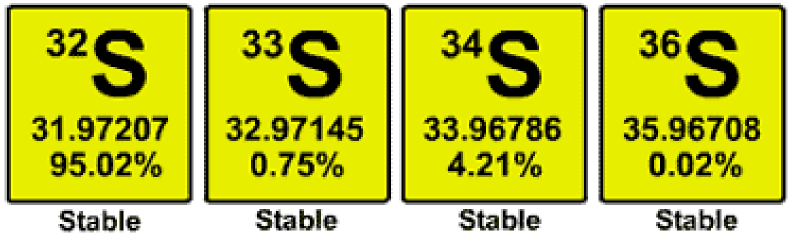
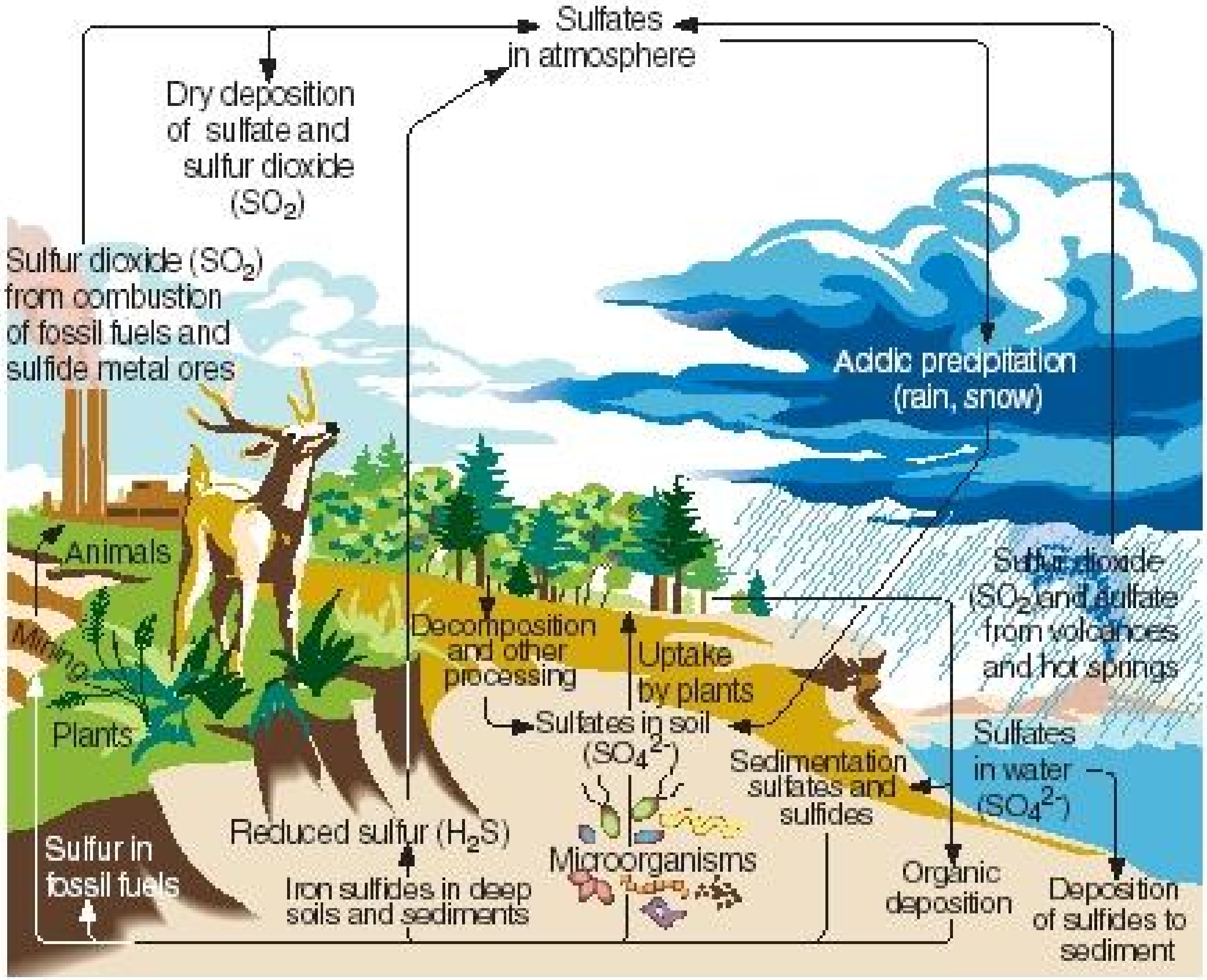
Sumpor



