

# Sulfur

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# Outline

- 1 Sulfur Allotropes
- 2 Technological Applications
- 3 Sulfate Reducing Bacteria
  - Biofilms
  - Sulfur Elsewhere

# Volcanic sulfur



# Sulfur as a Commodity

## Commercial sources of sulfur

- Sulfur is pale yellow, odorless, brittle solid, which is insoluble in water but soluble in carbon disulfide
- Sulfur is used in the vulcanization of natural rubber
- Sulfur is also used extensively in making phosphatic fertilizers
- A tremendous tonnage is used to produce sulfuric acid

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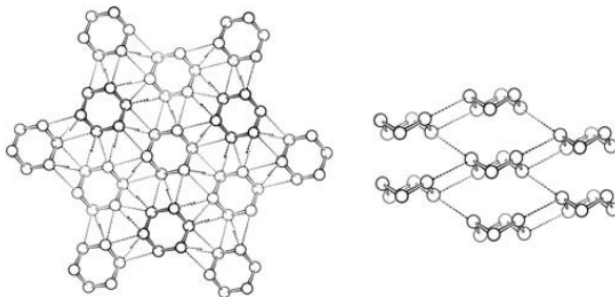
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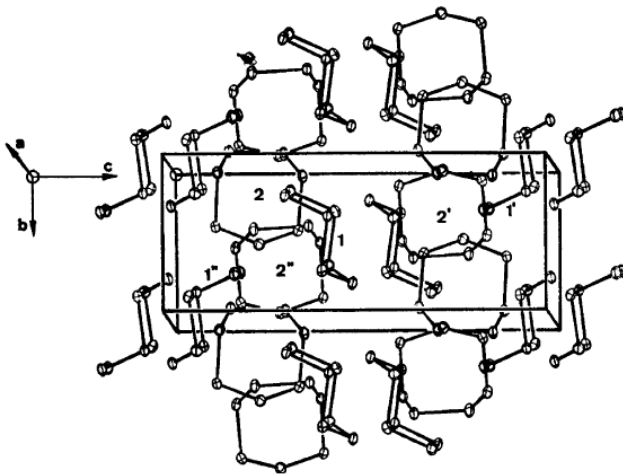
# Synthetic Sulfur Allotropes

$S_6$  is densely packed with close intermolecular contacts



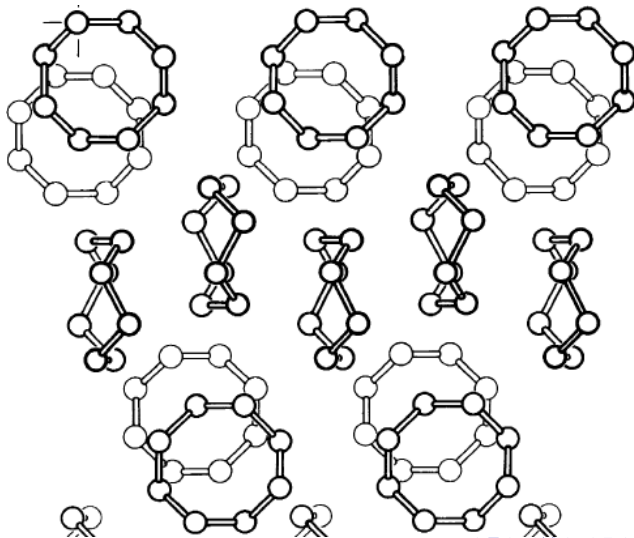
# Synthetic Sulfur Allotropes

$S_{7-\delta}$  is less densely packed with close intermolecular contacts



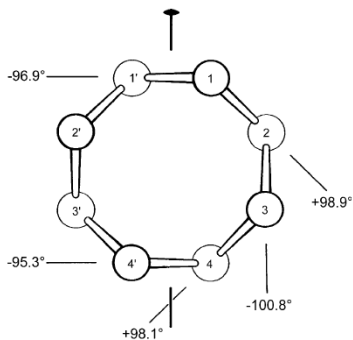
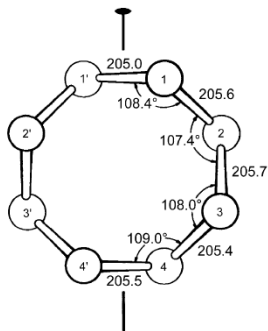
# Orthorhombic $\alpha$ -Sulfur

