Pore Scale Control of Gas and Fluid Transport at Shale Matrix-Fracture Interfaces

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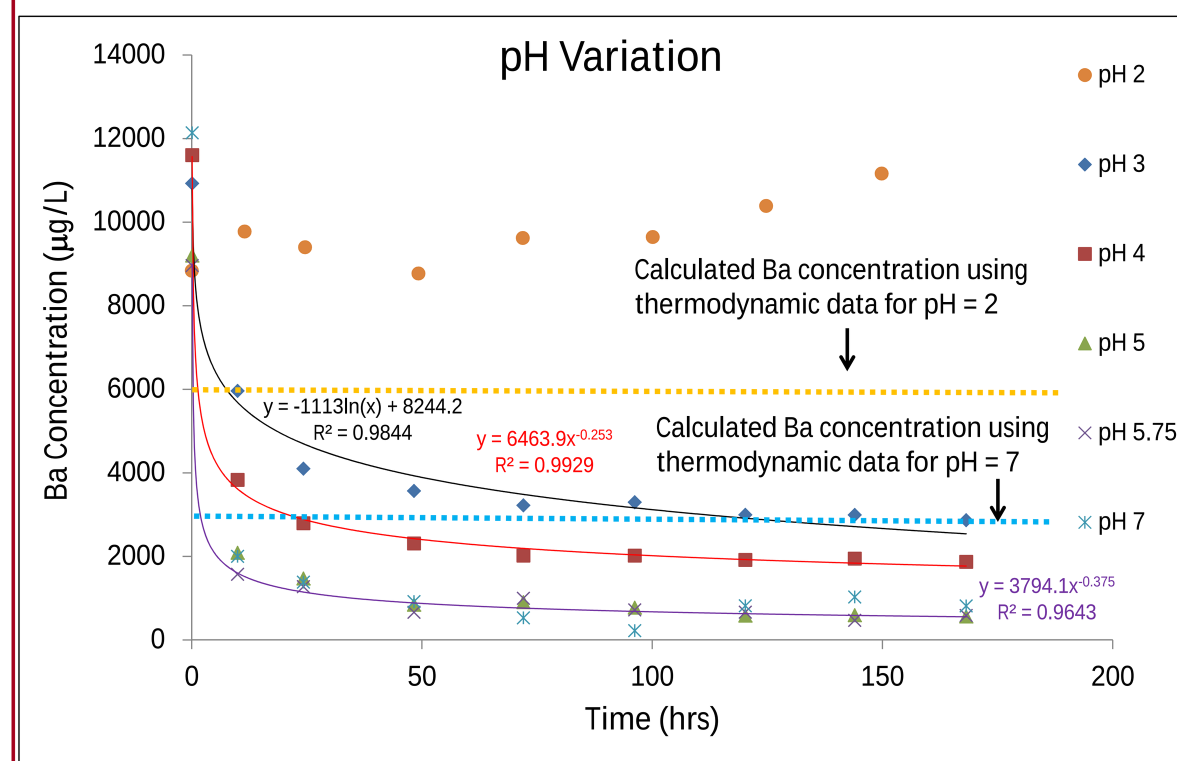
Geochemical controls over barite formation:

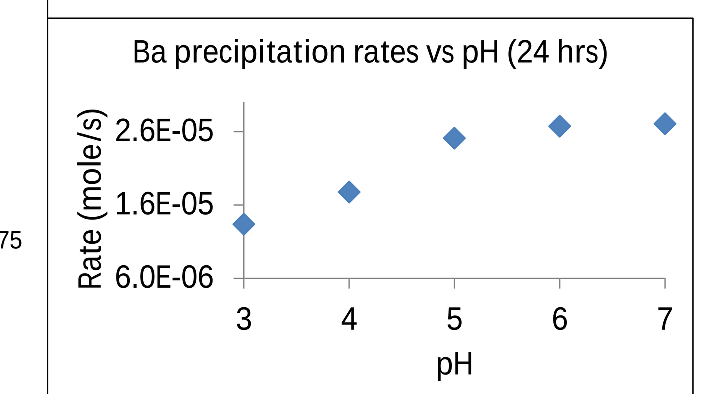
- Barium is ubiquitous in hydraulic fracturing systems
  - > 1 g/kg oil/gas shales
  - > 10 g/kg drilling mud
  - > 5 g/L produced water
- Depending on the shale play, barite precipitation is highly problematic
- Barite has low solubility for sulfates (Ksp = 10-9.34)
- Numerous sources of Ba:
  - Barite
  - BaCO3
  - Ba sorbed to clays
  - Ba-infused drilling mud
- Unknown if organic additives in fracture fluid inhibit or enhance barite precipitation