^{32}S
31.97207
95.02%
Stable
^{33}S
32.97145
0.75%
Stable
^{34}S
33.96786
4.21%
Stable
^{36}S
35.96708
0.02%
Stable



Sulfates in atmosphere
Dry deposition of sulfate and sulfur dioxide (SO_2)
Sulfur dioxide (SO_2) from combustion of fossil fuels and sulfide metal ores
Acidic precipitation (rain, snow)
Animals
Mining
Plants
Sulfur in fossil fuels
Decomposition and other processing
Uptake by plants
Sulfates in soil (SO_4^{2-})
Sulfur dioxide (SO_2) and sulfate from volcanoes and hot springs
Sulfates in water (SO_4^{2-})
Sedimentation sulfates and sulfides
Reduced sulfur (H_2S)
Microorganisms
Iron sulfides in deep soils and sediments
Organic deposition
Deposition of sulfides to sediment

δ-notacija:

$$\delta^{34}S = \left(\frac{\left({}^{34}S/{}^{32}S\right)_{uzorak} - \left({}^{34}S/{}^{32}S\right)_{standard}}{\left({}^{34}S/{}^{32}S\right)_{standard}} \right) \times 1000\ ‰$$

α-notacija:

$$\alpha = \frac{\left({}^{34}S/{}^{32}S\right)_{uzorak1}}{\left({}^{34}S/{}^{32}S\right)_{uzorak2}}$$

$$1000 \ln \alpha = \delta_1 - \delta_2$$

Standard: Troilit (FeS) iz željeznog meteorita (Cañon Diablo, Arizona)
$^{32}S/^{34}S=22,22$ *(sumpor iz bazičnih stijena ima gotovo identičan sastav)*

Kem. sastav: 7,1% Ni, 0,46% Co, 0,26% P, ~ 1% C, ~ 1% S, 80 ppm Ga, 320 ppm Ge, 1,9 ppm Ir.
Vrijeme pada: Prije 20.000 – 40.000 god.

Fe-meteorit pronađen 1891 u Cañonu Diablo, Arizona

Frakcionacija:

1. Redukcija sulfata anaerobnim bakterijama

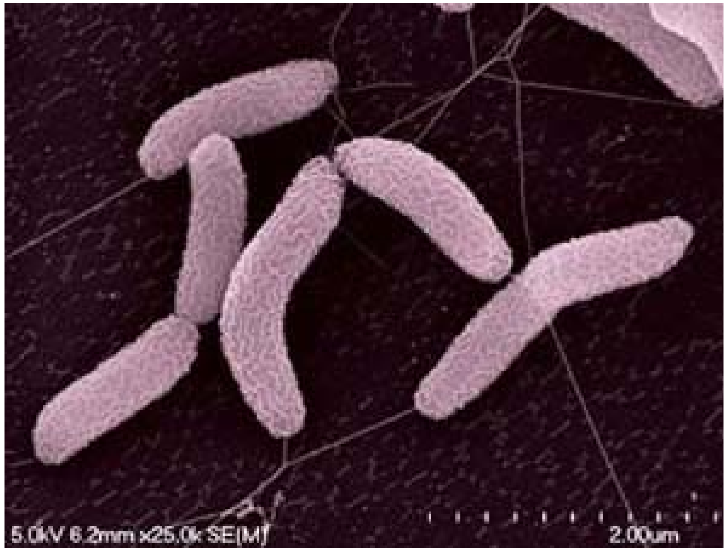
$$SO_4^{2-} + C_{org} \leftrightarrow H_2S + CO_2 + H_2O$$