$S_8$  is the most stable form of sulfur



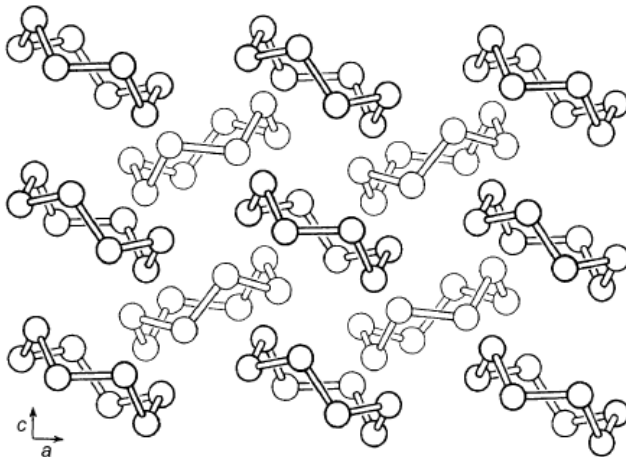
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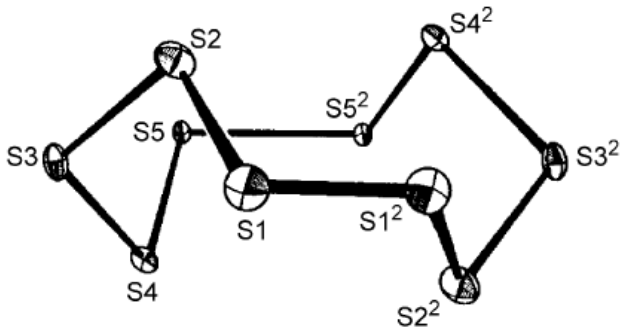
# $\gamma$ -Sulfur

$\gamma$ -S<sub>8</sub> exhibits a "sheared pennyroll" packing motif



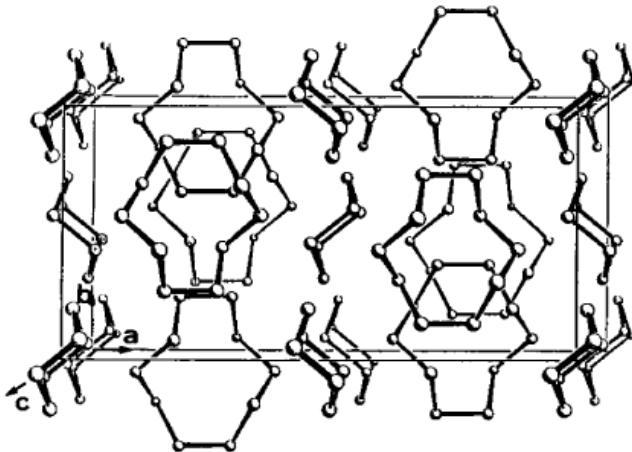
# Molecular Decasulfur

Wouldn't this make a great point group question?

