Structural characterization of natural UO$_2$ at pressures up to 82 GPa and temperatures up to 2200 K

STEEVE GRÉAUX,$^{1,*}$ LAURENT GAUTRON,$^{1,**}$ DENIS ANDRAULT,$^{1,3}$ NATHALIE BOLFAN-CASANOVA,$^3$ NICOLAS GUIGNOT,$^{4,**}$ AND JULIEN HAINES$^5$

$^1$Laboratoire des Géomatériaux et Géologie de l’Ingénieur, Université Paris-Est Marne la Vallée, France
$^2$Institut de Minéralogie et de Physique des Milieux Condensés, Paris, France
$^3$Laboratoire Magnas et Volcans, Université Blaise Pascal, Clermont-Ferrand, France
$^4$European Synchrotron Radiation Facility, Grenoble, France
$^5$Institut Charles Gerhardt Montpellier, Université de Montpellier, Montpellier, France

ABSTRACT

Uranium is one of the main heat sources in the Earth, as about 25% of the total heat is produced by the radioactive decay of U. The location of U in the deep mantle is then essential for a better understanding of the geodynamics and thermal behavior of the Earth. For the first time, the crystal structure of natural simple dioxide UO$_2$ was determined by X-ray diffraction with synchrotron radiation (ESRF, Grenoble, France), in situ in a laser-heated diamond-anvil cell at pressures and temperatures relevant to the deep Earth’s mantle. Fluorite-type UO$_2$ displays a new sequence of phase transitions at high P and T, with a cubic modified fluorite $Pa\bar{3}$ observed at 18 GPa, and an orthorhombic $Pbc\bar{a}$ structure from 33 GPa up to 82 GPa. Using a second-order Birch-Murnaghan equation of state, we calculated room-pressure bulk modulus $K_0 = 166(7)$ GPa with pressure derivative $K'_0 = 4.0$ for the $Pa\bar{3}$ structure, and $K_0 = 225(8)$ GPa with $K'_0 = 4$ for the $Pbc\bar{a}$ structure. The expected $Pnma$ cotunnite structure was not observed but is not excluded at pressures higher than 82 GPa. Since UO$_2$ displays a $Pbc\bar{a}$ structure stable up to 82 GPa and presents a density much higher than the average density of the surrounding mantle, UO$_2$ could be a host of U in the deep lower mantle.

Keywords: Heat sources, uranium oxide, X-ray diffraction, crystal structure, deep mantle

INTRODUCTION

Uranium is one of the main radioactive heat sources of the Earth. It is estimated that about 11 TW of the 44 TW heat flux measured at the Earth’s surface, is generated by radioactive decay of U$^{235}$ and U$^{238}$ (Hellfrich and Wood 2001; Turcotte et al. 2001). Uranium is expected to be mainly present in the Earth’s mantle (Turcotte et al. 2001); therefore about 9 TW is assumed to be produced by U in the mantle, with the main part (65%, about 6 TW) generated in the lower mantle. Turcotte et al. (2001) estimated that about 60 000 to 75 000 thousand million tons of U could be stored in the lower mantle.

The analysis of mid-ocean ridge basalts (MORB) revealed that the upper mantle is depleted in radiogenic elements, and produces only about 2–6 TW. Matching the observed heat flux at the Earth’s surface, would then require a deep extra heat source (Kellogg et al. 1999). Such primitive material could be present in small domains (<10 km) throughout the lower mantle (Albarède 2005) or in a compositionally distinct layer enriched in dense and radiogenic material, at the base of the lower mantle (Kellogg et al. 1999; Van der Hilst et al. 1999), or at the bottom of large regional domes (Davaille et al. 2005). In any case, this primitive material would exchange heat but little mass with the convecting upper mantle, and it is expected to remain stable and to be poorly mixed up to the present (Samuel and Farnetani 2003).

About 55 wt% of the total U of the Earth is expected to be present in such deep reservoirs in the lower mantle (Turcotte et al. 2001), but we do not know the mineralogy of U in the P-T conditions of this region. Uranium could be incorporated in major silicate phases of the mantle or exist as large or small heterogeneities in the whole lower mantle. The location of the radiogenic elements in the Earth is a key point to constrain the thermal and dynamic behavior of our planet. The investigation of their location starts with the study of simple actinide oxides at P and T that occur in the Earth’s deep interior. In this work, we focus on U, and study the behavior of natural uraninite UO$_2$ brought to the P-T conditions of the lower mantle. We used a natural sample to better constrain the mineralogy of U within the deep Earth.

Simple oxides with an AO$_2$ composition were intensively investigated at high pressure to understand and predict the high pressure behavior of SiO$_2$ polymorphs, and because of their interesting properties in material science. It is common to classify the AO$_2$ oxides at room P and T, in function of the