$$\xrightarrow[\textit{obogaćenje na } ^{32}S]{\textit{bakterije}}$$

2. Ravnotežne reakcije izmjene (^{34}S se koncentrira u spojevima s višim oksid. stanjem)

Biogena frakcionacija

Desulfovibrio desulfuricans
anaerobna bakterija, sulfat služi kao oksidans



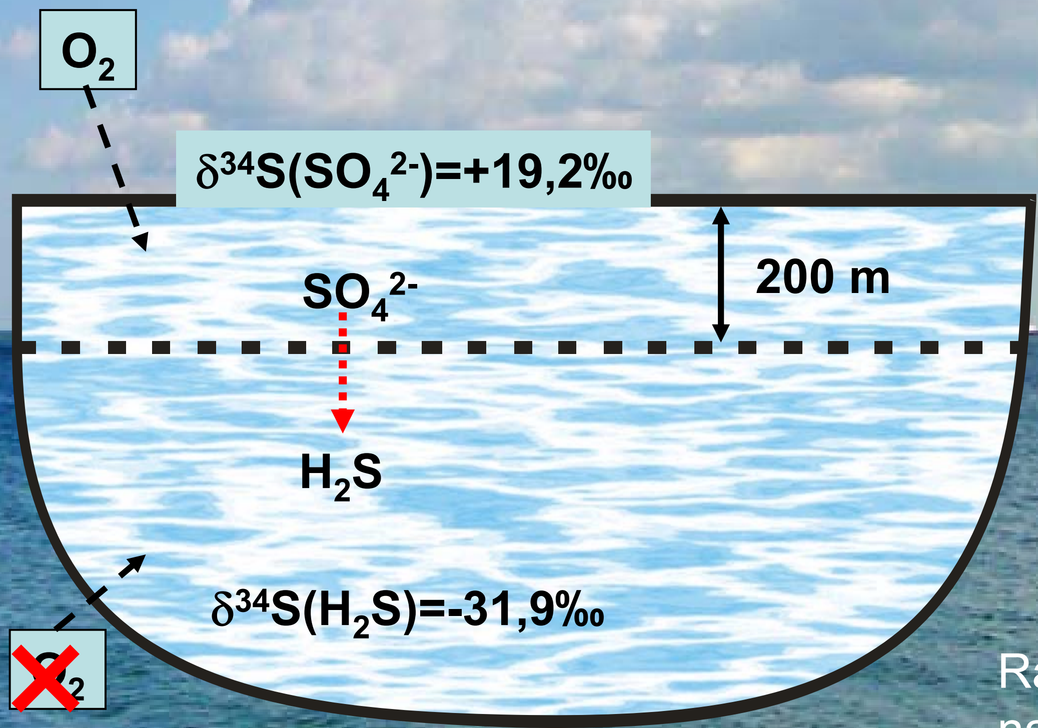
$$^{34,32}SO_4^{2-} + C_{org} \underset{\textit{bakterije}}{\leftrightarrow} {}^{32,34}H_2S + H_2O + CO_2 + \text{Energ.}$$

$$O_2 + C_{org} \leftrightarrow H_2O + H_2O + CO_2 + \text{Energ.}$$ (aerobne bakterije i životinje)

Stupanj frakcionacije: - različit i zavisi o vrsti hrane, količini SO_4^{2-}, temperaturi, itd.
- prosječno 40-50‰, a u laboratoriju i do 75‰

Otvoreni sustav:

