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# Geological Survey of Canada Scientific Presentation 142

# The subsurface sulphur system following hydraulic stimulation of unconventional hydrocarbon reservoirs: assessing anthropogenic influences on microbial sulphate reduction in the deep subsurface, Alberta

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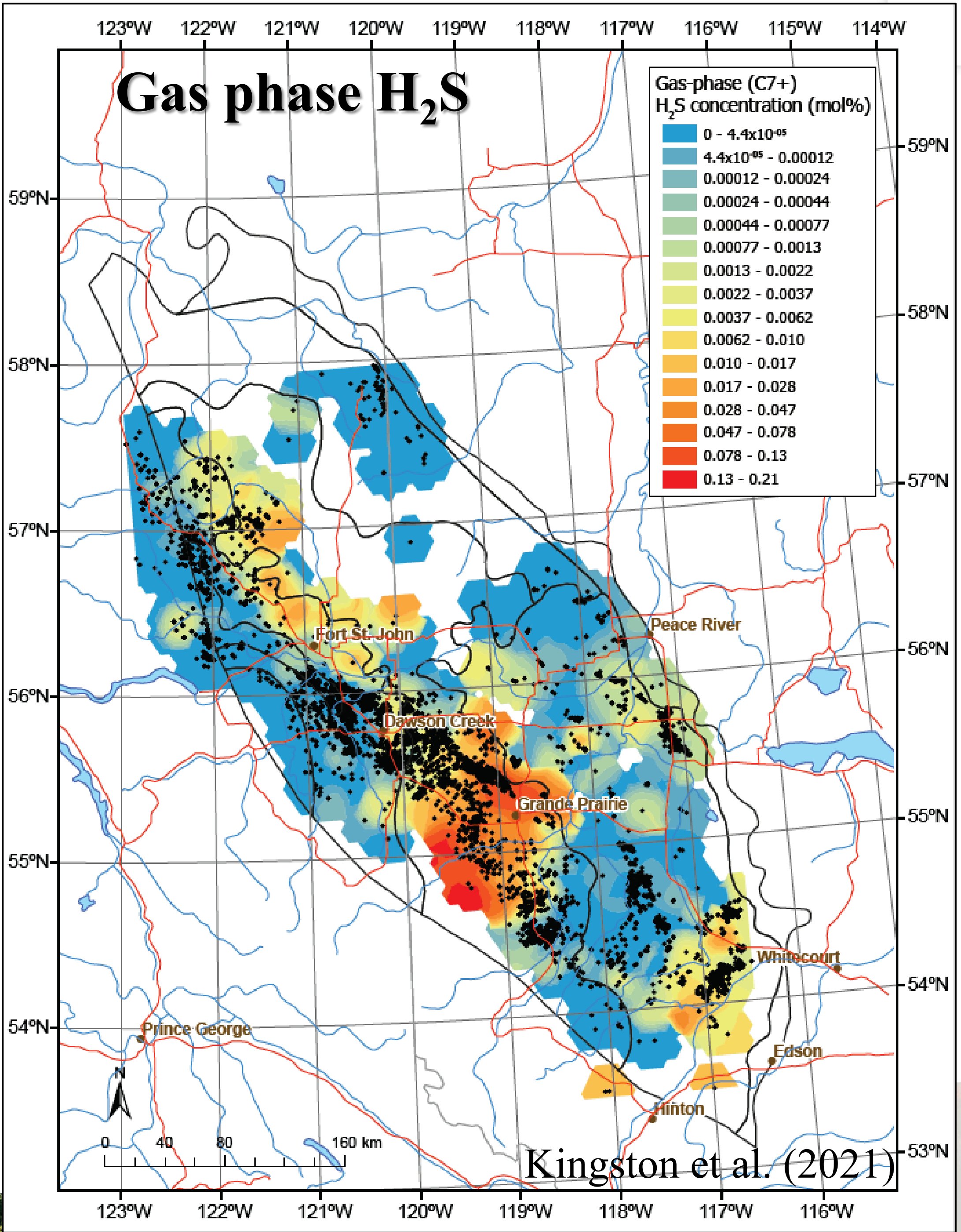
# Traditional Territorial Acknowledgement

I acknowledge that I am working on the traditional territories of the people of the Treaty 7 region in Southern Alberta. These are the Tsuut’ina First Nation, the Stoney Nakoda First Nation (including people of the Chiniki, Bearpaw, and Wesley), and the Blackfoot Confederacy (which includes people of the Siksika, Kainai, and Piikani). This region is also home to Métis Nation of Alberta, Region III.

# Motivation

- Sour gas makes up ~1/3 of the gas produced in Alberta
- Montney Formation is Canada's most productive gas reservoir
- Essential to understand $H_2S$ formation processes to protect people and infra-structure in hydrocarbon producing regions
- **$H_2S$ formation associated with HF poorly understood, research gap**




Kingston et al. (2021)

# Hydraulic fracturing

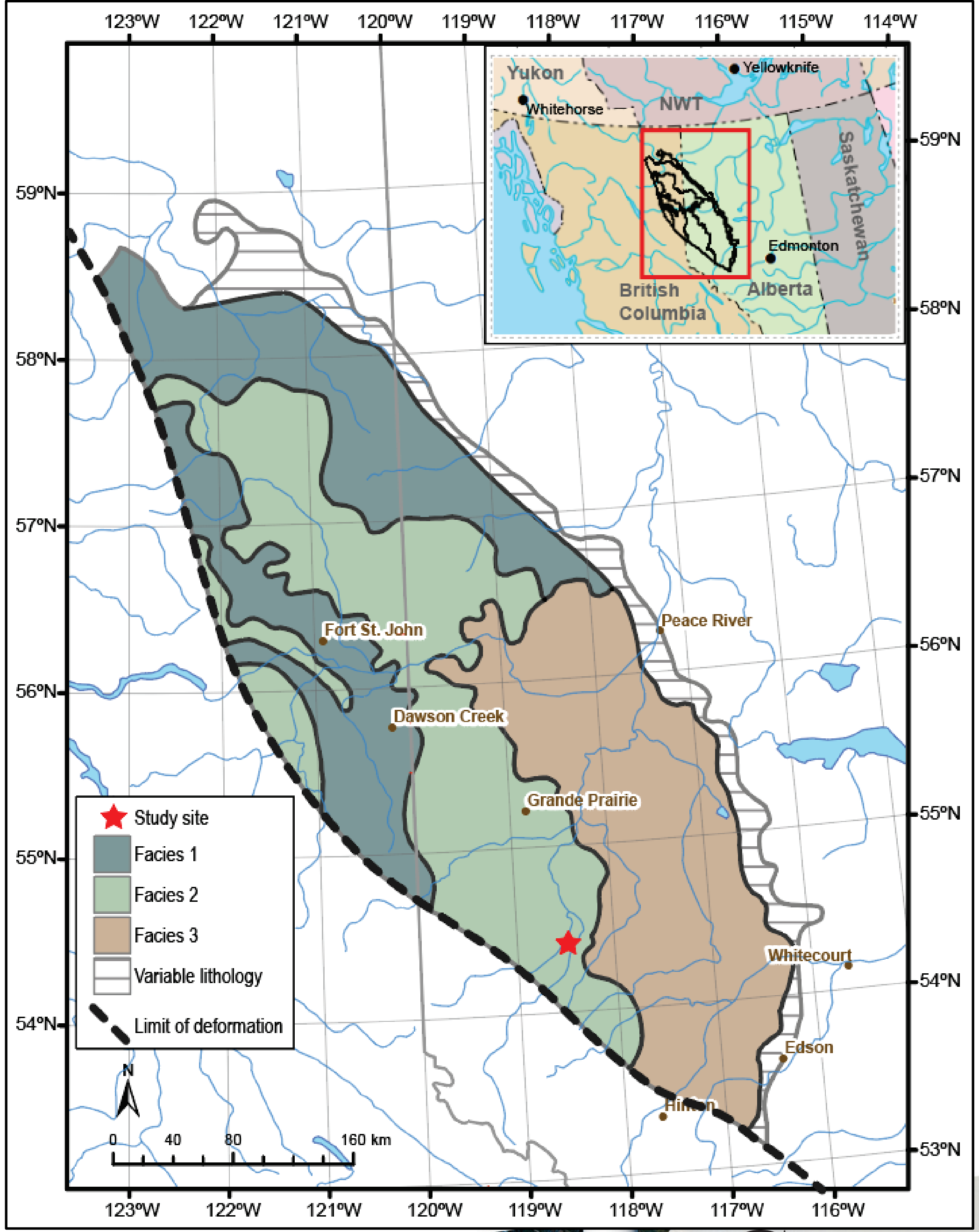
- High pressure injection of water, chemicals, and sand
- Used to enhance hydrocarbon production from low permeability reservoirs
- What are the chemical and biological effects in the subsurface