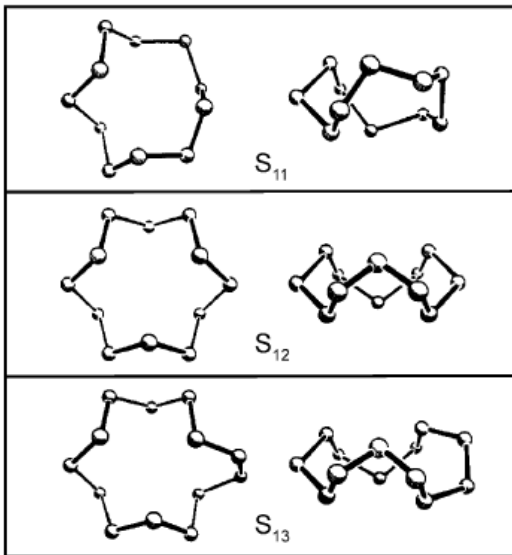


# $S_6 \cdot S_{10}$

An allotrope consisting of two different molecular forms of an element

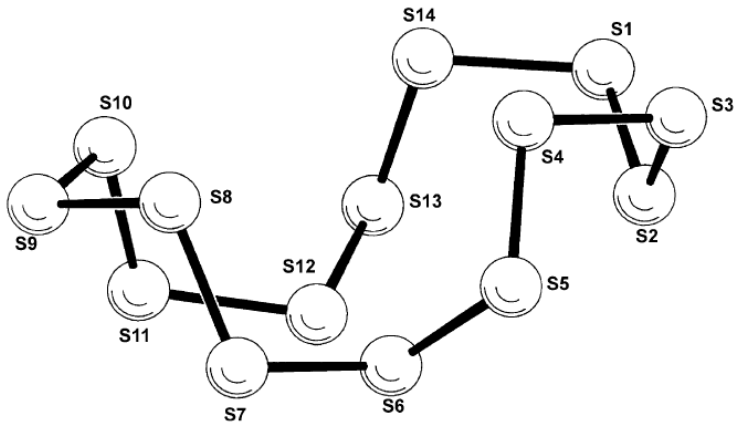


# Larger Sulfur Rings

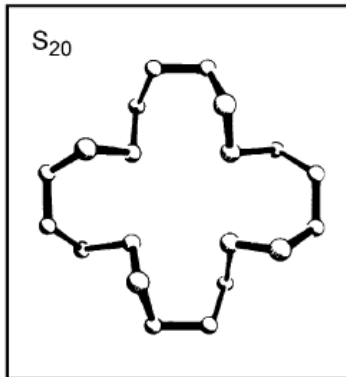
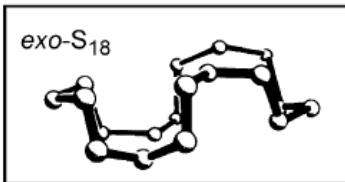
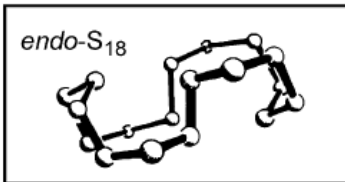




