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## Uranium in the Earth's lower mantle

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[1] The distribution of the radiogenic heat sources strongly influences the geodynamics and thermal behaviour of the Earth. About 11 TW is produced by the radioactive decay of uranium (25% of the total heat flux at Earth surface), and 55% of this energy comes from the lower mantle. Here we report the first experimental evidence that aluminous CaSiO<sub>3</sub> perovskite is the major, or even the only, host of uranium in the Earth lower mantle, since such a phase is able to incorporate up to 35 wt% UO<sub>2</sub> (or 4 at% of U). The aluminous Ca-perovskite could be the main U-bearing constituent of a dense and radiogenic reservoir proposed in a recent model and located in the bottom half of the lower mantle. **Citation:** Gautron, L., S. Greaux, D. Andraut, N. Bolfan-Casanova, N. Guignot, and M. A. Bouhifd (2006), Uranium in the Earth's lower mantle, *Geophys. Res. Lett.*, 33, L23301, doi:10.1029/2006GL027508.

### 1. Introduction

[2] About 70% of the total heat flux (44 TW) at the Earth surface comes from the radioactive decay of uranium, thorium and potassium [Helffrich and Wood, 2001], with 11 TW accounting for U alone. Uranium is known to be mainly present in the mantle and it is assumed that 50 wt% of total U in the Earth is stored in the lower mantle [Turcotte *et al.*, 2001]. The location of radioactive heat sources in the Earth's mantle is a key point to constrain the thermal and dynamic behaviour of our planet. As only few data are available, question remains as to know if uranium can form separate phases or incorporate the main mineral phases present in the Earth's mantle.

[3] The behaviour of uranium at P,T conditions of the mantle, was mainly investigated through HP-HT stability of simple compounds like UO<sub>2</sub> or USiO<sub>4</sub> [Liu, 1980, 1982] and U partitioning between solid and liquid silicates [Corgne and Wood, 2002, 2004; Corgne *et al.*, 2005; Knittle, 1998; Hirose *et al.*, 2004]. However it is essential to perform solid-solid reactions at high P and T to investigate the uranium mineralogy in the Earth's mantle. And there are no such available data.

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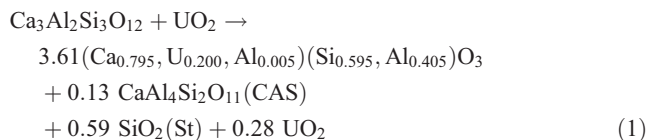
### 2. Materials and Methods

[4] With a large cationic size, calcium is a good candidate for its substitution by uranium. In the lower mantle, calcium is present in the CaSiO<sub>3</sub> perovskite which is the third important major phase (about 7 wt% or 5 mol%). To investigate the possible hosting of U by this phase, synthetic glasses of either grossular Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> or wollastonite CaSiO<sub>3</sub> composition were mixed with uraninite UO<sub>2</sub> (mix with U content up to 4.5 at%). A 1000 ton multi-anvil press (MAP) and a membrane-type laser-heated diamond anvil cell (DAC) were used to bring samples to the stability field of CaSiO<sub>3</sub> perovskite (see auxiliary material<sup>1</sup> Table S1). MAP samples were examined using Electron Probe Micro-Analysis (EPMA), Analytical Scanning Electron Microscopy (ASEM) and X-ray micro-diffraction ( $\mu$ -XRD) while DAC samples were characterized by angle dispersive X-ray diffraction using a synchrotron radiation at the European Synchrotron Radiation Facility (ESRF) (see description of methods in auxiliary material).

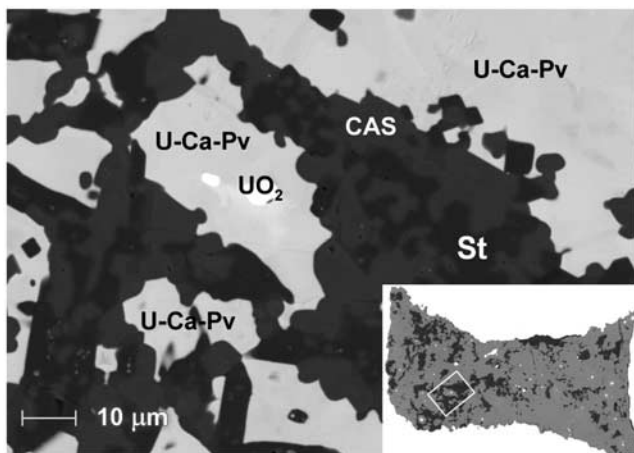
### 3. Results

[5] The major phase in MAP samples is a new U-bearing Ca-Al silicate phase with a stoichiometry CaSiO<sub>3</sub> (run MA 323, Figure 1). Both EPMA and ASEM analyses of this phase yielded a composition (wt%) as follows: CaO, 28.00; SiO<sub>2</sub>, 23.75; Al<sub>2</sub>O<sub>3</sub>, 12.65; UO<sub>2</sub>, 35.60. The incorporation of U is coupled to that of Al since no uranium enters the CaSiO<sub>3</sub> phase when no aluminium is present in the system (run MA 250). Together with the U-bearing Al-CaSiO<sub>3</sub> phase, we observed accessory phases like the CAS phase of composition CaAl<sub>4</sub>Si<sub>2</sub>O<sub>11</sub> [Gautron *et al.*, 1996, 1999] and stishovite SiO<sub>2</sub>.