# $H_2S$ formation mechanisms associated with Hydraulic Fracturing

- Adsorption of $H_2S$ on fresh generated surfaces during frac, leads to slow release of $H_2S$
- Migration of $H_2S$ from layers with elevated $H_2S$ (could even be cross formation boundaries)
  - Will be affected by pressure gradients
- Kerogen cracking (Type IIS)
- MSR or TSR of injection fluids (HFF components or seawater)
- **MSR of *in situ* sulfate**

# Study site

- SW portion of the Montney Basin
- Depths:
  3,300-3,400 m
- Regionally intense use of HF
- Issues with production of $H_2S$ following HF
- Multiple geochemical studies ongoing in this region



# Materials

- Sample drilling muds and cuttings during drilling process
- Sample core material

- Sample hydraulic fracturing fluids
- **Time series of produced water**
  - **flowback and formation**

# Sample Strategy

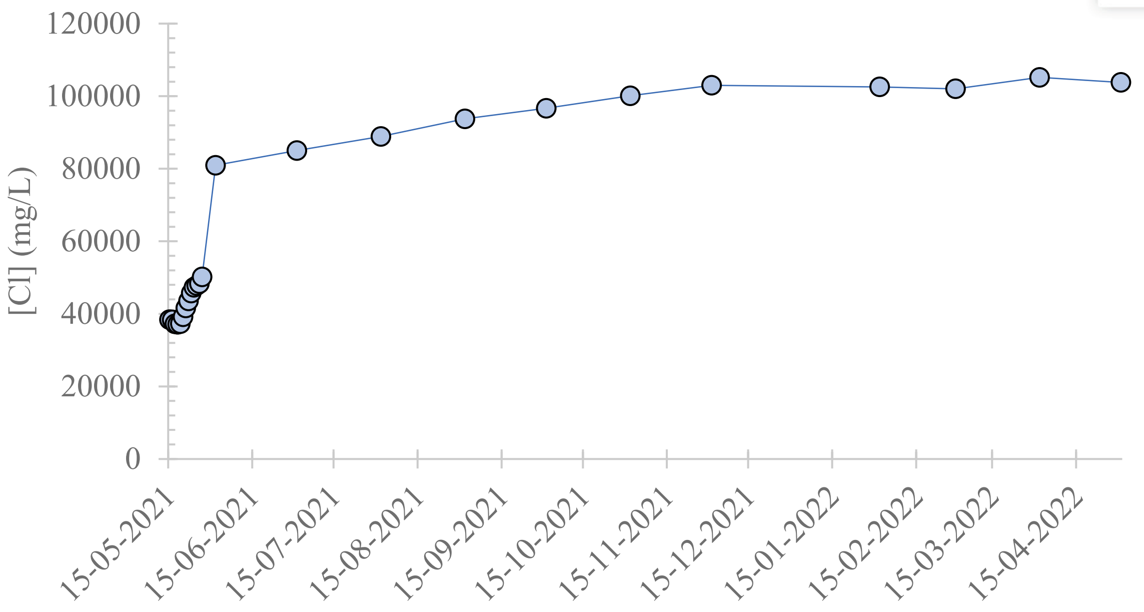
- 4 x 1 L samples
  - Geochemistry
    - 1 L untreated cooled
    - 1 L treated with Cadmium acetate to trap sulfides (CdS = yellow)
  - Microbiology
    - 1 L untreated cooled
    - 1 L untreated frozen
- Transported to lab and analyzed/processed as quick as possible

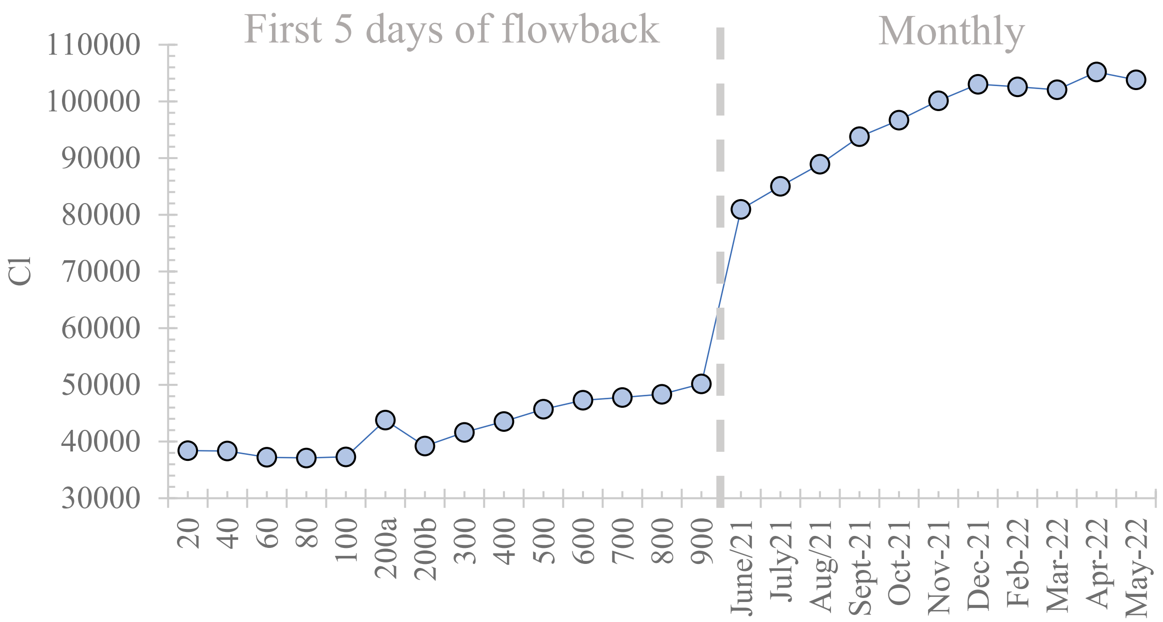
# Analytical

- Aqueous geochemistry
  - EC, RW, pH, TDS
  - $HCO_3$, Cl, Br, $NO_2$, $NO_3$, $PO_4$, $SO_4$
  - Al, B, Ba, Ca, Fe, K, Li, Mg, Mn, Na, Si, Sr
- Stable isotope geochemistry
  - Water: $\delta^{18}O$ and $\delta^{2}H$
  - Sulfate: $\delta^{34}S$ and $\delta^{18}O$
  - Sulfide: $\delta^{34}S$
- Microbiology
  - 16S rRNA sequencing
  - Incubations

