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Investigating native H₂ generation by alteration of Fe-rich olivine within Precambrian granitoid crust through HREM

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1 : IFPEN, France ; 2 : LFCR, Univ. Pau et Pays de l'Adour, France ; 3 : MNHN-IMPMC, Sorbonne Universités, France ; 4 : IPGP, Univ. De Paris, France ; 5 : KGS, Univ. of Kansas, USA



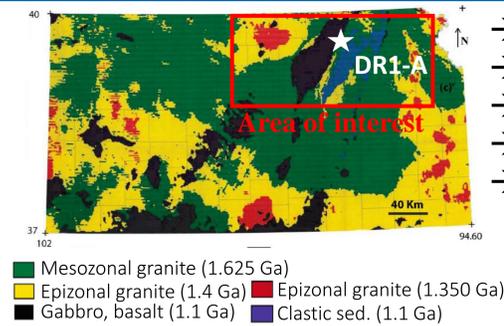
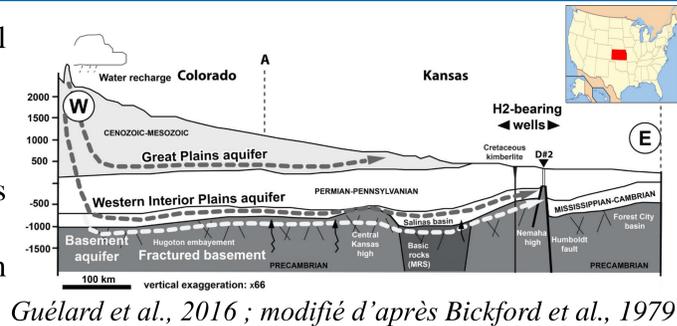
P35B – 22136 : Asteroids, Meteorites and Moons : Inner Solar System Processes II



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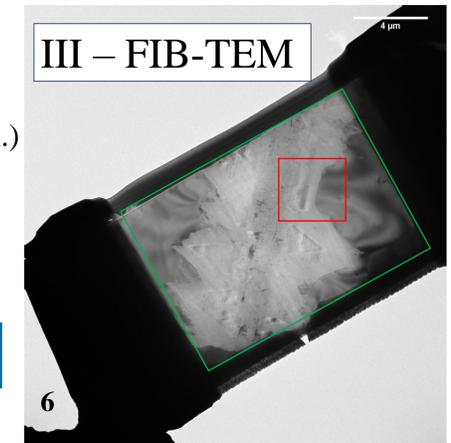
I – Context and methods

- Sample “K2” ∈ H₂-emitting DR1-A well in Kansas (USA)
 - Nemaha anticline
 - Humboldt crustal fault
- Basement = Precambrian granitoids (contains Fe-rich minerals)
- Mid-Rift System = multi-km accumulation of mafic rocks of 1.1 Ga → aborted rift



- Petrographic obs.
- XRD
- SEM-EDS (15 keV – Zeiss Gemini)
- STXM-XANES (709 keV – SOLEIL syn.)
- TEM (200 keV) on FIB section (FEG)

First hypothesis of H₂ generation:
 $2Fe^{2+}O + H_2O \rightarrow Fe_2^{3+}O_3 + H_2$

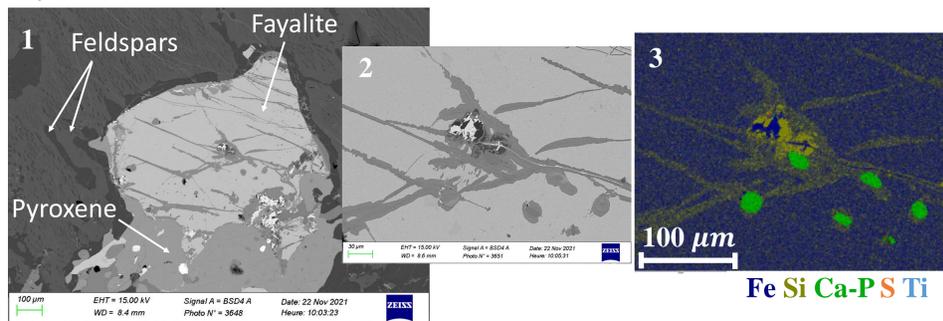


TEM images show typical chlorite and serpentine/smectite interstratified crystallization structure.