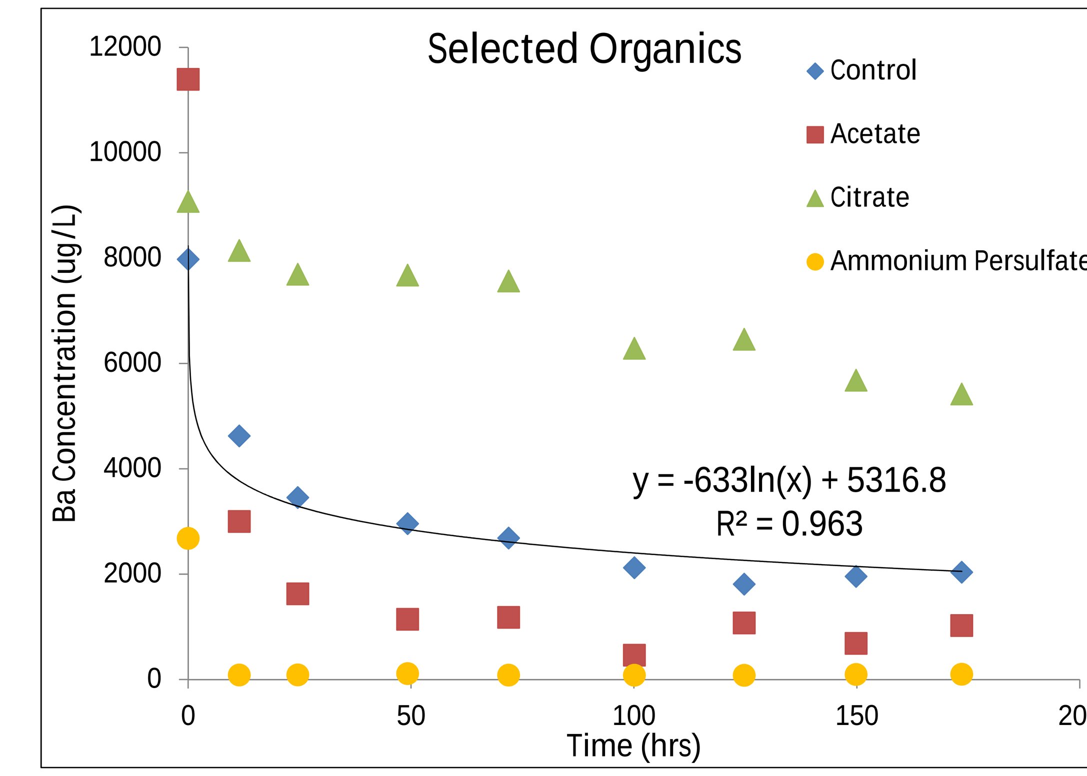
METHODS

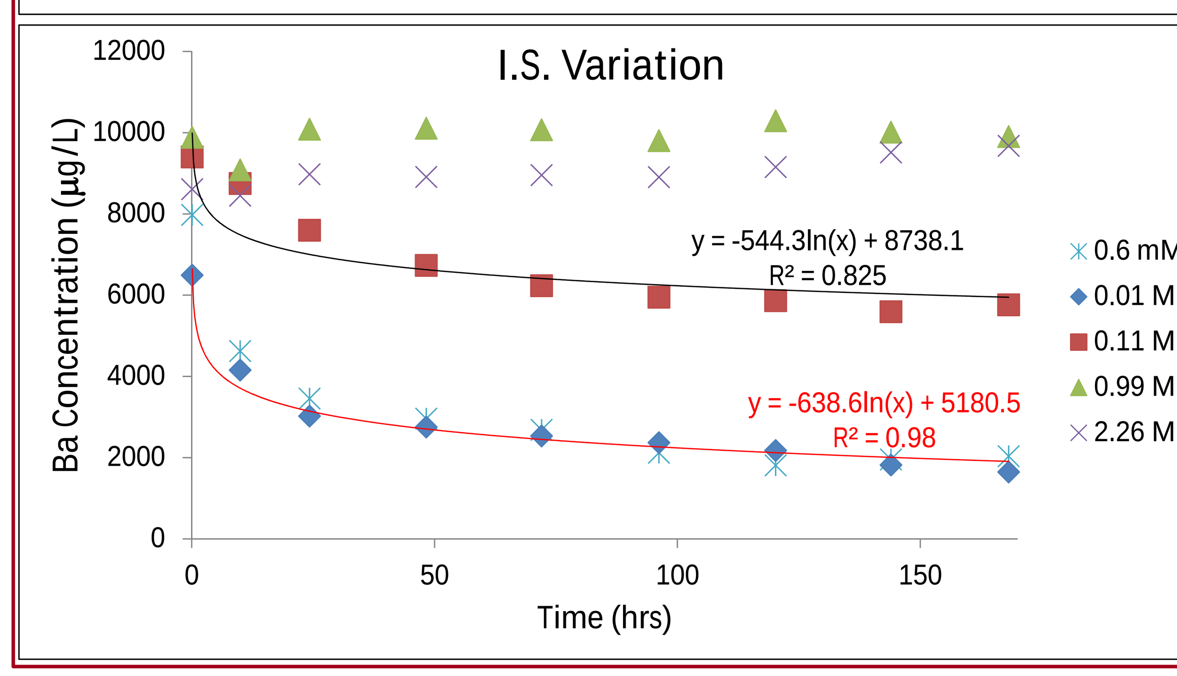
- 0.1 mM $BaCl_2/Na_2SO_4$ (I.S. = 0.6 mM)
- Organics (concentration set to literature values, I.S. ~0.6 mM): Ethylene glycol, polyethylene glycol, methanol, acetate, kerosene, guar gum, citrate, glutaraldehyde, benzene, ammonium persulfate, Marcellus-derived bitumen
- pH: 2, 3, 4, 5, 6, 7 (adjusted with HCl)
- I.S.: 0.6 mM, 0.01 M, 0.1 M, 1 M, 2.6 M (adjusted with NaCl)
- 80 °C incubation
- Constant mixing using end-over-end tumbler
- Incubation time 1 week with sampling every 24 hours
- Filter size 0.02 mm
- Ba concentrations measured with ICP-OES

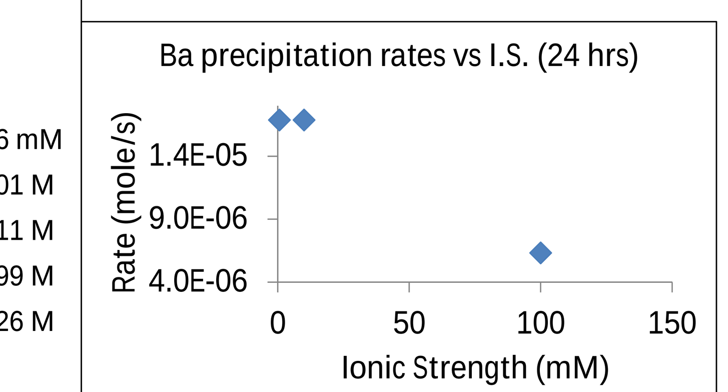
RESULTS











CONCLUSIONS

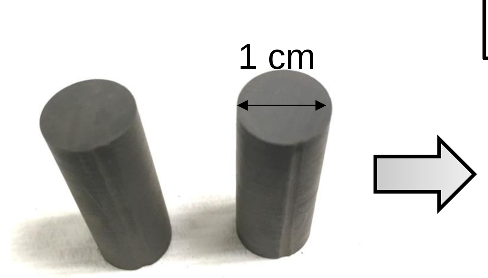
- pH and Ionic Strength have a strong influence on barite precipitation
  - ≤ pH 2 and High I.S. (≥0.99M) lower halts precipitation
- Ethylene glycol (anti-scaling agent) has no effect on barite scale production
- Citrate, guar gum, glutaraldehyde, and polyethylene glycol slow precipitation
- Marcellus-derived bitumen, acetate, benzene, and methanol enhance precipitation
- Ammonium persulfate significantly enhance precipitation with ~2/3 of total Ba precipitated in 6 minutes
- Core scale experiment show that barite scale formation precipitation was most obvious in shales with high pH buffering capacity
- Scale formation on the shale surface inhibits Fe leaching from shale matrixes.
- Permeability measurements for shale matrixes before and after reaction are in progress