[6] U<sup>4+</sup> is expected to be the dominant oxidation state for U during mantle processes [Wood *et al.*, 1999] (see auxiliary material). We expect U to enter the dodecahedral Ca site in the CaSiO<sub>3</sub> perovskite. The substitution of Ca<sup>2+</sup> by U<sup>4+</sup> can easily be charge balanced by the substitution of two Si<sup>4+</sup> by two Al<sup>3+</sup>. This is the first experimental evidence of such a substitution mechanism for the incorporation of U in a high-pressure silicate phase. This mechanism explains the major role played by Al in our samples. The reaction between grossular and uraninite UO<sub>2</sub> (sample MA-323) is the following:



<sup>1</sup>Auxiliary material data sets are available at ftp://ftp.agu.org/apend/gl/2006gl027508. Other auxiliary material files are in the HTML.



**Figure 1.** Backscattered electron image of the MA-323 sample synthesized at 18 GPa and 2000 K for 12 hours. The U-bearing Al-CaSiO<sub>3</sub> (U-Ca-Pv) is the major phase of the sample (light grey, see inset). In addition to this phase, we observe the CAS phase (CaAl<sub>4</sub>Si<sub>2</sub>O<sub>11</sub>), SiO<sub>2</sub> stishovite (St), and a small amount of UO<sub>2</sub>.

[7] According to this mechanism, Al excess could also enter the Ca site [Andraut *et al.*, 1998]. U-saturation appears to be achieved for 35 wt% of UO<sub>2</sub> (4 at% of U).

[8] All micro-diffraction spectra display six strong reflections which we explained with a tetragonal symmetry for the perovskite lattice (space group P4/mmm), with lattice parameters  $a = 3.6396(2)$  Å and  $c = 3.6536(2)$  Å, and a zero pressure volume of  $48.398 \pm 0.004$  Å<sup>3</sup> ( $V_0$  (MAP)).

[9] The crystal structure and stability field of the U-bearing Al-CaSiO<sub>3</sub> phase was also investigated by angle dispersive X-ray diffraction performed in situ in a laser-heated diamond anvil cell at the ESRF, at pressures up to 54 GPa.

[10] At 31 GPa and 2400 K, the diffraction pattern of sample DAC-02 is well explained by a mixture of Ar and a new P4/mmm tetragonally distorted Ca-perovskite (auxiliary material Figure S1). Line intensities are compatible with site occupancies derived from the chemical analysis of MAP samples. These results are perfectly compatible with MAP experiments and U-substitution-mechanism proposed in equation (1). The Ca-bearing mantle perovskite is able to host large amounts of U with limited symmetry change.

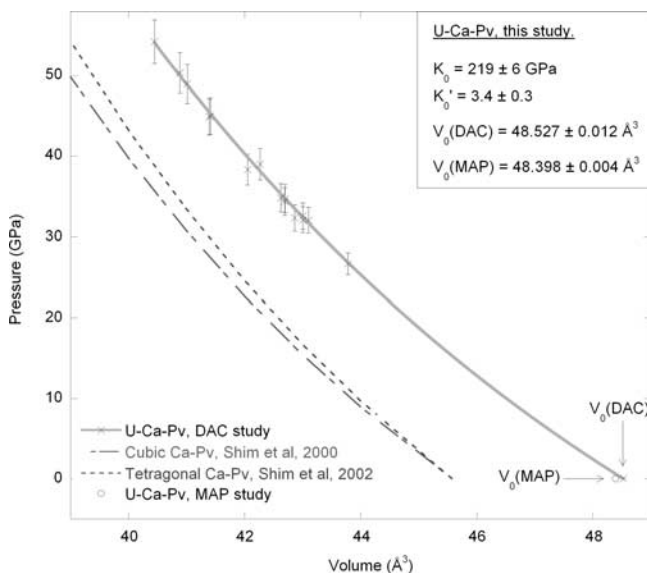
[11] Using a third order Birch-Murnaghan equation of state for the U-bearing Al-CaSiO<sub>3</sub> perovskite, we calculated room-pressure bulk modulus  $K_0 = 219 \pm 6$  GPa, with pressure derivative  $K'_0 = 3.4 \pm 0.3$ . Since the U-bearing Al-CaSiO<sub>3</sub> perovskite is stable at ambient P-T conditions, unit cell volume in standard conditions could be refined to  $V_0$  (DAC) =  $48.527 \pm 0.012$  Å<sup>3</sup> (Figure 2). It is about 7% higher than the volume of a pure CaSiO<sub>3</sub> perovskite ( $V_0 = 45.58$  Å<sup>3</sup> [Shim *et al.*, 2000]): such dilatation is probably due to the insertion of a larger Al<sup>3+</sup> cation in octahedral site compared to Si<sup>4+</sup>. This effect, together with the insertion of a smaller U<sup>4+</sup> cation compared to Ca<sup>2+</sup> in dodecahedral site, is compatible with a distorted perovskite unit cell lattice. Note the good agreement between the  $V_0$  obtained from DAC and MAP experiments, within only 0.25% difference.