Npr. Crno more



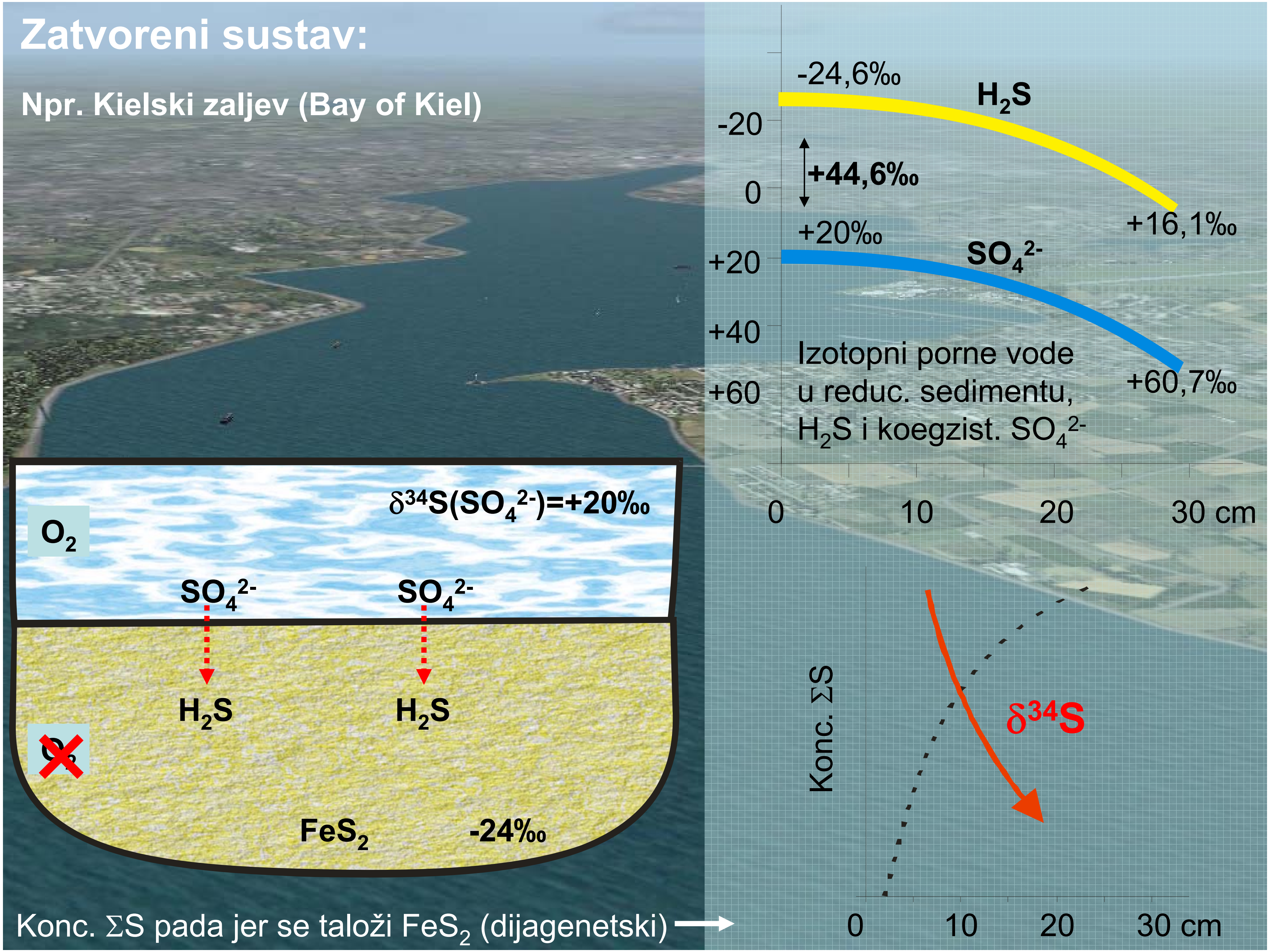
$\Delta_{(SO4,\ H2S)} = \delta^{34}S(SO_4^{2-}) - \delta^{34}S(H_2S)$

$= konst$

$= (+19,2\ ‰) - (-31.9\ ‰)$

$= 51.1\ ‰$

Razlika je konstantna jer se sulfat trajno nadoknađuje u otvorenom sustavu


Zatvoreni sustav:
Npr. Kielski zaljev (Bay of Kiel)
δ34S(SO42-)=+20‰
O2
SO42-
SO42-
H2S
H2S
O2
FeS2
-24‰
Konc. ΣS pada jer se taloži FeS2 (dijagenetski)
-24,6‰
H2S
-20
+44,6‰
0
+16,1‰
+20‰
SO42-
+20
+40
Izotopni porne vode
u reduc. sedimentu,
H2S i koegzist. SO42-
+60,7‰
+60
0
10
20
30 cm
Konc. ΣS
δ34S
0
10
20
30 cm