Fluid-Shale Permeability Controls

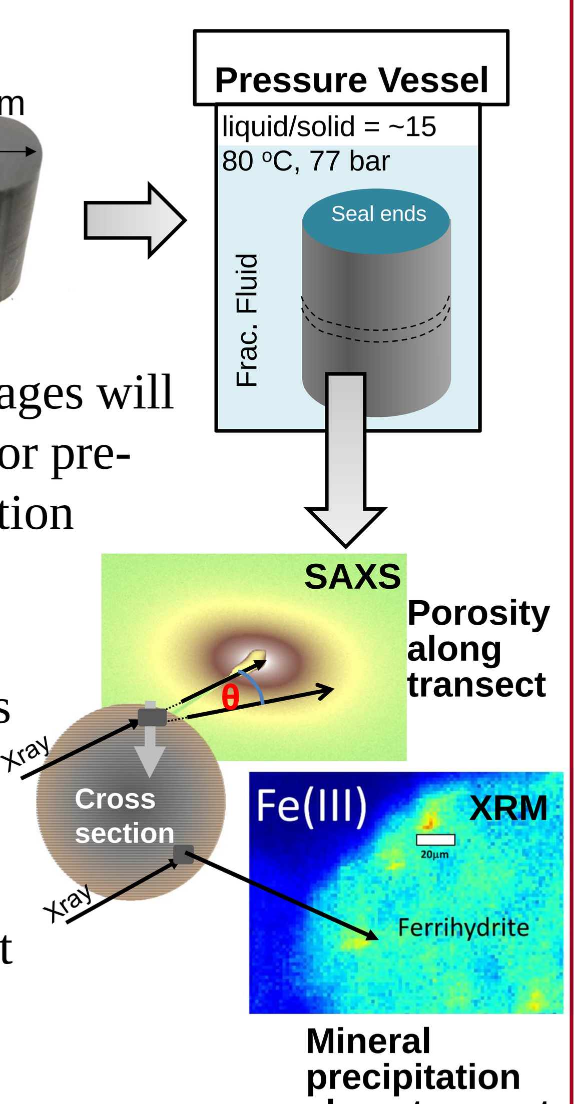
- Alteration in porosity, diffusivity, and permeability of shale matrix can affect the efficiency of hydrocarbon production
- A few studies on chemical reactions with shale samples were conducted using fractured cores and shale sands, focusing on fracture surface alteration
- We aim at examine chemical reactions in shale matrixes, and seed answers to several questions:
  - How **deep the reactions penetrate** into the matrix? Is it in mm or µm scale?
  - Does **porosity** alter in nanoscale or microscale?
  - What are the effects on **diffusivity** and **permeability** of the matrix?
  - How would **mineralogy** of the shale affect the results?
  - How barite **scale formation** affect alteration of the shale matrix?

METHODS

- Whole cores of Marcellus and Eagle Ford were reacted at 80 °C and 77 bar for three weeks at both dissolution- and precipitation-favorable conditions.

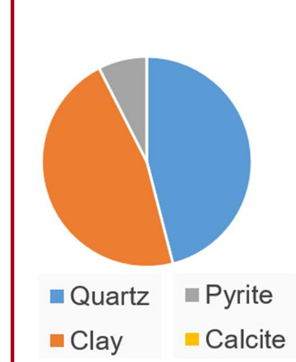


- Micro-CT images will be collected for pre- and post-reaction cores.
- Cross sections of the pre-reaction and post-reaction cores were cut for analyses.