# S<sub>14</sub>, Tetradecasulfur

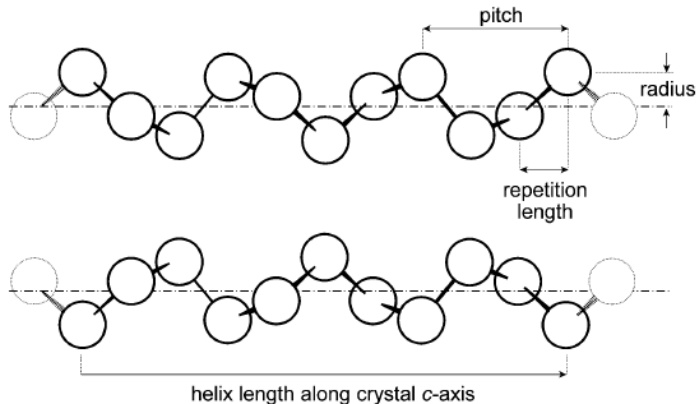


# S<sub>18</sub> and S<sub>20</sub>



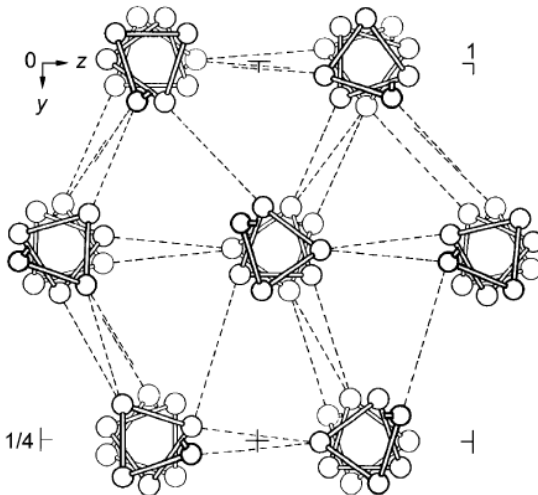
# Fibrous Sulfur

This allotrope exhibits infinite helical chains of sulfur



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# Lithium Sulfur Batteries

## Carbon@Sulfur Composites for High-Power Lithium Sulfur Batteries

- Among cathode materials for secondary lithium batteries, elemental sulfur has the highest theoretical capacity,  $1672 \text{ mA h g}^{-1}$
- This is at least ten times greater than that of commercially used transition-metal phosphates and oxides
- The electrochemical redox reaction:  $16\text{Li} + \text{S}_8 \rightleftharpoons 8\text{Li}_2\text{S}$
- Lithium-Sulfur is considered a promising candidate for electric and hybrid electric vehicles

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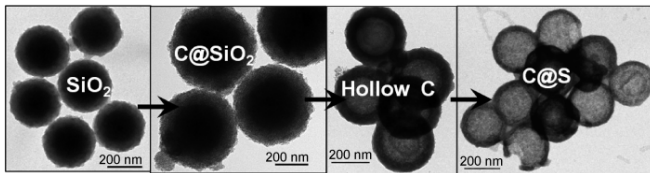
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# C@S Nanocomposites

TEM images of mesoporous, hollow carbon capsules generated by a template-based approach



# Sulfur-Containing Polymers

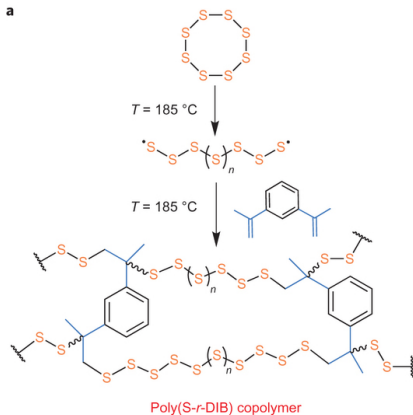
Elemental sulfur is a byproduct of petroleum refining (HDS)





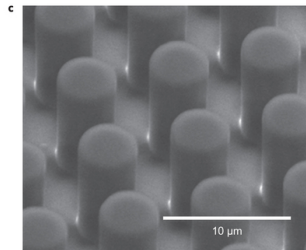
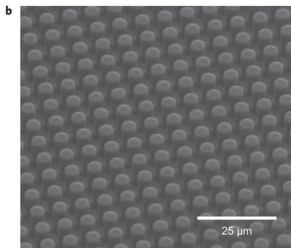
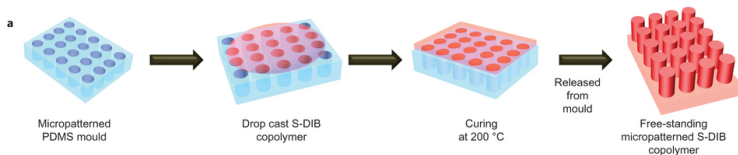
# Sulfur-Containing Polymers

A new process given the name "inverse vulcanization"



# Sulfur-Containing Polymers

Imprint lithography of poly(S-r-DIB) copolymers to form micropatterned films with 70% S



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# Sulfate Reducing Bacteria

One of the oldest forms of life on Earth

- They can be traced back billions of years in the geologic rock record to the Early Archean (3900 to 2900 million years ago)
- Oxygen concentrations in Earth's atmosphere were low
- Ancient sulfate-reducing bacteria left their first mark on their environment in pyrite minerals ( $\text{FeS}_2$ ) as old as 3400 million years
- Today, these microorganisms are widespread in marine and terrestrial aquatic environments
- Their ability to adapt to extreme physical and chemical conditions enables them to play an important role in global geochemical cycles
- There is evidence of their role in the generation of ore deposits