# Time series sampling

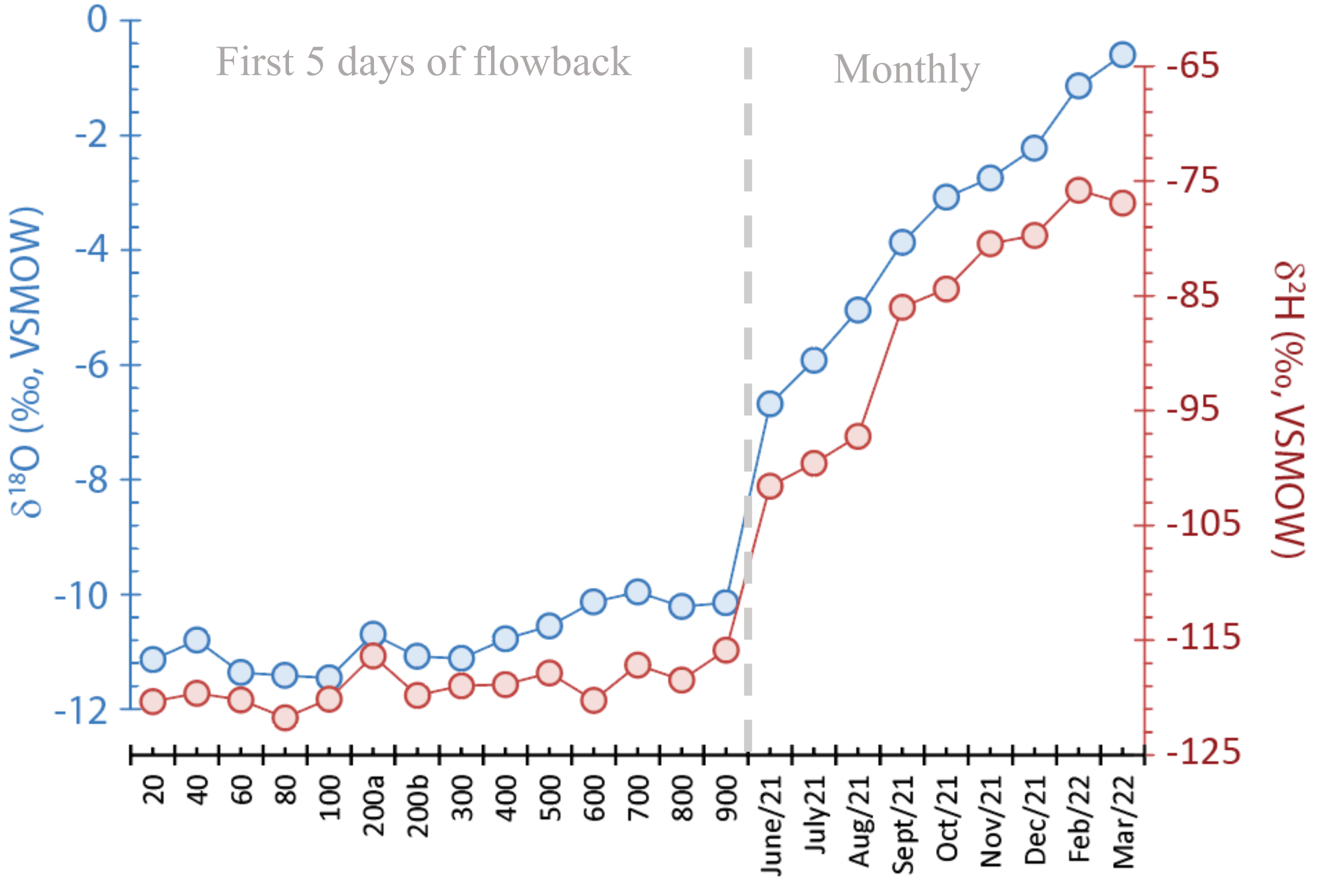
- Initial flowback May 4th to 9th
- 1 sample every 20 $m^3$ to 100 $m^3$
  1 sample every 100 $m^3$ to 1600 $m^3$
  1 sample every 200 $m^3$ to 2000 $m^3$
  Monthly samples to 1 year from frac
- 900 $m^3$ after 120 hours (5 days)
- 14 samples taken initially, 25 to date



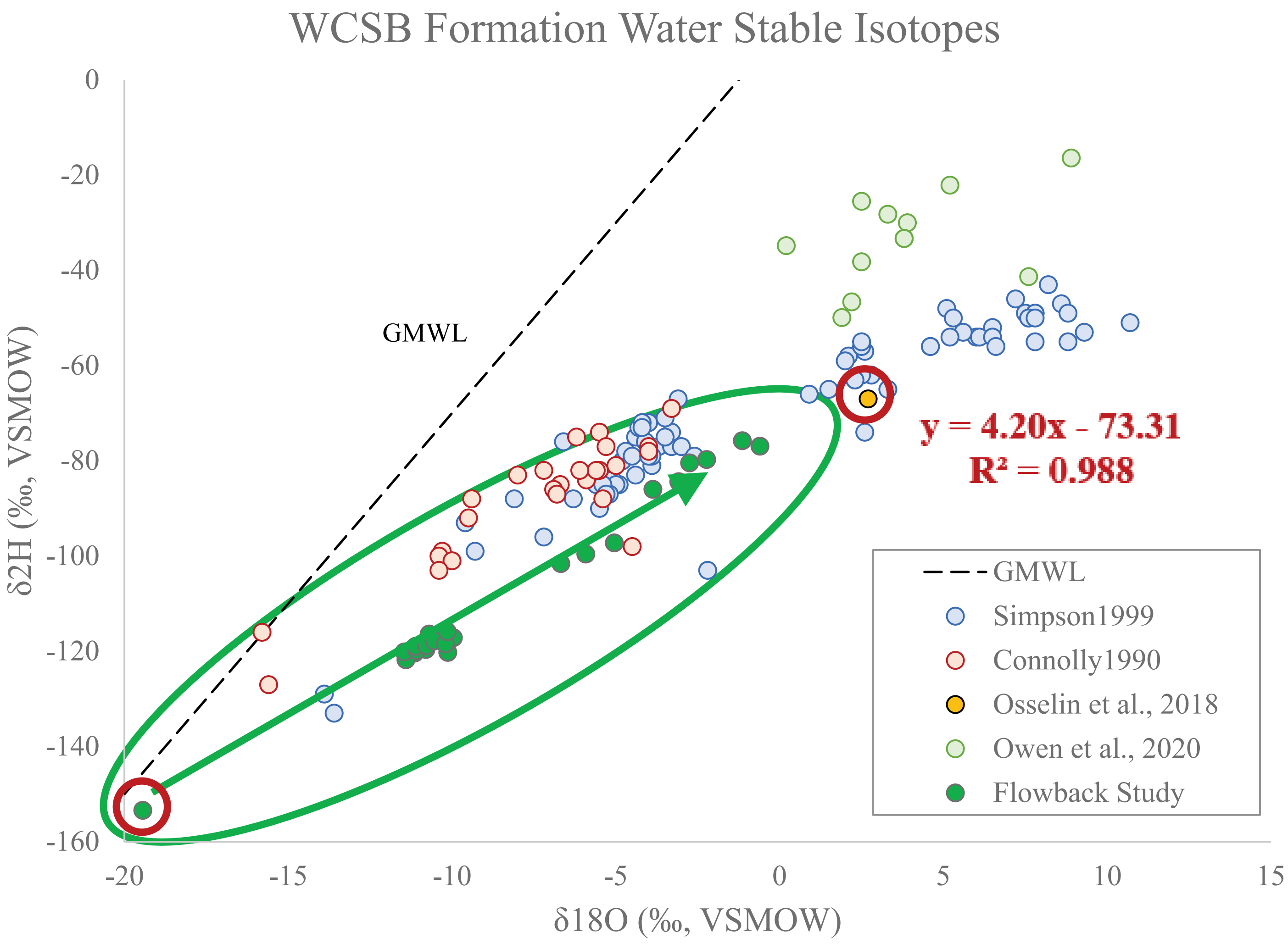
# Water Isotope Time Series

- $\delta^{18}O$ and $\delta^{2}H$ values increase over time representing increased production of formation waters
- Note change in scale