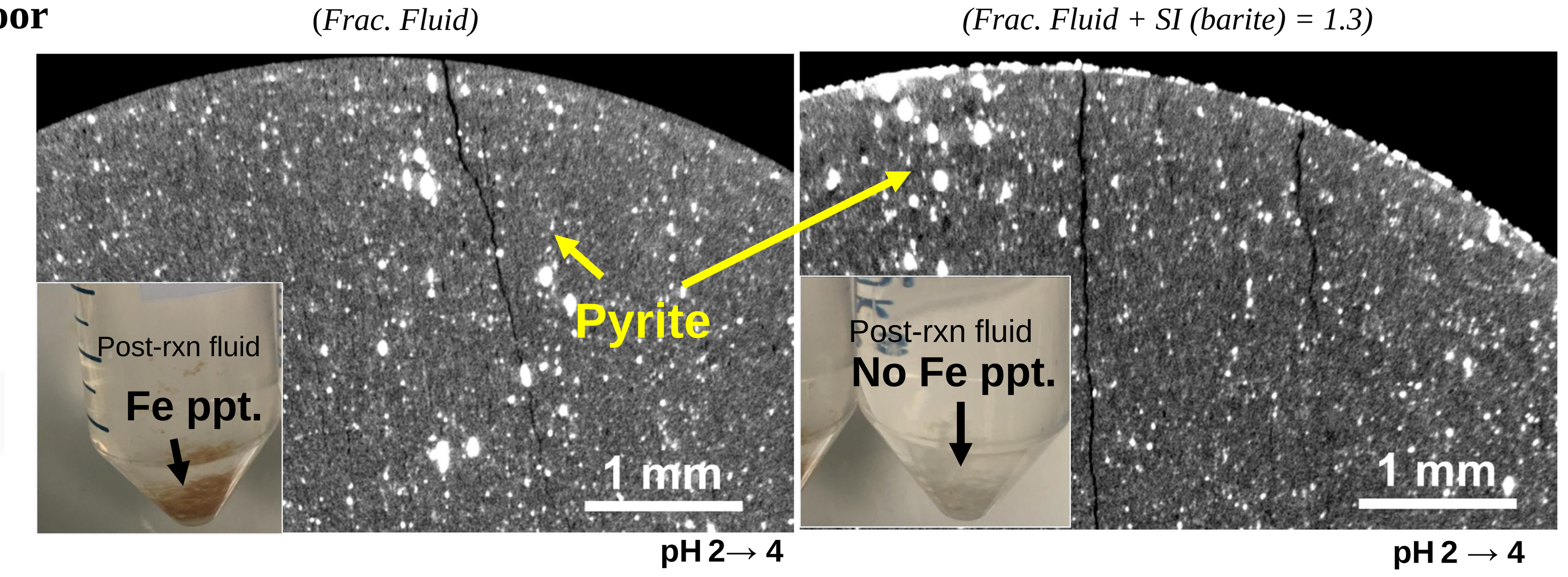


RESULTS

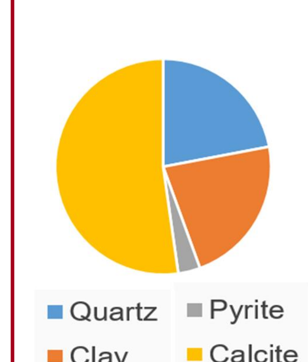
Marcellus (Pennsylvania): Carbonate-Poor



