# Clay minerals trap hydrogen in the Earth's crust: Evidence from the Cigar Lake uranium deposit, Athabasca

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ABSTRACT

Hydrogen ($H_2$)-rich fluids are observed in a wide variety of geologic settings including gas seeps in serpentinized ultramafic rocks, sub-seafloor hydrothermal vents, fracture networks in crystalline rocks from continental and oceanic crust, and volcanic gases. Natural hydrogen sources can sustain deep microbial ecosystems, induce abiotic hydrocarbons synthesis and trigger the formation of prebiotic organic compounds. However, due to its extreme mobility and small size, hydrogen is not easily trapped in the crust. If not rapidly consumed by redox reactions mediated by bacteria or suitable mineral catalysts it diffuses through the rocks and migrates toward the surface. Therefore, $H_2$ is not supposed to accumulate in the crust. We challenge this view by demonstrating that significant amount of $H_2$ may be adsorbed by clay minerals and remain trapped beneath the surface. Here, we report for the first time $H_2$ content in clay-rich rocks, mainly composed of illite, chlorite, and kaolinite from the Cigar Lake uranium ore deposit (northern Saskatchewan, Canada). Thermal desorption measurements reveal that $H_2$ is enriched up to 500 ppm (i.e. 0.25 $mol\,kg^{-1}$ of rock) in these water-saturated rocks having a very low total organic content (<0.5 wt%). Such hydrogen uptake is comparable and even exceeds adsorbed methane capacities reported elsewhere for pure clay minerals or shales. Sudoite (Al–Mg di-trioctahedral chlorite) is probably the main mineral responsible for $H_2$ adsorption in the present case. The presence of multiple binding sites in interlinked nanopores between crystal layers of illite-chlorite particles offers the ideal conditions for hydrogen sorption. We demonstrate that 4 to 17% of $H_2$ produced by water radiolysis over the 1.4-Ga-lifetime of the Cigar Lake uranium ore deposit has been trapped in the surrounding clay alteration haloes. As a result, sorption processes on layered silicates must not be overlooked as they may exert an important control on the fate and mobility of $H_2$ in the crust. Furthermore, the high capacity of clay minerals to sorb molecular hydrogen may also open up new opportunities for exploration of unexpected energy resources and for $H_2$ storage based on geo-inspired materials.

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## 1. Introduction

In the Earth's crust, hydrogen ($H_2$) concentration results from a complex balance between the deep mantle source input, the crustal production and consumption and the transport mechanisms of the molecule such as liquid/vapor partitioning, diffusion and advection. Besides being continuously released from the mantle, hydrogen is formed in the crust as a product of the hydration of ultramafic or peralkaline rocks (e.g. Neal and Stanger, 1983;

Charlou et al., 2002; Mayhew et al., 2013; Potter et al., 2013), by water radiolysis (Dubessy et al., 1988; Lin et al., 2005), as well as by some thermophilic bacteria (Huber et al., 1986; Hoehler et al., 2001). A portion of the produced $H_2$ is consumed either by lithospheric chemotrophes using $H_2$ for energy (Nealson et al., 2005; Sherwood Lollar et al., 2007), or by thermochemical redox reactions such as carbonate or sulfate reduction (e.g. Horita and Berndt, 1999; McCollom and Seewald, 2001; Proskurowski et al., 2008; Truche et al., 2009). The remaining is supposed to be vented in the oceans or the atmosphere. It is also possible that a large part of $H_2$ produced is retained beneath the subsurface and remains adsorbed at the surface of minerals. This potential sink or

reservoir is currently ignored in the $H_2$ budget and distribution in the crust (Cannat et al., 2010; Sherwood Lollar et al., 2014; Worman et al., 2016). Few laboratory experimental studies seem to indicate that hydrogen physisorption is feasible at the surface of clay minerals (Gil et al., 2009; Didier et al., 2012; Edge et al., 2014; Mondelli et al., 2015). However, the conditions (cryogenic temperature, dry and outgassed samples, pure synthetic swelling clays) used in these experiments are not representative of geologic settings complicating any attempts at extrapolation.

Here, we report hydrogen concentration in the mineralized area and in the clay alteration halo surrounding the Cigar Lake uranium orebody. The massive and focused presence of $UO_2$ led to pore water radiolysis and therefore to a localized $H_2$ production (Liu and Neretnieks, 1996; Bruno and Spahiu, 2014). The simple lens-shaped geometry of the deposit (2200 m long, by 25–100 m wide, by 1–20 m high) and its depth ($\sim$430 m), which precludes effects from recent weathering and erosion, provide a unique opportunity to study hydrogen behavior in sedimentary and basement rocks. Results provide clear evidence for hydrogen adsorption at the surface of clay minerals, and show that this process is far from being negligible in controlling hydrogen fate and mobility in the crust.