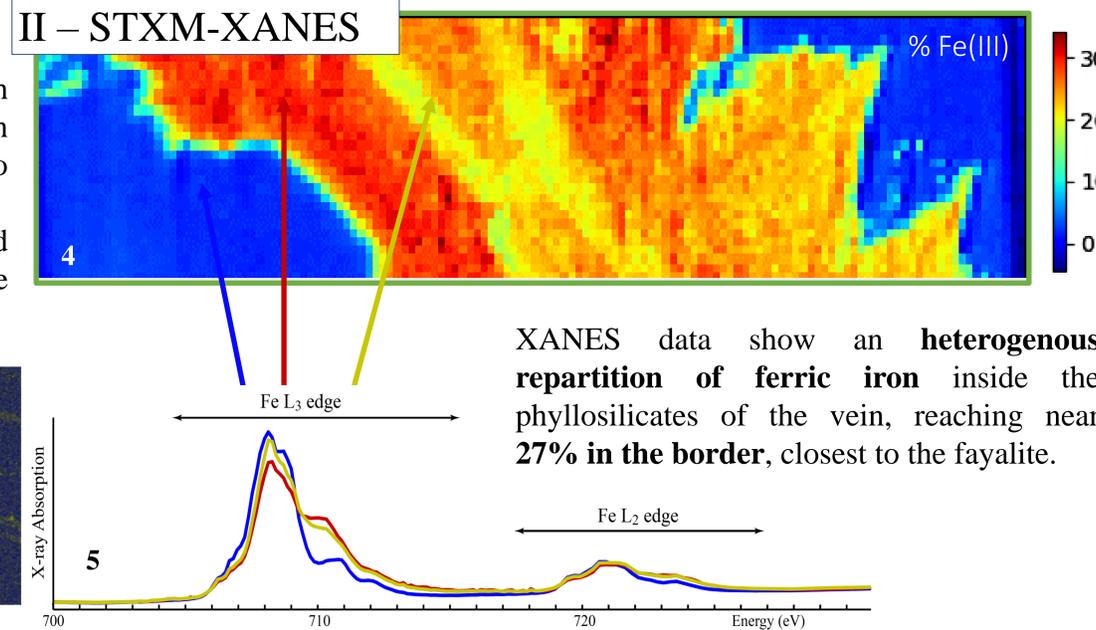
II – HREM Results

I – SEM-EDS

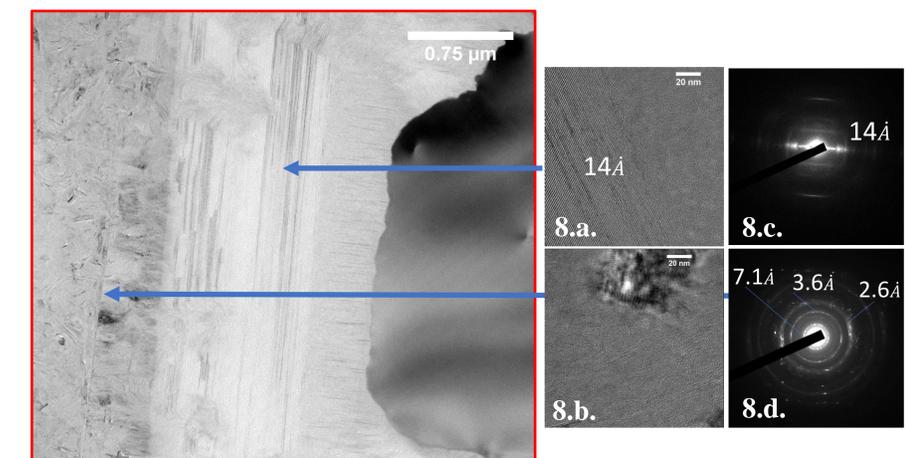
The majority of the sample is composed of sanidine and albite. Fe-rich amphiboles and pyroxenes are associated with **Fe-rich olivines** which are **fractured and altered**. Accessory phases such as apatite are also present. The fractures are filled with **two Fe-rich phyllosilicates**. Iron oxide and occasionally iron sulphurs are found in the fractures or at the rim of the fayalite.