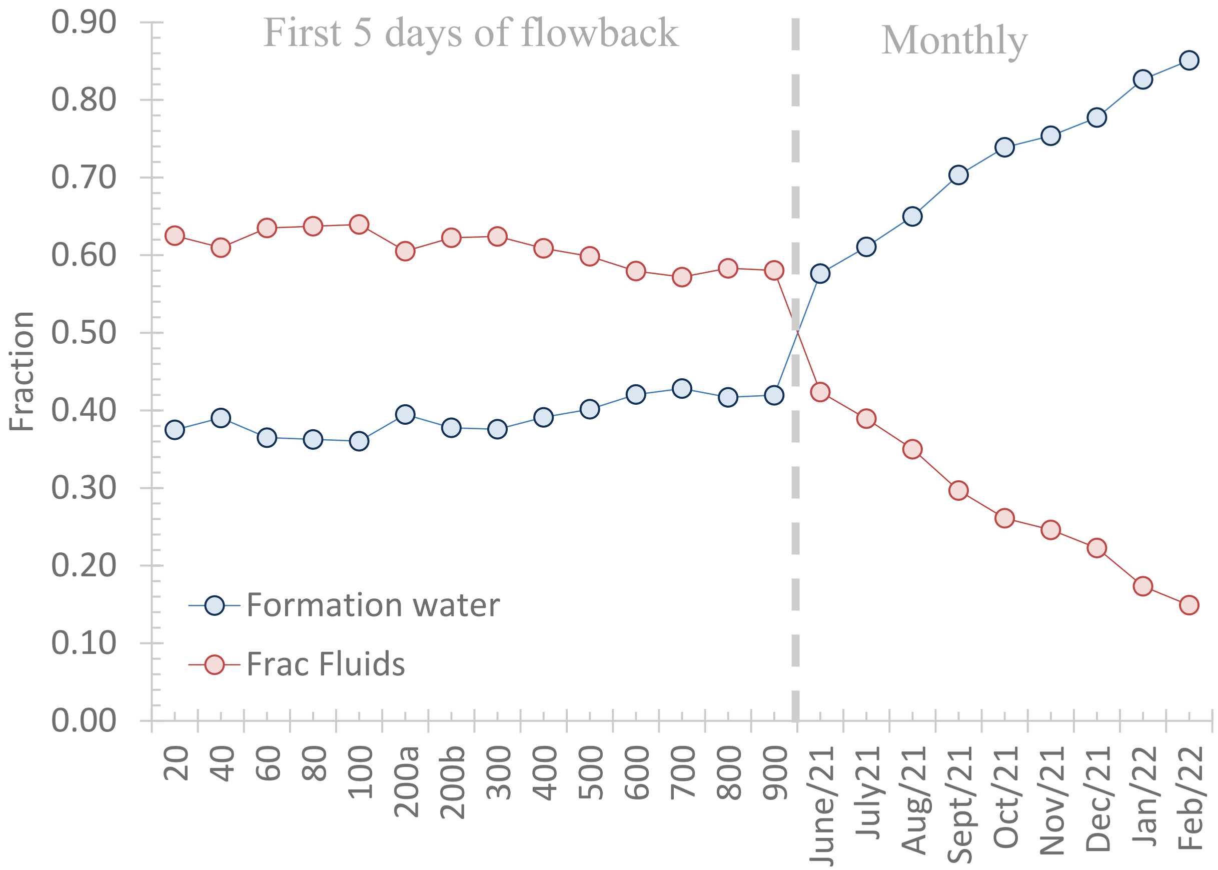
# Water Isotopes

- Overview of WCSB formation waters and flowback study
- Evolves from surface water composition (HFF) to formation water
- Model water data using two δ18O end-members
  - Initial frac fluid: -19.4 ‰
  - Formation water: 2.7 ‰ (Osselin et al., 2018)
- Similar results using δ2H



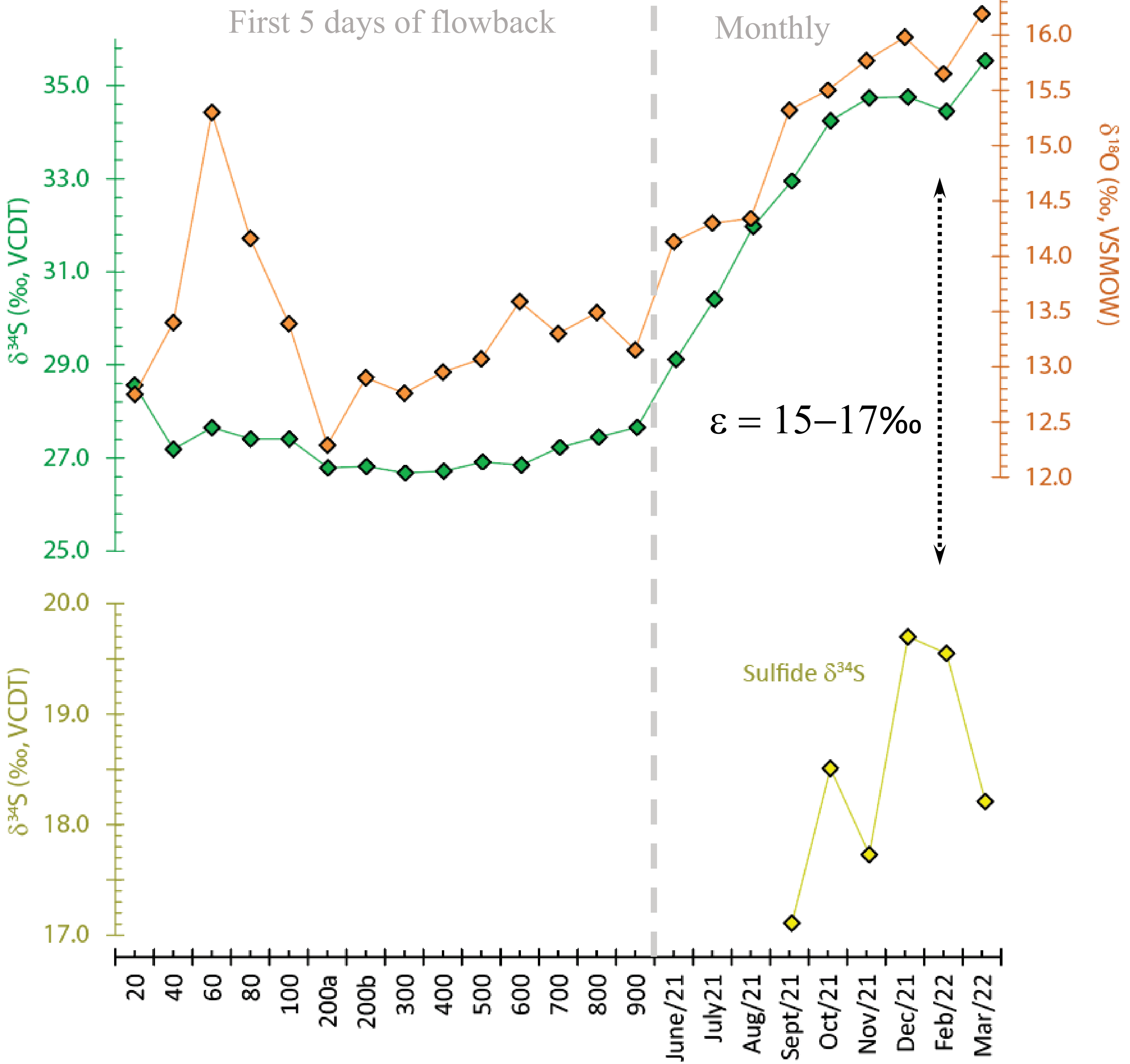
# Water mixing model

- Flowback begins with 63% HFF fluid
- Significant production of formation water
  - Could have implications for effectiveness of **biocide** in the subsurface