It is noticeable that the U-bearing Al-CaSiO<sub>3</sub> perovskite is more compressible than any Ca-perovskite previously observed [Shim *et al.*, 2000, 2002; Yusa *et al.*, 1995]. Both a smaller cation (U) in the Ca site and a bigger cation (Al) in the Si site could contribute to make the U-Al Ca-perovskite more compressible.

#### 4. Geophysical Implications

[12] In this work we show that the U-bearing Al-CaSiO<sub>3</sub> perovskite is stable up to at least 54 GPa (Figure 2). The density of this new phase containing 35 wt% UO<sub>2</sub> is calculated to be about 25% higher than that of pure CaSiO<sub>3</sub> perovskite. The combined incorporation of uranium and aluminium in the Ca-perovskite gives even higher density and higher compressibility to this phase which is therefore likely to remain at all lower mantle depths.

[13] Our results evidence that Al is necessary for the incorporation of U in the CaSiO<sub>3</sub> perovskite. In a pyrolitic lower mantle, the CaSiO<sub>3</sub> perovskite could contain up to 1.6 wt% Al<sub>2</sub>O<sub>3</sub> [Hirose, 2002], and then we calculate that up to 4.1 wt% UO<sub>2</sub> (0.36 at% U) could be inserted in this phase, according to our results. On the other hand, in a case of a non-uniform composition of the CaSiO<sub>3</sub> perovskite throughout the lower mantle, this study demonstrates that this latter phase is able to incorporate large amounts of U. As the U content of the lower mantle is about 60,000 to 75,000 milliard tons [Turcotte *et al.*, 2001], all the uranium present in this region could be easily stored via its insertion in the Al-CaSiO<sub>3</sub> perovskite. As thorium is expected to behave similarly to uranium, aluminous CaSiO<sub>3</sub> perovskite is candidate to be the main or even the only host of radiogenic actinide heat sources in the lower mantle.



**Figure 2.** Isothermal compression curve of the U-bearing Al-CaSiO<sub>3</sub> perovskite (U-Ca-Pv), (DAC-02, see auxiliary material Table S1). The  $K_0$  and  $K'_0$  values are calculated using third order Birch-Murnaghan equation of state. The U-bearing Al-CaSiO<sub>3</sub> perovskite is 7% and 14% more compressible than cubic ( $K_0 = 236 \pm 4$  GPa [Shim *et al.*, 2000]) and tetragonal ( $K_0 = 255 \pm 5$  GPa [Shim *et al.*, 2002]) pure CaSiO<sub>3</sub> perovskite, respectively.

[14] HP-HT uranium partitioning between solid and liquid silicates showed that U is a highly incompatible element when in contact with Mg-rich silicates [Corgne and Wood, 2004; Knittle, 1998]. However, other studies [Corgne and Wood, 2002; Corgne et al., 2005; Hirose et al., 2004] revealed that U clearly partitions to the CaSiO<sub>3</sub> perovskite in presence of melts, for P-T conditions of the lower mantle. HP-HT solid-liquid reactions are performed to investigate the differentiation of the early mantle from a magma ocean. Then, one can imagine a scenario where part of Ca-perovskite could have been significantly enriched in U during its crystallization from the magma ocean. This could have led to the formation of U-rich Ca-perovskite which could display a significant density contrast with the bulk mantle, and then could have sunk towards the base of the lower mantle. Then U-rich Ca-perovskite could be present in a deep layer as proposed by Kellog et al. [1999], or in small domains (<10 km) made of primordial material still present in the mantle as proposed by Albarède [2005]. In any case, according to previous studies and ours, the incompatible behaviour of U is severely put into question.

[15] As mentioned above, a recent model of mantle convection [Kellog et al., 1999; van der Hilst and Karason, 1999; Davaille, 1999] proposes the presence of a compositionally distinct layer enriched in dense and radiogenic material, roughly at the bottom half of the lower mantle (1600 to 2900 km depth). This layer, about 4% denser than the overlying mantle, would exchange heat but little mass with the convecting upper mantle, and it is expected to remain stable and to be poorly mixed until present-day time [Samuel and Farnetani, 2003]. We believe that U can be stabilized in such a deep layer in the Al-bearing CaSiO<sub>3</sub> perovskite. U is expected to remain stable in the lowermost mantle as it is located in a very dense phase. In the case of a deep layer containing the aluminous Ca-perovskite as the main host of uranium and possibly thorium as mentioned above, this kind of bottom heating could generate about 60% of the total radioactive heat produced in the Earth's mantle.

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