II – STXM-XANES



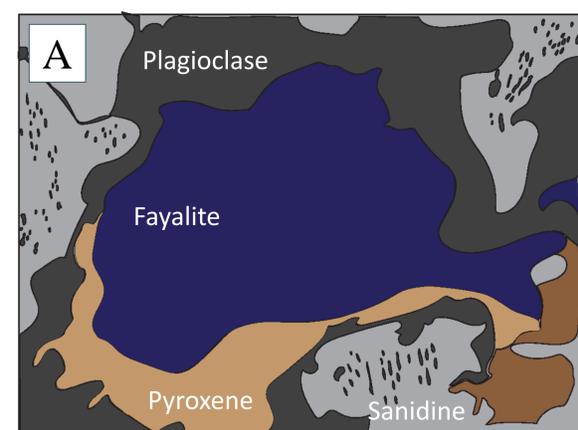
6 – TEM image of the FIB section of the fayalite vein (green rectangle is the XANES map, red rectangle is the TEM image n°7; 7 – TEM image of one area of interest in the FIB section; 8.a & 8.b – HR TEM images of the two phyllosilicates – 8.c & 8.d – Electronic diffraction of the two phyllosilicates.



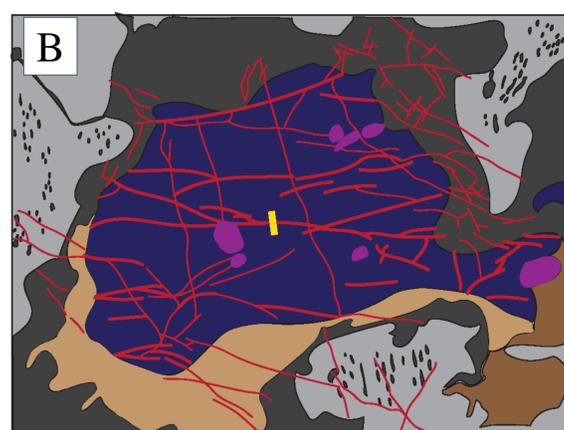
1 – SEM image of the fractured and altered Fe-rich olivine in K2 sample. Red line is the FIB section; 2 – SEM image of the vein; 3 – SEM-EDS map of one of the fayalite vein's; 4 – XANES map of ferric iron (%) in the fayalite and the vein; 5 - X-ray Absorption spectrum of iron of the fayalite and the vein (Bourdelle et al., 2013 et Le Guillou et al., 2018)

→ How is native H₂ produced in intracratonic context?

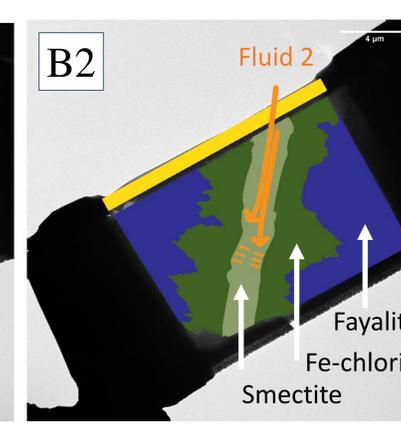
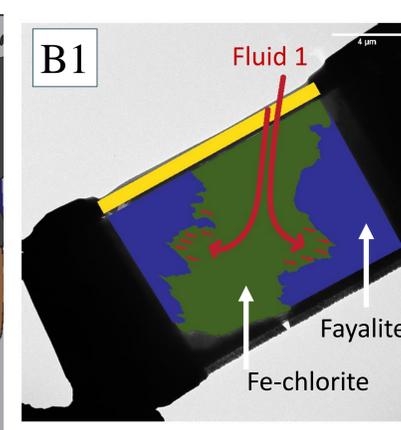
III – Chronology of formation, fracturation, alteration and crystallisation



A – **Fayalite crystallization** in the Precambrian granitoid basement :
 - Type-A granite
 - Metamorphic fayalite



