### Hydrogen Sulfide (H<sub>2</sub>S) in the Permian Basin\*

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#### **Abstract**

Hydrogen sulfide (H<sub>2</sub>S) is a hazardous and toxic gas component, which increases the cost of oil and gas exploration, development and production. Meanwhile, H<sub>2</sub>S is a natural tracer reflecting hydrocarbon flows during geological period and during production. Investigating and understanding the distribution of H<sub>2</sub>S concentration may increase the reliabilities of H<sub>2</sub>Srisk prediction and hydrocarbon resource assessment. In this work, we focus on the interpretation of H<sub>2</sub>S in the Permian Basin (western Texas and southeastern New Mexico). H<sub>2</sub>S concentration in natural gas (associated or non-associated) produced from the Permian Basin varies from several parts per million (ppm) to over 100,000 ppm (10 %) volumetrically. Over 85% of the gas streams are H<sub>2</sub>S-rich (>100 ppm), and over 40% of the gas streams are extremely rich in H<sub>2</sub>S (>10,000 ppm, or 1 %). H<sub>2</sub>S-rich gas exists in both conventional and unconventional reservoirs, and in all sub-basins and shelf areas. Generally, H<sub>2</sub>S concentration is higher in the shallower formations (Guadalupian) than in the deeper ones (Leonardian and Wolfcampian), and it is higher in the Central Basin Platform than in the Midland and Delaware sub-basins. The high concentration levels indicate that the main source of H<sub>2</sub>S is neither bacterial sulfate-reduction (BSR) nor the reactions involving sulfate components in drilling fluids. Consequently, modifying drilling fluids or adding biocides (to kill sulfate-reducing bacteria) has no impact on H<sub>2</sub>S concentration. The general trend of decreasing H<sub>2</sub>S concentration with thermal maturity and with gas-to-oil ratio (GOR) indicates that H<sub>2</sub>S is unlikely from thermochemical sulfate-reduction (TSR). The widely spread anhydrite and gypsum layers in the Permian formations are not a significant source of H<sub>2</sub>S due to the low thermal stress experienced by these formations. Cracking of Type IIS kerogen during source rock maturation is most likely the main source of H<sub>2</sub>S in the Permian Basin. H<sub>2</sub>S vertical distribution along the boundary of the Central Basin Platform reflects fluid migration paths. The increase of H<sub>2</sub>S

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concentration during the course of production could be due to the heterogeneous distribution of  $H_2S$  in the reservoir, and to the adsorption of  $H_2S$  on fresh rock surfaces after hydraulic fracturing.

### **References Cited**

Hill, C.A., 1995, H<sub>2</sub>S related porosity and sulfuric acid oil-field karst: AAPG Memoir 63, p. 301-305.

Xia, D., and G.S. Ellis, 2016, Coupled Kinetic and Fluid Dynamic Models to Understand H<sub>2</sub>S Occurrence in Unconventional Petroleum Reservoirs: Theme 5: Understanding Petroleum System Chemistry from Source Rocks to Produced Hydrocarbons II: URTeC, August 1-3, 2016, San Antonio, TX.







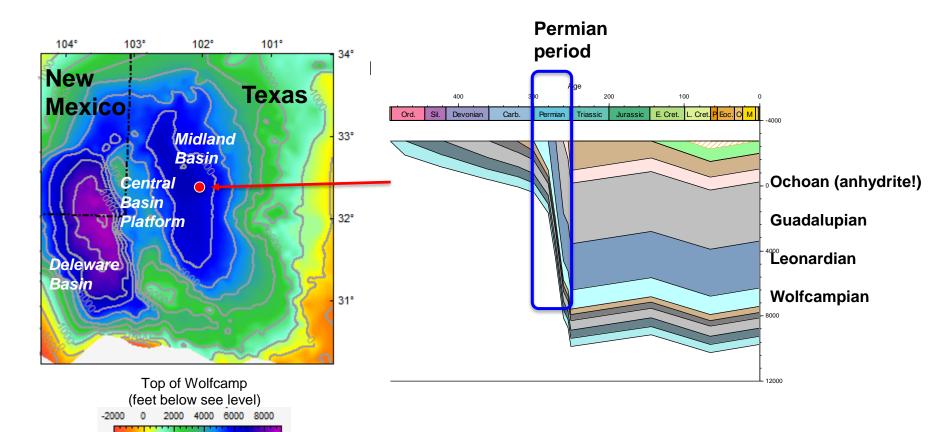
# Hydrogen Sulfide (H<sub>2</sub>S) in the Permian Basin