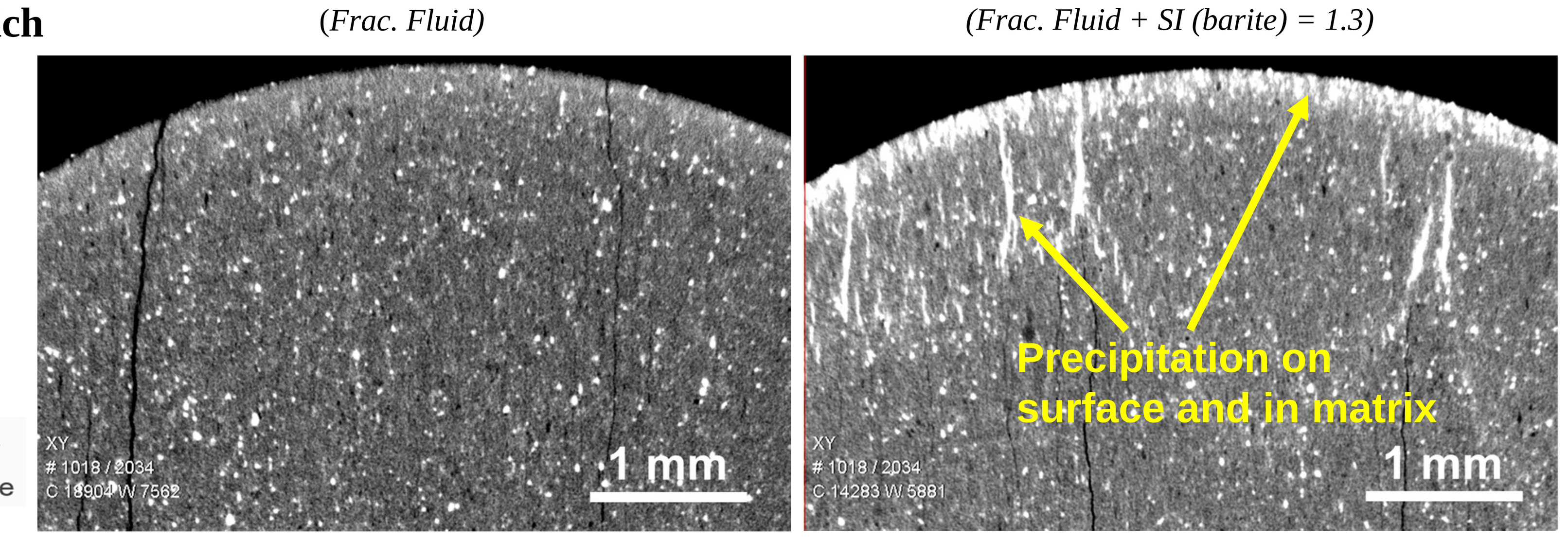
Dissolution-favorable *(Frac. Fluid)* | **Precipitation-favorable** *(Frac. Fluid + SI (barite) = 1.3)*



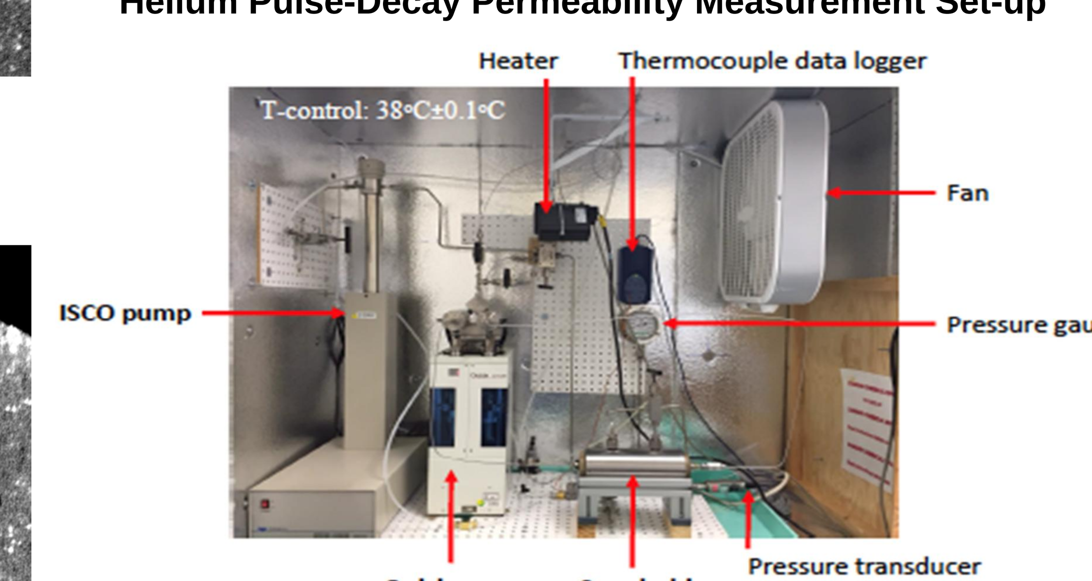
Eagle Ford: Carbonate-Rich



Dissolution-favorable *(Frac. Fluid)* | **Precipitation-favorable** *(Frac. Fluid + SI (barite) = 1.3)*



Helium Pulse-Decay Permeability Measurement Set-up



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