B – **Fracturation** (in red) and alteration of the fayalite



B1 – **First step of alteration and crystallization**
 B2 – **Second and actual step of alteration and crystallization**

To remember

- Fractured and altered fayalite (Fe₂SiO₄) in the Precambrian basement
- Fe-rich serpentine/ chlorite crystallisation + iron oxide
- 26.6% of Fe³⁺ in the border of the veins

BICKFORD, M. E. et LEWIS, Richard D. U-Pb geochronology of exposed basement rocks in Oklahoma. *Geological Society of America Bulletin*, 1979, vol. 90, no 6, p. 540-544 ; BOURDELLE, Franck, BENZERARA, Karim, BEYSSAC, Olivier, et al. Quantification of the ferric/ferrous iron ratio in silicates by scanning transmission X-ray microscopy at the Fe L_{2,3} edges. *Contributions to Mineralogy and Petrology*, 2013, vol. 166, no 2, p. 423-434 ; LE GUILLOU, Corentin, BERNARD, Sylvain, DE LA PENA, Francisco, et al. XANES-based quantification of carbon functional group concentrations. *Analytical Chemistry*, 2018, vol. 90, no 14, p. 8379-8386 ; GUELARD, Julia, BEAUMONT, Valérie, ROUCHON, Virgile, et al. Natural H₂ in Kansas: Deep or shallow origin?. *Geochemistry, Geophysics, Geosystems*, 2017, vol. 18, no 5, p. 1841-1865.

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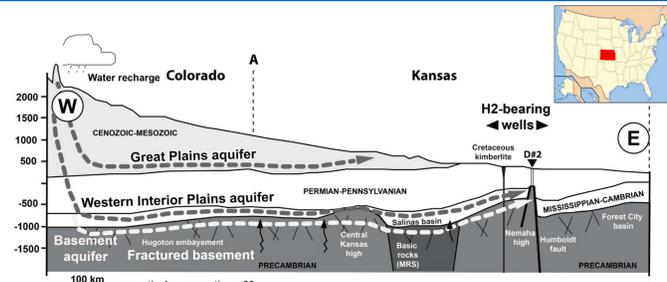
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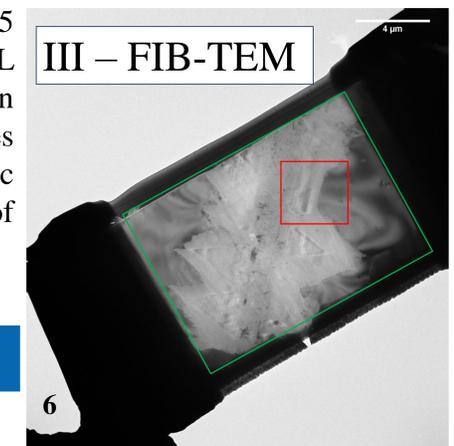
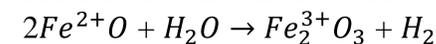
I – Context and methods

We studied drill cores obtained from the H₂-emitting DR1-A well located in Kansas (USA). The well is aligned along the Nemaha anticline highlighted by the Humboldt crustal fault. In this area the basement is mainly composed of Precambrian granitoids rich in ferromagnesian minerals but westward it has been intruded by the Mid-Rift System, a 1.1 Ga aborted rift (multi-km accumulation of mafic rocks).



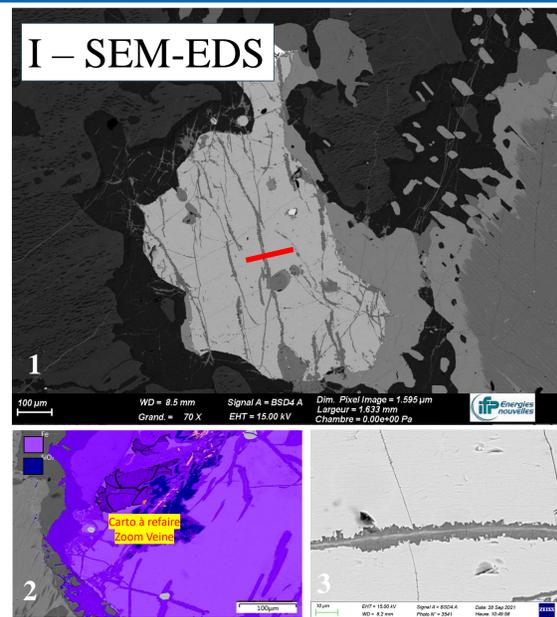
Guélard et al., 2016 ; modifié d'après Bickford et al., 1979