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### **Geology of Permian Basin**

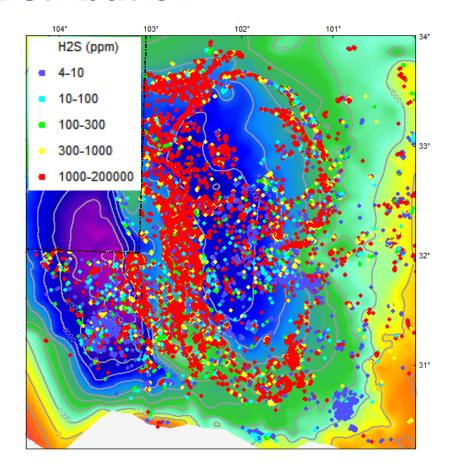


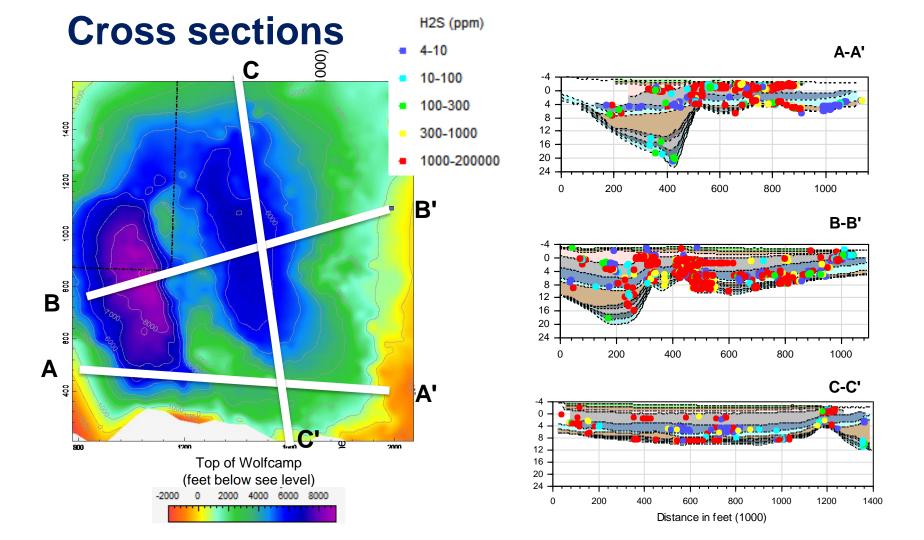
### H<sub>2</sub>S Data

- Data source: Texas Railroad Commission (RRC)
- ~40,000 data points
- Analysis time: 1976 2016
- Location & depth assigned based on our Trinity project
- Reservoir types:
  - Conventional & unconventional
  - Clastic & carbonate rocks
  - Vertical & horizontal wells

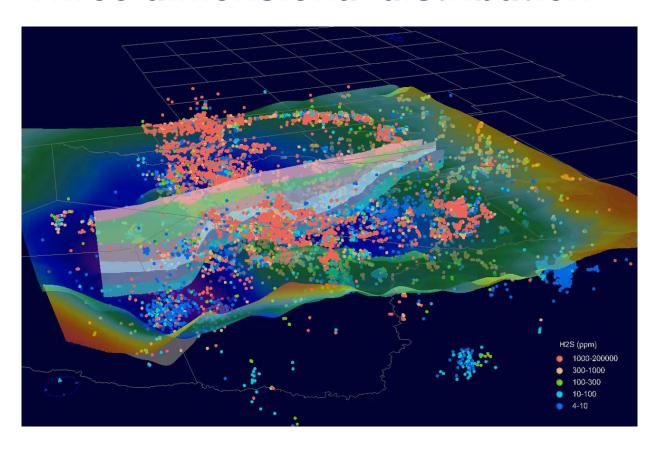
### **Lateral distribution**

- H<sub>2</sub>S-rich gas more concentrated in shallow locations:
  - Central-basin platform
  - Reefs