## 2. Geological setting

The Cigar Lake U deposit is located at the eastern rim of the Athabasca Basin (Saskatchewan province, Canada) at the unconformity between the sandstones of the Manitou Falls formation and the Aphebian metasediment basement known as the Wollaston Group (Bruneton, 1993). It is one of the many unconformity type sandstone-hosted U deposits of Proterozoic age that characterize the Athabasca Basin uranium province (Jefferson et al., 2007). The deposit was formed around 1.4–1.5 Ga ($1461 \pm 47$ Ma) ago by hydrothermal processes, but several remobilizing events occurred especially within the range 300–400 Ma (Fayek et al., 2002). The massive and extremely focused uranium mineralization is mainly uraninite and pitchblende $UO_{2+x}(s)$ with some subordinate coffinite. Total estimate reserves at Cigar Lake are 601,800 tons of ore at average U grade of 14.2 wt%, with local concentration reaching values as high as 60 wt% (Scott Bishop et al., 2016). The deposit is characterized by a series of alteration haloes geometrically arranged around the orebody, decreasing in intensity with increasing distance from the ore surface. The haloes comprise a massive clay zone of varying thickness (up to 30 m) immediately surrounding the orebody and mostly derived from the hydrothermal alteration of the sandstones, conglomerates, and basement rocks. The clay matrix directly associated with the high-grade mineralization consists of illite and sudoite (di-trioctahedral Al–Mg-chlorite) changing upward and outward to illite and kaolinite in the sandstones (Percival and Kodama, 1989; Percival et al., 1993; Billault et al., 2002). In the basement, the illite–sudoite clay alteration assemblage is superimposed to the initial metamorphic muscovite and Fe–Mg trioctahedral chlorite. The massive orebody is almost exclusively sandstone-hosted and has sharp contacts with the highly argilitized basement below. Right above the orebody, a 5 m thick ferric rich illite–hematite–siderite rim occurs.

## 3. Materials and methods

### 3.1. Petrographic, mineralogical and textural analysis

The core samples were collected during a drilling campaign carried out by Cameco Corporation in 2014. Their exact location is reported in Table 1. Rock samples were characterized by microscopic observations under reflected light and by scanning electron microscopy (SEM). Unoriented bulk powders and oriented clay aggregates were characterized by X-ray diffraction using a D8 Bruker diffractometer (Co K$\alpha$, 40 kV, 40 mA). The clay mineral fraction ($<2$ μm) was extracted from samples by application of the Stoke's law and deposited on glass slides, which were analyzed three different ways: i) oriented clay mineral fraction, ii) ethylene glycol saturated, and iii) heated at 550 °C during 4 h. Each diffractogram was measured in the 2-$\theta$ domain. Whole-rock samples were analyzed for Fe and U concentration by ICP-OES.

The specific areas of the rock samples were obtained using the BET method on a Belsorp-Max apparatus using a cross sectional area on nitrogen (0.163 nm$^2$). Solids were outgassed overnight at 150 °C down to a $3.0 \times 10^{-5}$ Pa before analysis with $N_2$ at 77 K. The presence of micropores in the sample was checked using the t-plot method. Pore size distributions were calculated following the BJH method by applying the Non-Local Density Functional Theory (NLDFT) method.

### 3.2. Thermal desorption analysis

Core samples were packed and sealed in gas tight double liner plastic-alumina bags of 3 to 5 kg immediately after being recovered at the surface. In order to make sure that no hydrogen was released during storage, the gas phase present in the bags was sampled before opening thanks to a syringe and analyzed by gas chromatography (GC). Hydrogen was never found in detectable amount ($<5$ ppmv) in these hermetic envelopes. Then, the rock samples were split in two aliquots: one was loaded without any pre-processing in a 500 mL inox Parr® flow-through autoclave for thermal desorption run and the other one was crushed ($<2$ mm, agate mortar) and dried for 48 h at 40 °C before the desorption run in order to remove free bulk water, while avoiding gas desorption. Once loaded with a known amount of sample ($\sim$250 g), the autoclave was flushed with argon to avoid oxidation in the presence of air, and heated up to 600 °C by step of 20 to 50 °C. The duration of each temperature step was $\sim$10 h, but longer steps (up to four days) were also tested to ensure the completeness of the desorption process at a given T. The autoclave was constantly flushed by argon at a flow rate of 0.1 l min$^{-1}$. The composition of the effluent gas was measured online by GC (Agilent® 490 Micro GC dual equipped with a 10 m Molecular Sieve 5A column and a 40 cm HayeSep A column) for $H_2$, He, $N_2$, $CH_4$, $CO_2$, and CO. The absolute concentration was calibrated to the area of the $H_2$, He, $CH_4$, and $CO_2$ peaks for standard gases. The estimated uncertainty in gas measurement is about 5%.

Batch thermal desorption runs were also performed (300 and 600 °C, 48 h, Ar) for comparison with the flow-through ones and bulk $H_2$ isotopic measurements. Hydrogen, recovered after these runs, was first purified in a vacuum glass line. $H_2O$, and $CO_2$ were trapped cryogenically with liquid nitrogen. Hydrogen was transferred into a special vessel with a septum using a Toepler pump. Hydrogen isotopic composition was measured by injecting 500 μL of headspace gas into a modified EA-IRMS (isotopic ratio mass spectrometry) system equipped with a 1 m Molecular Sieve 5A methane separation column in line with a GV Isoprime IRMS. Hydrogen isotopic composition was expressed as $\delta$D value with a reference to Vienna standard mean ocean water (V-SMOW):

$$\delta D\text{‰} = \left[ (D/H)_{\text{sample}} / (D/H)_{\text{standard}} - 1 \right] \times 1000 \tag{1}$$

where D is deuterium, and the standard is V-SMOW. Total error incorporating both accuracy and reproducibility is $\pm 10$‰ with respect to V-SMOW.