. Consequently, the evaluation of Xe content should be preferentially based on *in situ* measurements as proposed in the present study.

Recent experiments have focused on the incorporation mechanism of Xe in olivine, one of the most widespread terrestrial minerals. Sanloup et al. (2011) studied Xe-bearing San Carlos olivine up to 7 GPa and 2000 K by *in situ* X-ray diffraction and Raman spectroscopy reporting shifts of lattice parameters in presence of Xe at high pressure and for temperatures above Xe melting point. Cell parameter *a* increases, *c* decreases (although *c* is strongly temperature dependent) while *b* is not affected. This lattice

distortion was interpreted as potentially due to Xe incorporation on Si sites, as Si release from olivine was observed. A new Raman mode, in presence of Xe, (disappearing within few minutes after quench) was also observed at  $786 \text{cm}^{-1}$  in presence of Xe at 0.9 GPa after heating at 1800 K. This new Raman band is close to the stretching of  $\text{XeO}_4$  at  $776 \text{cm}^{-1}$  (Gerken and Schrobilgen, 2002), and is in the Si–O stretching region of olivine (Noël et al., 2006). As for other heavy rare gases, Ar was not observed to substitute to Si in olivine up to 7 GPa–2000 K (Sanloup et al., 2011). In the absence of studies devoted to the incorporation of Kr in minerals at depth, we can temporarily conclude that this mechanism is specific to Xe and of major relevance to the ‘Missing Xe’ issue.

First-principles calculations represent a powerful complementary approach to identify incorporation sites of trace elements in minerals. Regarding Xe in silicates only two theoretical studies are so far available. Probert (2010) investigated different incorporation mechanisms of Xe in  $\alpha$ -quartz, but the lack of related measurements prevents definitive conclusion. Kalinowski et al. (2014) investigated Xe incorporation in fibrous silica, which can be found on Earth in moganite or chalcodine (Hopkinson et al., 1999). Computed Raman spectra of Xe-bearing fibrous silica possibly reproduce observations for Xe-rich quartz (Sanloup et al., 2002) and  $\text{XeO}_2$  (Brock and Schrobilgen, 2011).

In the present work, we study the structure, stability and vibrational properties of different incorporation sites of Xe in olivine, by means of first-principles calculations based on density functional theory (DFT). These theoretical results are then compared to the experimental data of Sanloup et al. (2011) to infer potential mechanisms of Xe storage in Earth’s interior.

## 2. METHODS

Various systems are investigated: two reference compounds ( $\text{XeO}_4$  molecule,  $\text{Xe}_3\text{O}_2$  condensed phase); pure forsterite ( $\text{Mg}_2\text{SiO}_4$ , the Mg-rich end member of the olivine series); Xe-bearing forsterite in which one Xe atom substitutes one Si (or Mg) atom or in which one Xe atom is added at an interstitial position. In all cases, the charge of the simulation cell is neutral. Xe-bearing forsterite is simulated using supercells of various sizes:  $2 \times 1 \times 2$ ,  $4 \times 1 \times 2$ ,  $3 \times 1 \times 3$ ,  $4 \times 2 \times 4$  (with respect to the forsterite unit cell containing 28 atoms) corresponding to a concentration of approximately 0.89, 0.45, 0.40, 0.11 at.% Xe (or 5.5, 2.8, 2.5, 0.72 wt% Xe), respectively.

All calculations are done within density functional theory (DFT) and the generalized gradient approximation (GGA-PBE) of Perdew et al. (1996), by using the PWscf code of the Quantum ESPRESSO package <http://www.quantum-espresso.org/>; Giannozzi et al., 2009). Norm-conserving pseudopotentials (Troullier and Martins, 1991) are used. Electronic wave-functions (charge-density) are expanded up to an energy cut-off of 80 (480) Ry. Equilibrium structures are obtained after full relaxation of atomic positions and cell parameters (total energy is converged within 1 mRy/atom and forces to less than  $10^{-4}$  Ry/au). Electronic k-point sampling of  $\text{Xe}_3\text{O}_2$  and pure forsterite

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