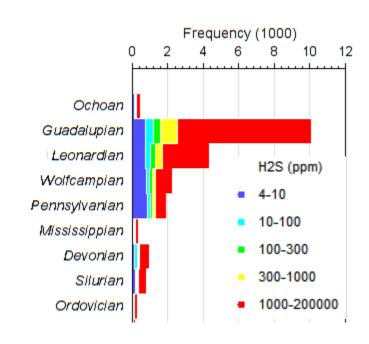


### Three dimensional distribution



## H<sub>2</sub>S distribution by reservoir age

- H<sub>2</sub>S-rich (>300 ppm)
   gas exists in all layers
- Younger formations more enriched of H<sub>2</sub>S
  - Unlikely due to TSR (thermochemical sulfate reduction)

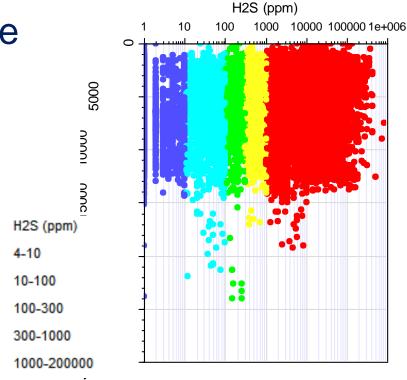


## H<sub>2</sub>S distribution by reservoir depth

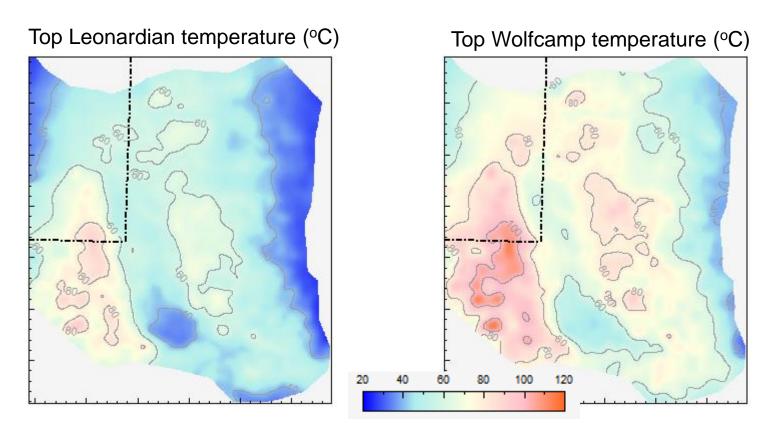
H<sub>2</sub>S-rich samples more concentrated in