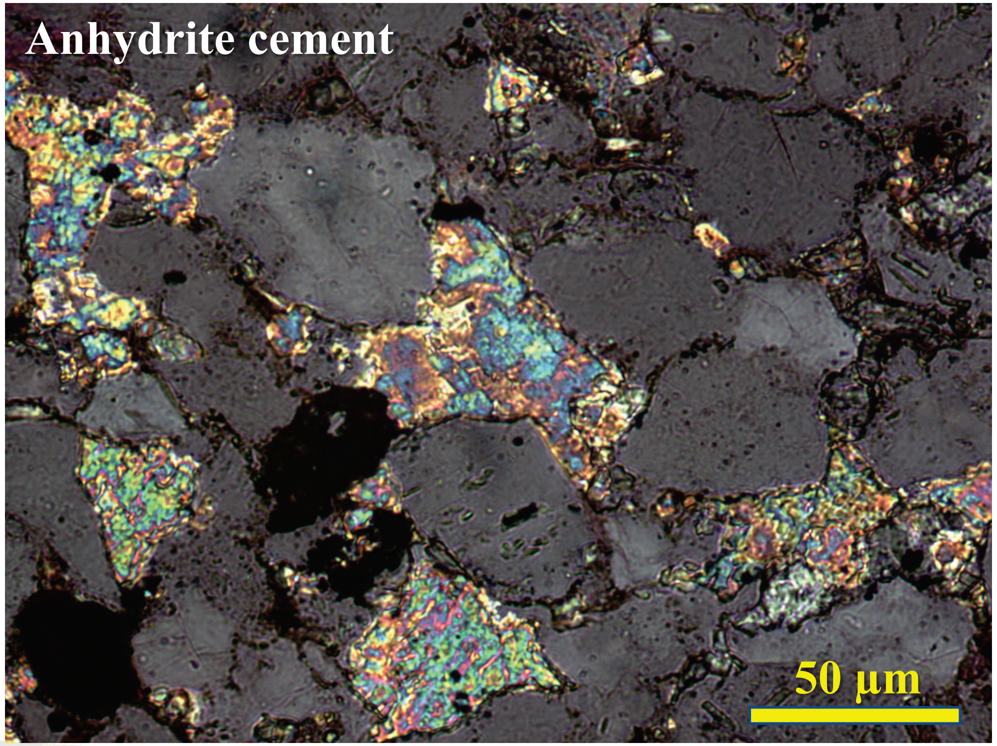
# Sulfate isotope time series

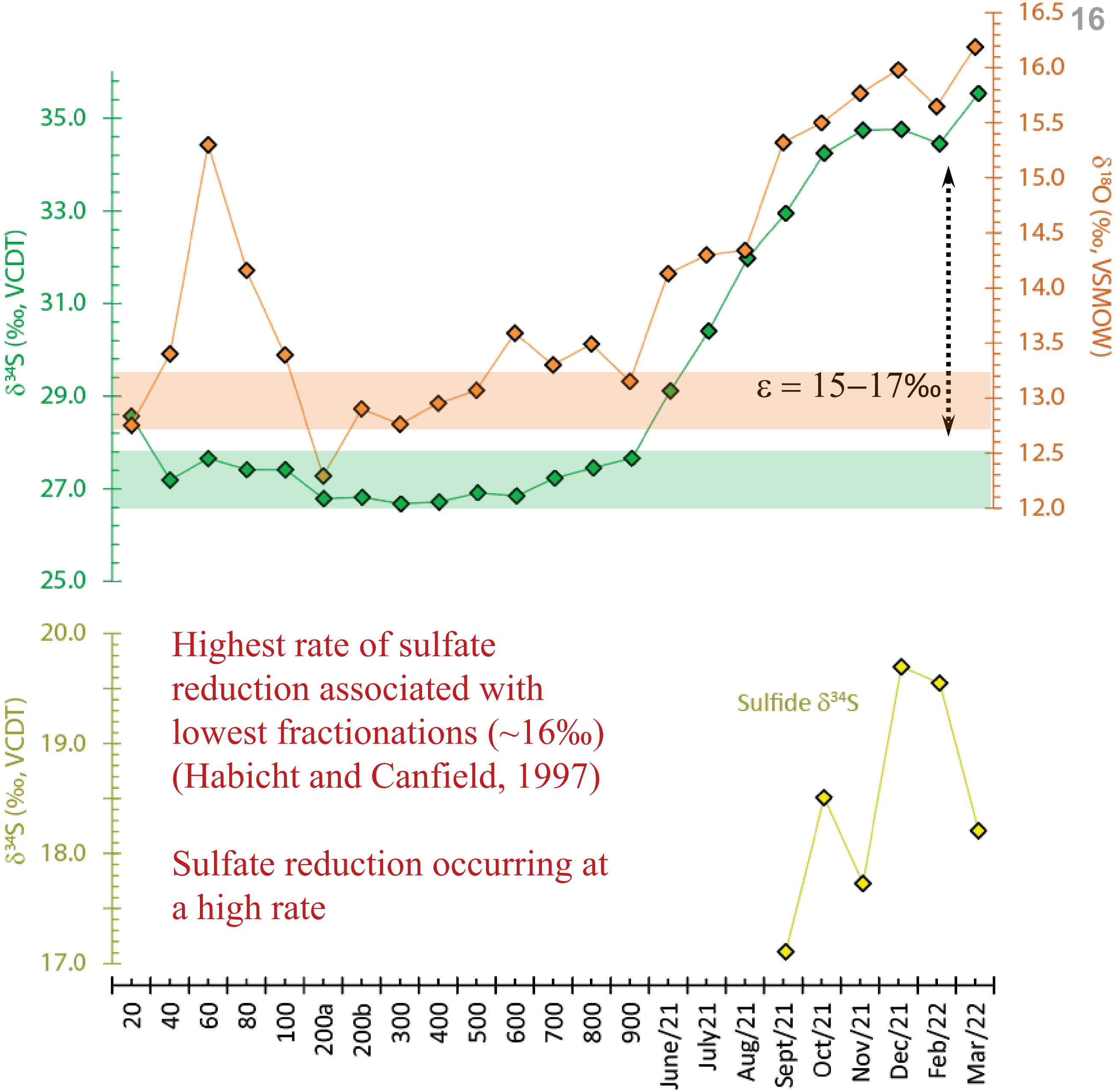
- $\delta^{34}S$ and $\delta^{18}O$ increase over time
- Sulfide observed in Sept-Mar samples
- Synchronous rise in **$\delta^{34}S$** values of sulfate and sulfide
- Fractionation between sulfate and sulfide consistently 15-17 ‰
- Likely MSR not TSR (Fm. temp = 85°C)



# Sulfate sources

- Persulfate breaker: $\delta^{34}S = 0.7 \pm 5$ ‰
- Oxidation of pyrite: $\delta^{34}S_{py} = -5$‰ (–35 to +20 ‰)
- Anhydrite cement: $\delta^{34}S = 22$‰, $\delta^{18}O = 15$‰
  - Initial $SO_4$ $\delta^{34}S_{FB} = 27$‰; $\delta^{18}O_{FB} = 13$‰



