Determination of the Mossbauer Isomer-Shift in High-Pressure Fe Minerals up to Earth's Core Conditions

JACQUES K DESMARAIS[1], JOHN S TSE[2], YUANMING PAN[3], SILVIA MARIA CASASSA[4]

[1]Department of Geological Sciences, University of Saskatchwan, 114 Science Place, SK S7N 5E2, Saskatoon, Saskatchwan, Canada; Dipartimento di Chimica Universita di Torino, Via Giuria 5,10125 Torino, Italy; jkd788@mail.usask.ca

[2]Department of Physics & Engineering Physics, University of Saskatchewan, 116 Science Place, SK S7N 5E2, Saskatoon, Saskatchewan, Canada; john.tse@usask.ca

[3] Department of Geological Sciences, University of Saskatchwan, 114 Science Place, SK S7N 5E2, Saskatoon, Saskatchwan, Canada; yuanming.pan@usask.ca

[4] Dipartimento di Chimica Universita di Torino, Via Giuria 5,10125 Torino, Italy;silvia.casassa@unito.it

Knowledge of the oxidation state (OS) of Fe in deep Earth minerals is key in reconstructing the redox history of the Earth. This has broad implications in terms of understanding ancient atmospheric conditions, as well as the dynamics of Earth's formation (1,2). One of the most powerful tools to determine OS in high-pressure Fe phases (HPFP) is Mossbauer spectroscopy, whereby the OS is determined through knowledge of the isomer shift (IS) (1,2). The IS is proportional to the total electron density, evaluated at the nucleus of the material in question, relative to that of body-centered-cubic (bcc) Fe. To this day the IS of HPFP up to Earth's core conditions (ECC) is largely unknown due in part to difficulties in carrying precise experiments at ECC. More generally, there are also relatively few theoretical calculations of the IS (especially in solids), because of difficulties in accurately determining the total density at the nucleus. Even in molecular systems, the theoretical calculation of the IS is highly challenging, sometimes requiring the use of huge basis-sets and/or relativistic calculations with sophisticated treatment correlation, that goes beyond conventional density functional theory (3,4). Here we determine the IS of dominant HPFP in Earth's interior (hexagonal-closed packed Fe and FeO) up to ECC through ab-initio calculations. The theoretical results are confirmed at upper mantle conditions against high-pressure Mossbauer experiments. The implications of the results are discussed in terms of Earth's formation and redox history.

[1] Gu et al., (2016) *Nature Geosciences* **9**, 723-727. [2] Frost et al, (2004) *Nature* **428**, 409-412. [3] Neese (2002) *Inorganica Chimica Acta* **337**, 181-192. [4] Hedegard et al (2014) *Phys. Chem. Chem. Phys.* ***16**, 4853-4863.*