Through petrographic observations, followed by XRD, SEM-EDS (15 keV – Zeiss Gemini), STXM-XANES (708.7 keV – SOLEIL synchrotron) and then TEM analysis (200 keV - FEG) on FIB thin section, we studied alteration of Fe-rich olivine and phyllosilicates generation in the aim of understanding H₂ production in intracratonic terrestrial contexts. First hypothesis is H₂ production by oxidation of iron coupled with reduction of water as followed :



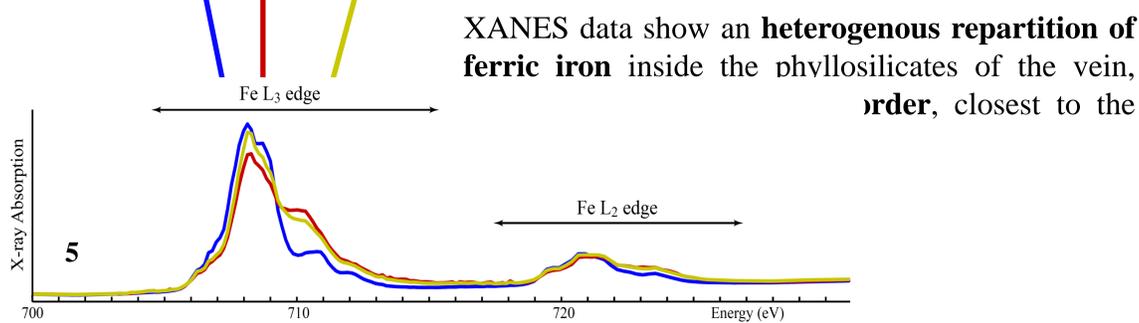
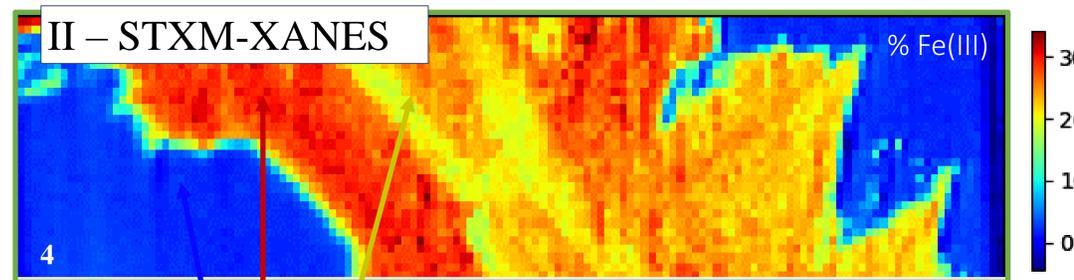
TEM images show typical chlorite and serpentine/smectite interstratified crystallization structure.

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1 – SEM image of the fractured and altered Fe-rich olivine in K2 sample. Red line is the FIB section area ; 2 – SEM-EDS map of one of the fayalite vein's ; 3 – SEM image of the vein