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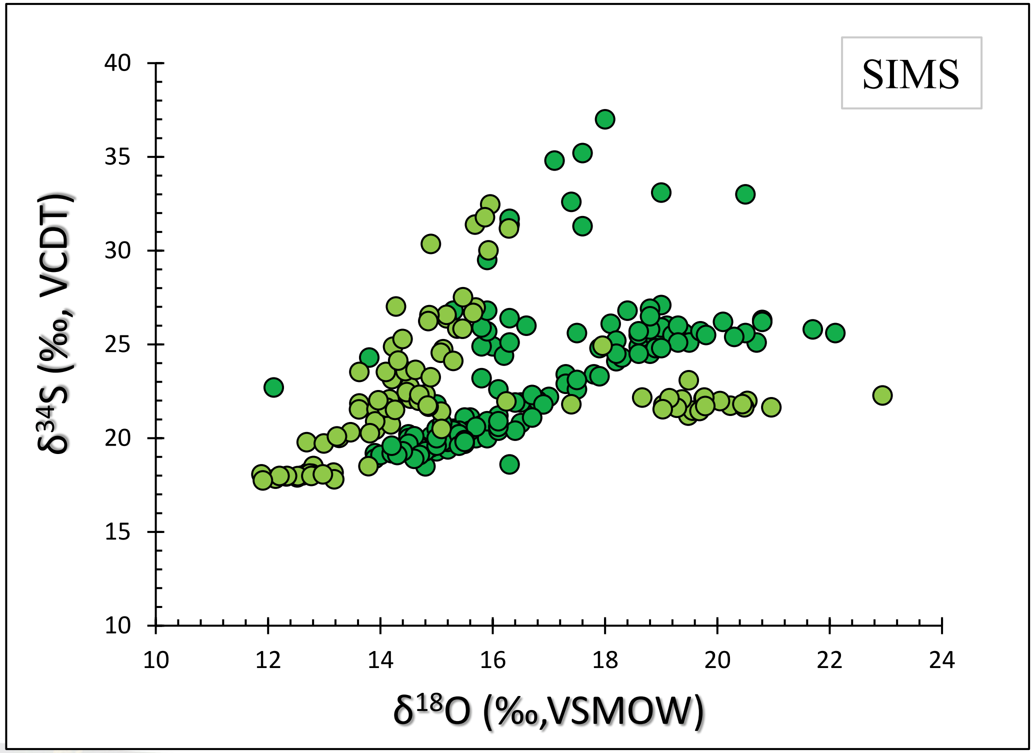
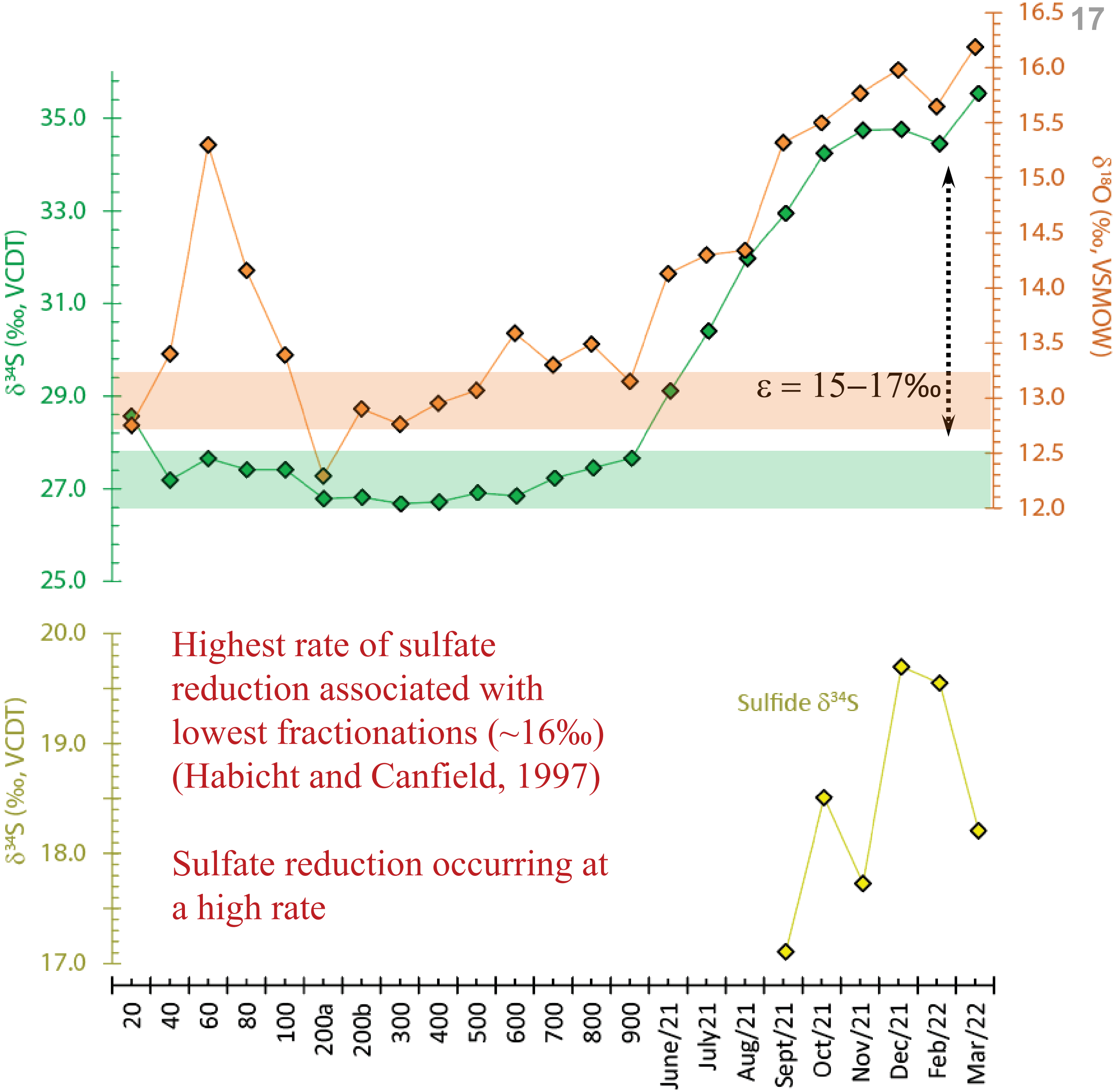


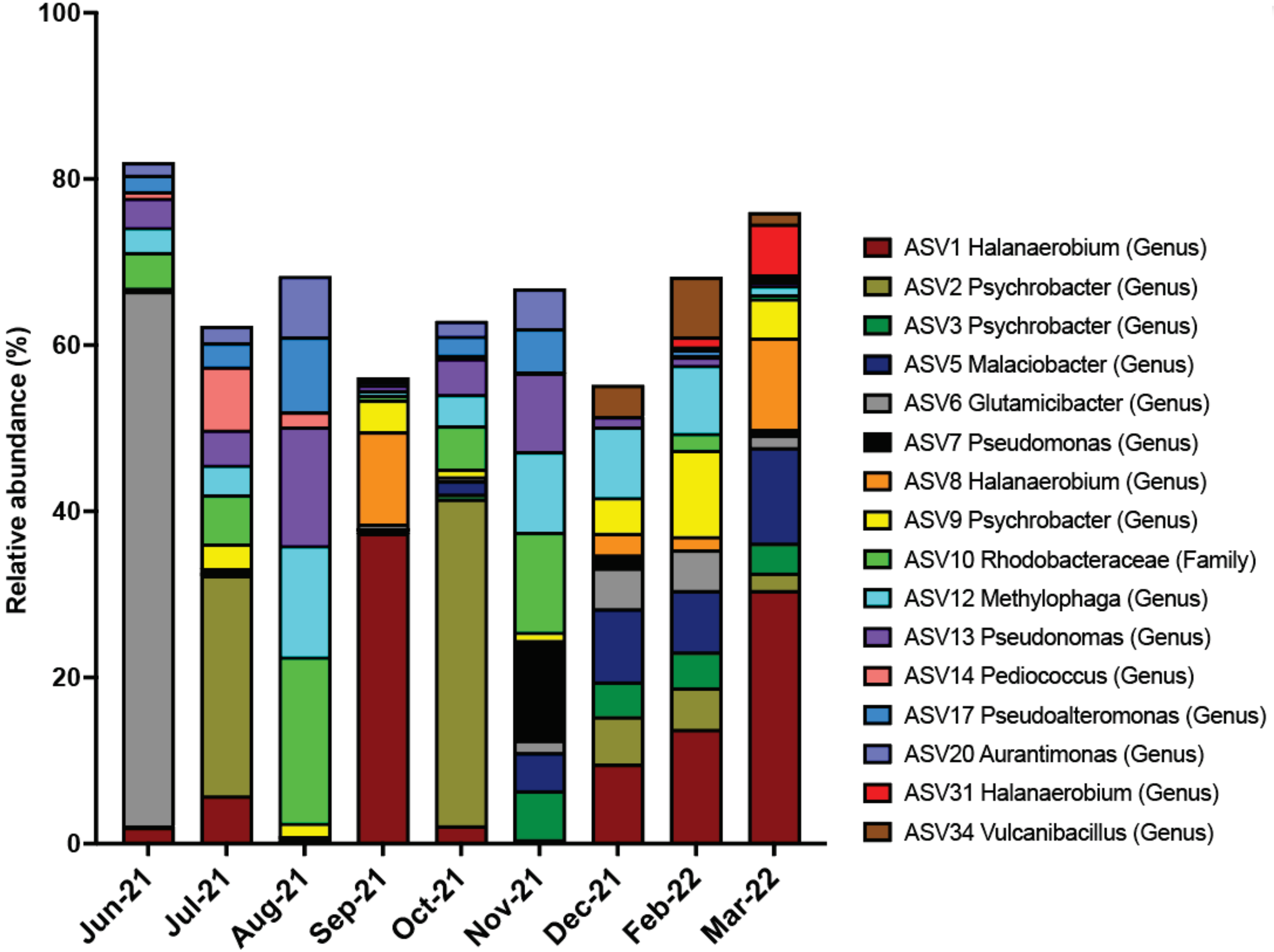




Highest rate of sulfate reduction associated with lowest fractionations (~16‰) (Habicht and Canfield, 1997)

Sulfate reduction occurring at a high rate

# Microbiology Time Series

- 16S rRNA sequencing
- Large changes in microbial populations through time
- SRM are not the dominant species (<5%)
- Shift from aerobic to anaerobic species through time