Fosilna goriva

Nafta

- Sadrži od 0,1 do 10% S
- Nafta iz istog ležišta ima konst. $\delta^{34}S$
- Nafte različite starosti mogu imati značajno različite $\delta^{34}S$
- H_2S is nafte sličan $\delta^{34}S$ (*nema frakcionacije*)
- H_2S, $\delta^{34}S \approx 15‰$ manji od suvremenog sulfata u moru (*budući da se sulfat mijenja su geol. starošću, možemo razmišljati o matičnoj stijeni iz koje je nastala nafta ili o putevima kroz koje je prošla na putu u sadašnji rezervoar*)

Ugljen

- Sadrži do 20% S
- Sumpor je prisutan kao pirit, markazit, Pb, Zn, Cu-sulfidi, organski sumpor (*npr. Raški ugljen sadrži do 10% organski vezanog sumpora*)
- $\delta^{34}S_{(ugljen)} \approx -30$ do $+24‰$ (zavisno o porijeklu npr. marinsko vs. terestričko)

Izotopna evolucija marinskog sulfata

- Oceani sadrže 1,3×10^{6} milijardi tona sumpora u obliku sulfata
- Moderni oceani $\delta^{34}S(SO_4^{2-})$= +20 ‰
- U fanerozojskim sulfatima (a time i u oceanu) δ^{34}S varira u širokom rasponu (*npr. +30 ‰ u kambriju, +10 ‰ u permu, +20 ‰ danas*)