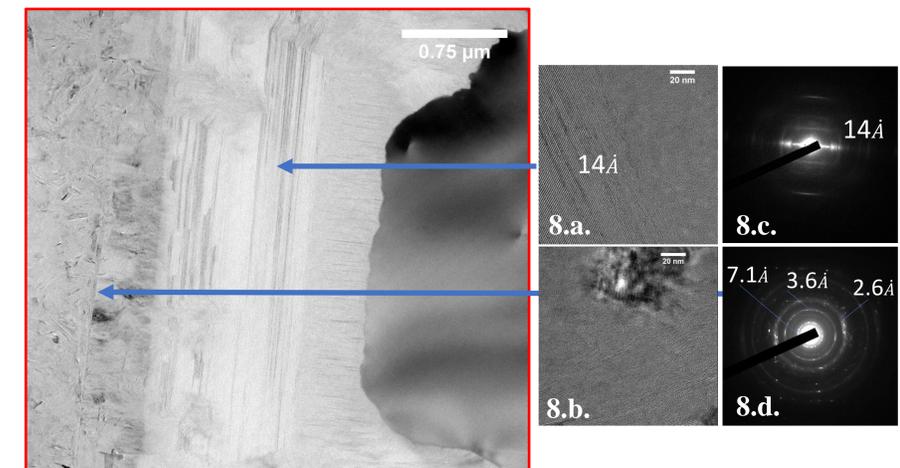
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4 – XANES map of ferric iron (%) in the fayalite and the vein ; 5 - X-ray Absorption spectrum of iron of the fayalite and the vein (Bourdelle et al., 2013 et Le Guillou et al., 2018) ; 4 – X-ray absorption spectra

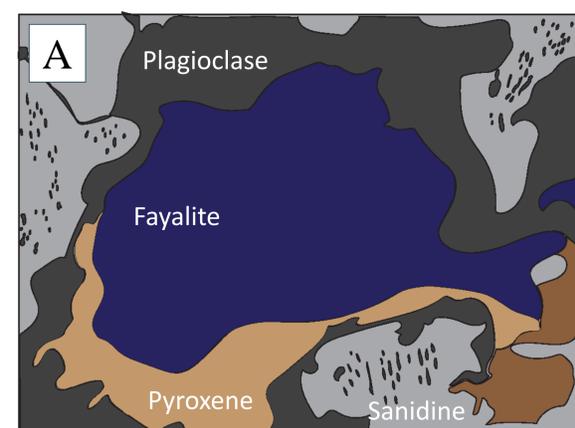
XANES data show an heterogeneous repartition of ferric iron inside the phyllosilicates of the vein, order, closest to the

6 – TEM image of the FIB section of the fayalite vein (green rectangle is the XANES map, red rectangle is the TEM image n°7 ; 7 – TEM image of one area of interest in the FIB section ; 8.a & 8.b – HR TEM images of the two phyllosilicates – 8.c & 8.d – Electronic diffraction of the two phyllosilicates.



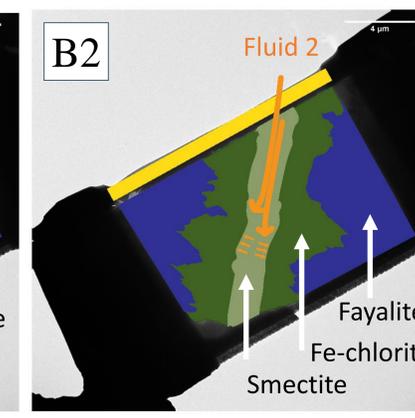
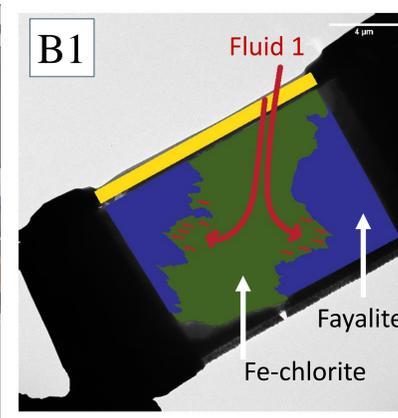
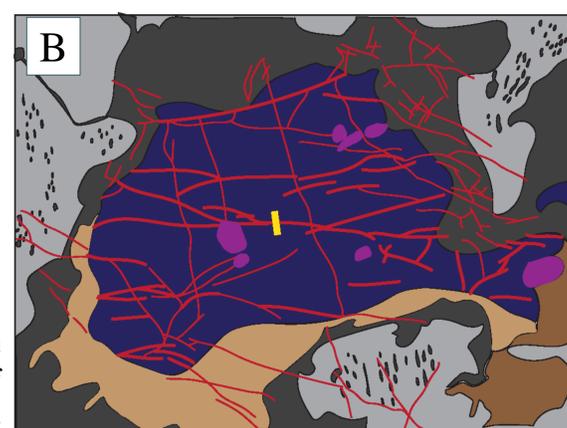
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