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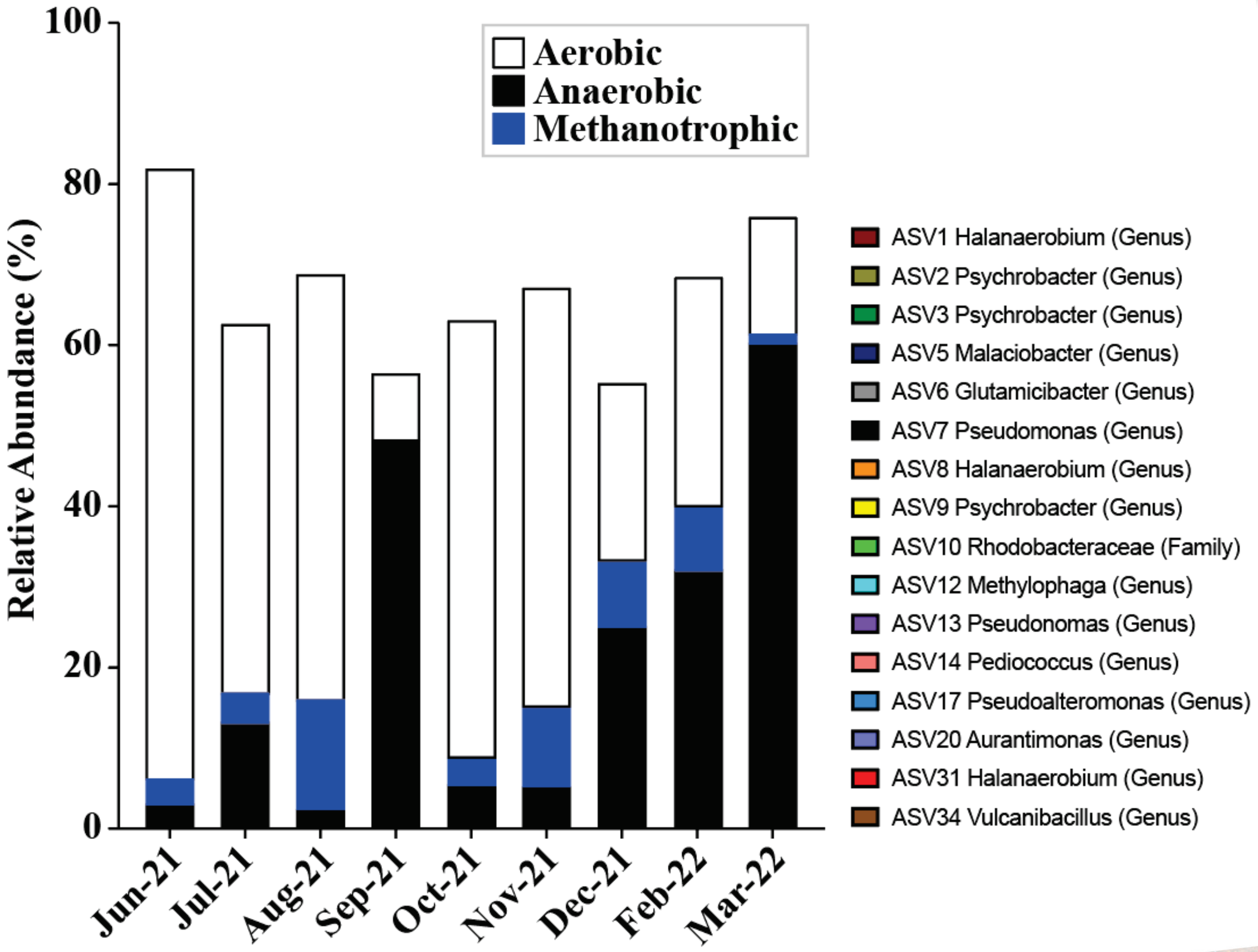
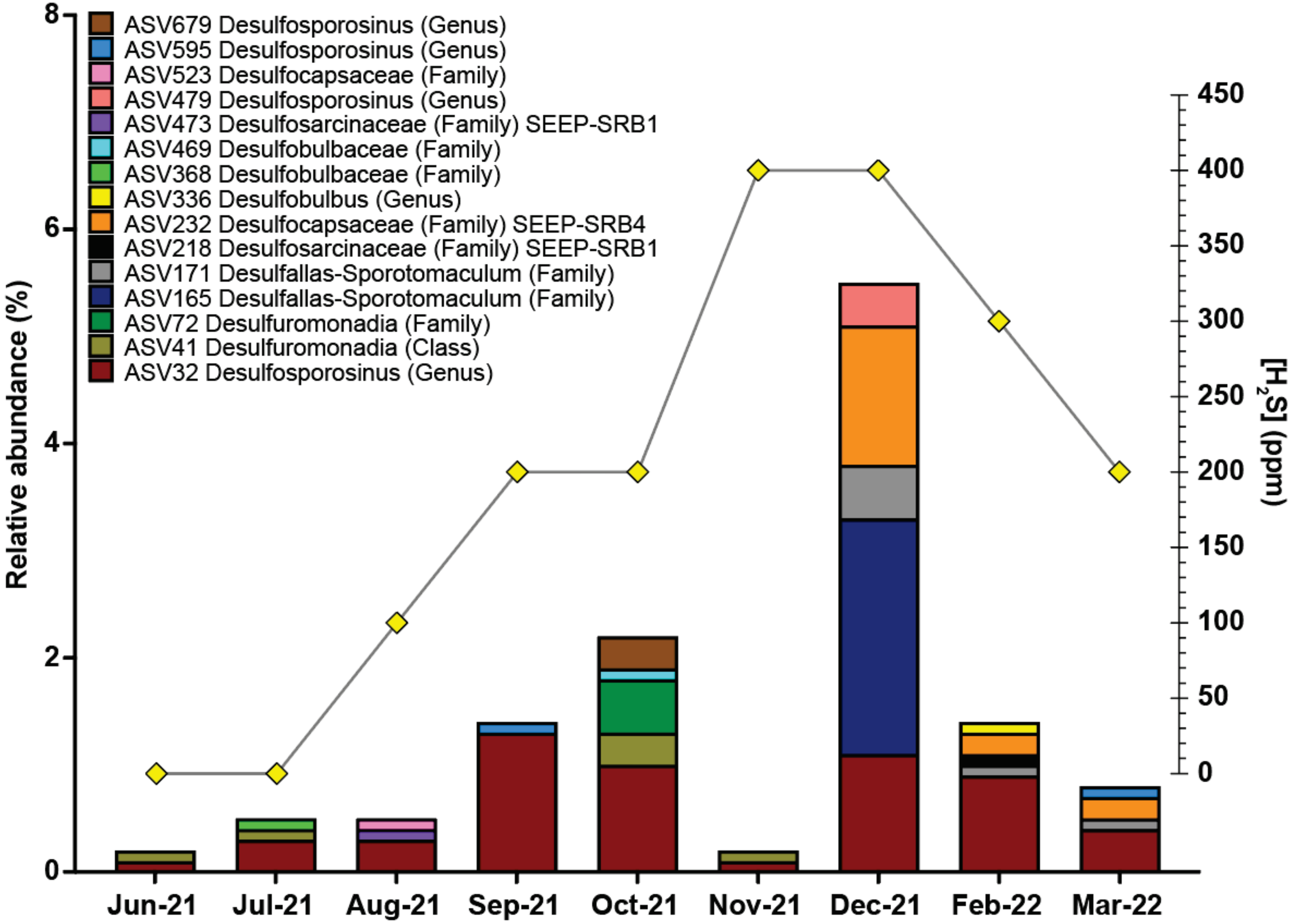