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- Sulfate-reducing bacteria can tolerate low levels of oxygen and can precipitate zinc sulfide minerals
- The sulfur cycle was strongly correlated with the carbon cycle throughout geologic history because the two cycles are intrinsically connected through microbial metabolism
- The sulfur cycle thus constitutes one of the best examples of the impact exerted by living organisms on geochemical cycles
- Sulfate-reducing bacteria use sulfate mainly as an electron acceptor (without assimilating sulfur) in the anaerobic oxidation of inorganic or organic substrates such as  $\text{H}_2$  +  $\text{CO}_2$ , lactate, acetate, and propionate

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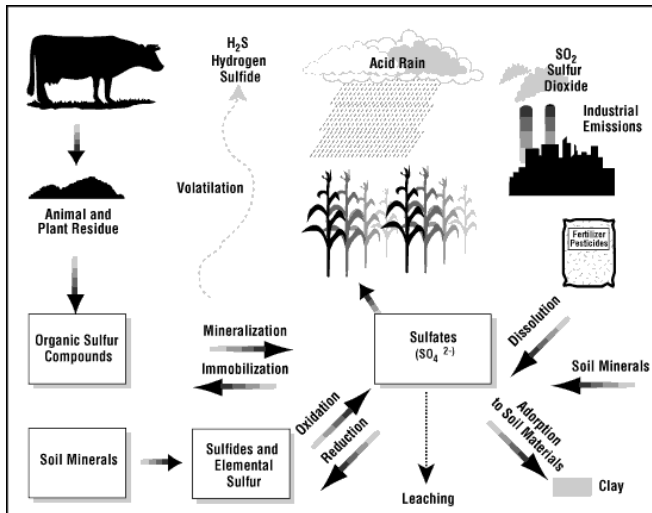


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# The Sulfur Cycle



# Sulfate Reducing Bacteria

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- As a consequence of their metabolism, large amounts of reduced sulfide ions are produced and accumulated in their natural habitats
- The sulfide ions combine with available metal ions to form insoluble products, most commonly  $\text{FeS}_2$ , leading to the production and transformation of natural mineral deposits
- Using scuba divers to gain access to a flooded mine tunneled into a Pb-Zn ore deposit, Labrenz et al. were able to retrieve samples containing microbial biofilms
- They demonstrated that the collected aerotolerant sulfate-reducing bacteria assemblage has the ability to form a pure precipitate of sphalerite ( $\text{ZnS}$ )

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- This observation has interesting implications for understanding how economic ZnS deposits may have formed
- Bacteria could be used to remove trace metals, such as Zn, As, or Se, from contaminated drinking water!
- Sulfate-reducing bacterial assemblages can accumulate metals to form a valuable ore deposit ( $\text{PbS}$ ,  $\text{ZnS}$ , or  $\text{FeS}_2$ ) while simultaneously promoting the dolomitization ( $\text{CaMg}(\text{CO}_3)_2$ ) of the host rock

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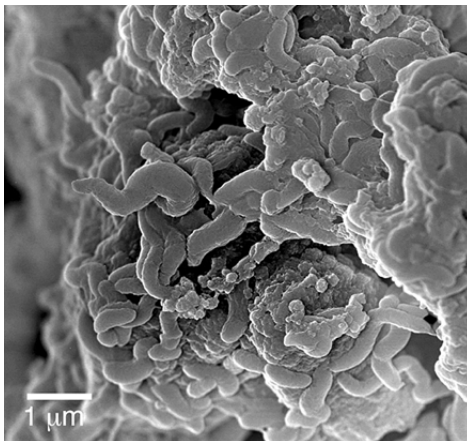
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# The role of microbes in ore deposit formation

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Scanning electron microscopy image of sulfate-reducing bacteria that are intimately associated with dolomite crystals

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