Unlikely due to TSR

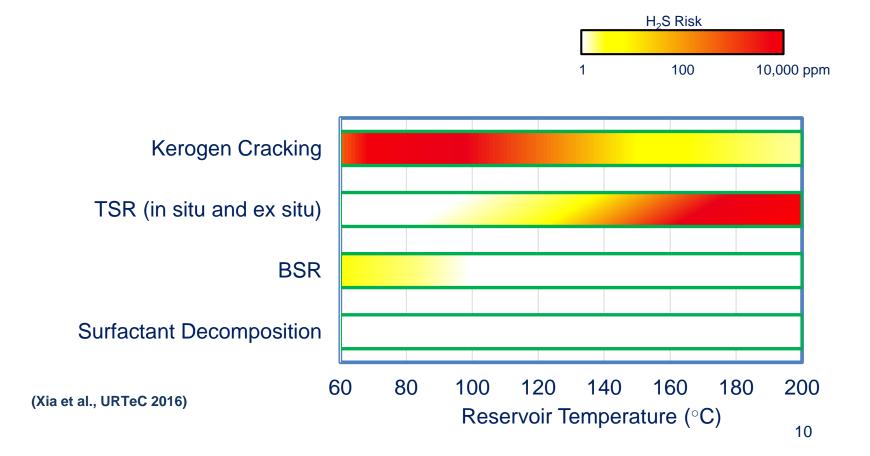
shallower depths



## **Current reservoir temperature: lower than TSR onset temperature**



### Possible H<sub>2</sub>S sources in shale plays

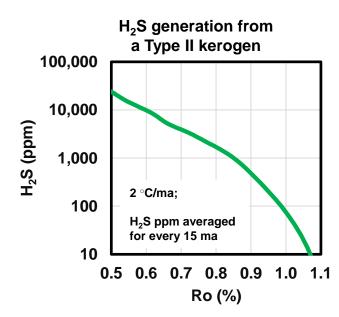


## Possible sources of H<sub>2</sub>S in Permian Basin

- Bacterial sulfate reduction: <u>unlikely</u>
  - Large amount of samples with H<sub>2</sub>S concentration over 10%
  - Similar trend in Eagle Ford, anhydrate absent!
- Reduction of anhydrite in Upper Permian anhydrite: <u>unlikely</u>
  - Low thermal stress
- Thermochemical sulfate reduction in deep layers:
  - Proposed by an early study (C. Hill, 1995)
  - Inconsistent to H<sub>2</sub>S vertical distribution
  - Unlikely
- Kerogen cracking: most likely

### Kerogen & bitumen cracking

- Sulfur abundant in carbonate source rock & bitumen
- C-S easier to break than C-C bonds
- H<sub>2</sub>S concentration <u>decreases</u> with thermal maturity



### Is there enough sulfur in kerogen?

CH<sub>4</sub> generation at low thermal maturity:

```
< 100 \text{ mL/g}_{TOC}, or < 70 \text{ mg}_{HC}/g_{TOC}
```

For 10 vol% H<sub>2</sub>S in natural gas:

corresponding to

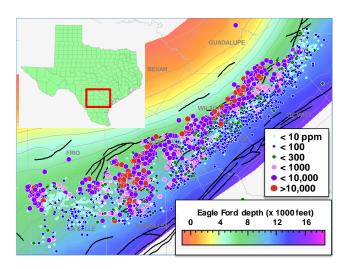
```
S wt% = 1.4%;
```

- atomic S:C = 0.005
- Not type IIS kerogen yet!
  - Type IIS kerogen: S wt% 8-14 %; atomic S:C ≥ 0.04

### Why data more messy than in Eagle Ford

- Shape:
   two basins vs. one monocline
- Thermal maturity window: narrow (Ro < 1.5 in Permian) vs. wide (Ro up to 2% in Eagle Ford)
- Reservoir layers: multiple vs. single
- Migration distance: long vs. short



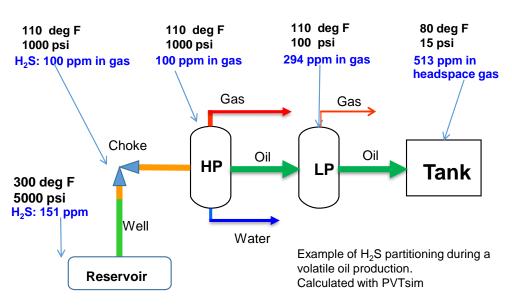


(Xia et al., URTeC 2016)

## H<sub>2</sub>S partitioning between different phases

 H<sub>2</sub>S more enriched in gas phase when pressure decreases

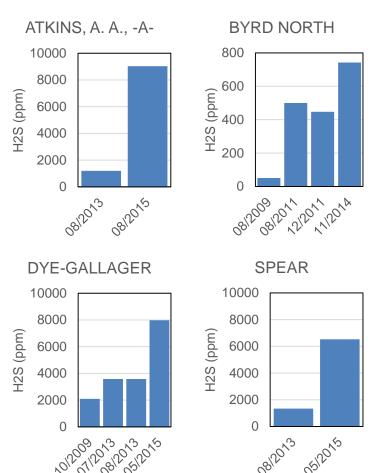
 H<sub>2</sub>S ppm in headspace gas of oil tank is high



(Xia et al., URTeC 2016)

## H<sub>2</sub>S ppm change with time

- May increase during production
  - Common in recent horizontal wells
- Mechanism:
  - Adsorption on fresh rock surfaces
  - Delayed flux from H<sub>2</sub>S-rich layer
     (Xia et al., URTeC 2016)



### **Conclusions**

- H<sub>2</sub>S in the Permian Basin:
  - More enriched in shallower reservoirs
  - Distribution mainly controlled by thermal maturity
  - Mainly from kerogen cracking (not necessarily Type IIS kerogen)
- Similar to observation in Eagle Ford
- H<sub>2</sub>S from kerogen cracking is common
  - Eagle Ford, Permian, Madison group (above Bakken), ...
  - Need to pay more attention (compared with TSR)

### **Acknowledgements**

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  - Dr. Changrui Gong (Apache)
  - Prof. Sun Yongge (Zhejiang University)