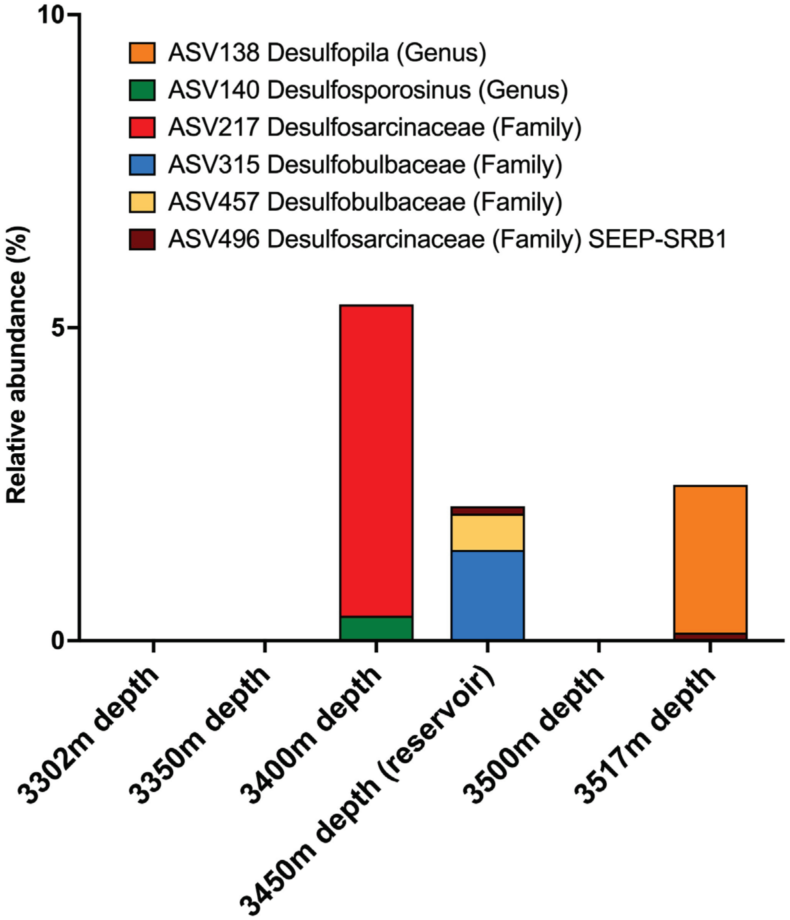
# Time series of SRM abundances

- Abundances of SRM variable over time
- Peak SRM abundances coincides with maximum [$H_2S$] in the gas stream
- Further evidence of microbial sulfate reduction and biological formation of $H_2S$ via MSR processes

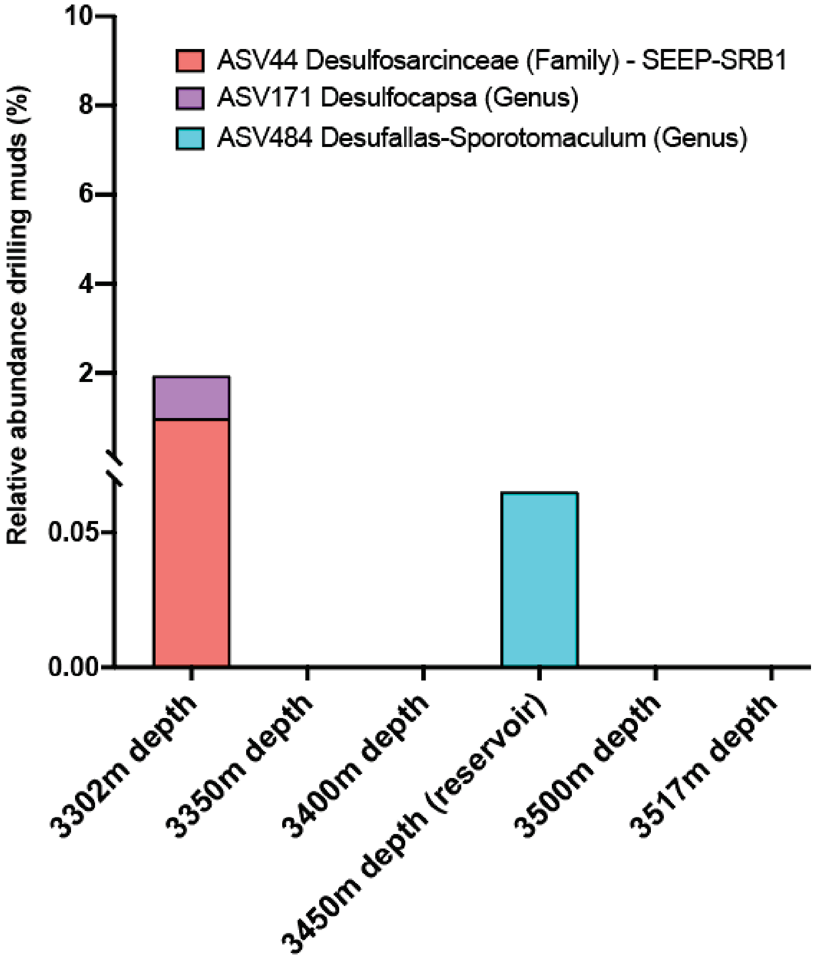


# Where do SRMs come from: endemic or introduced?

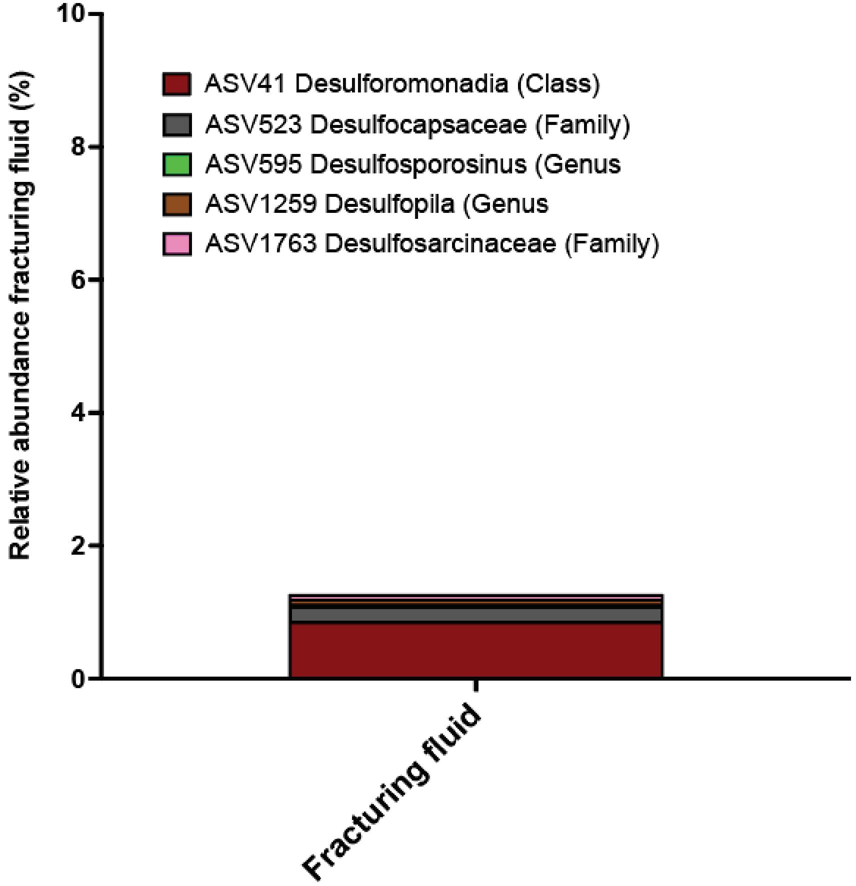
## Drill cuttings




## Drilling muds




## Fracturing fluid



# Conclusions

- Water isotope modeling indicates initial produced fluids are ~60% HFF suggesting a dilution of biocide in the subsurface
- Sulfur isotope fingerprinting of sulfur sources suggests that *in situ* sulfate cements are the most likely source of sulfate in produced waters
- Sulfur isotope fractionation between sulfate and sulfide in produced water strongly suggests $H_2S$ is produced *in situ* via MSR
- Microbial rRNA analysis shows SRM are present and occur in varying abundance over the course of produced water sampling
  - Abundance of SRM is strongly correlated with $H_2S$ concentrations in produced gas
- Differences between microbial populations in drilling muds and drill cuttings provides evidence of potentially endemic versus introduce species
- We suggest that hydraulic fracturing process results in the injection of nutrients into a nutrient-limited deep biosphere stimulating biological activity and promoting $H_2S$ production

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