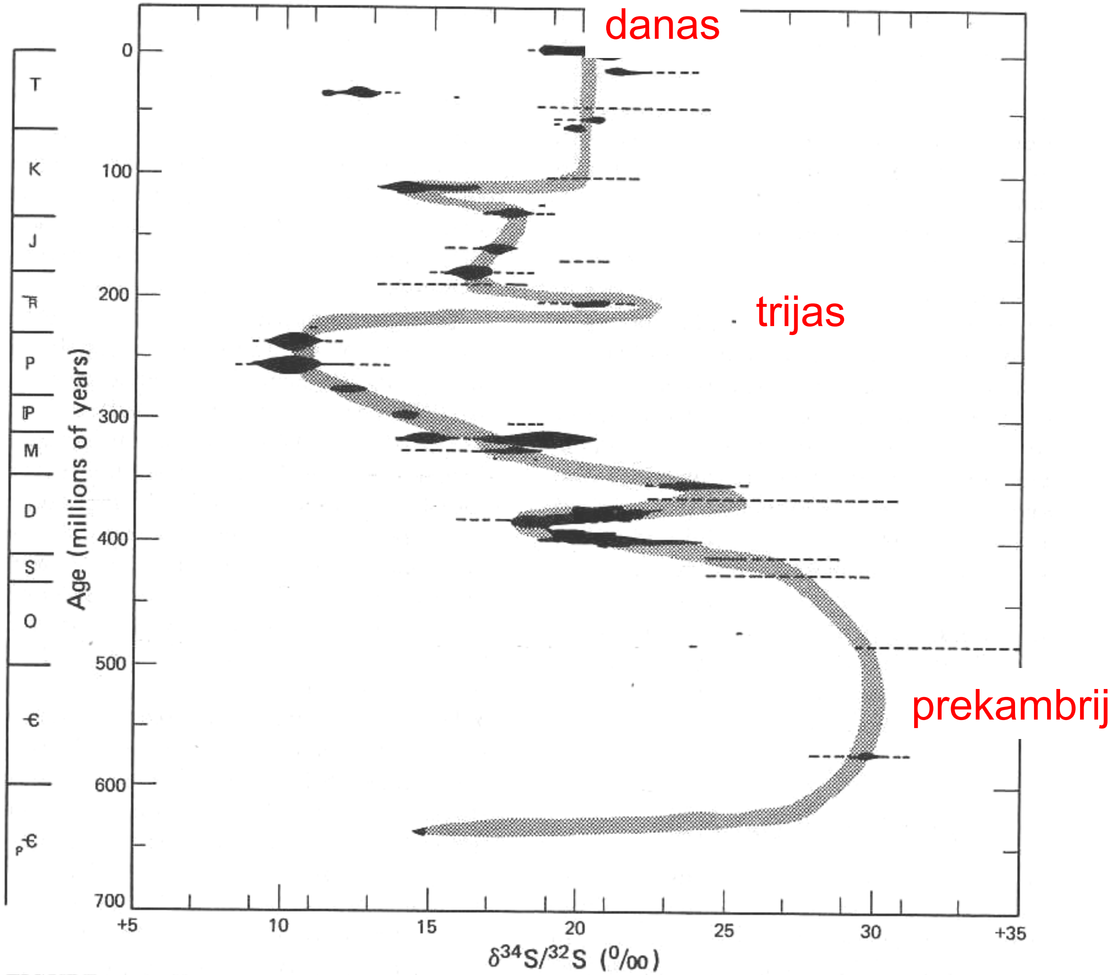


FIGURE 21.2 Variation of the isotopic composition of marine sulfate during Phanerozoic time. (Reproduced from Figure 5 (p. 120) of Holser, W. T. and I. R. Kaplan, Chemical Geology, vol. 1, No. 2, 93–135, 1966, by permission of Elsevier Scientific Publishing Co.)

Sulfidna rudna ležišta

Rane nade da ćemo određivanjem izotopnog sastava sulfida prepoznati da li su ležišta sulfida sedimentna ($\delta^{34}S<0‰$) ili magmatska ($\delta^{34}S\approx0‰$) izjalovila su se.

Npr. Singenetska, dijagenetska i epigenetska sedimentna ležišta mogu pokazivati široku lepezu $\delta^{34}S$ vrijednosti ovisno o razvoju u “otvorenom” ili “zatvorenom” sustavu.

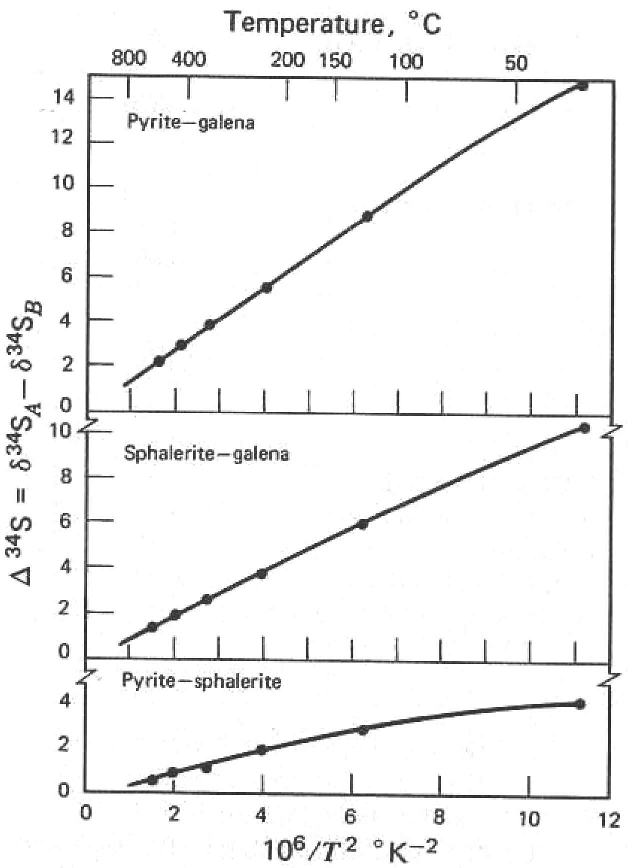
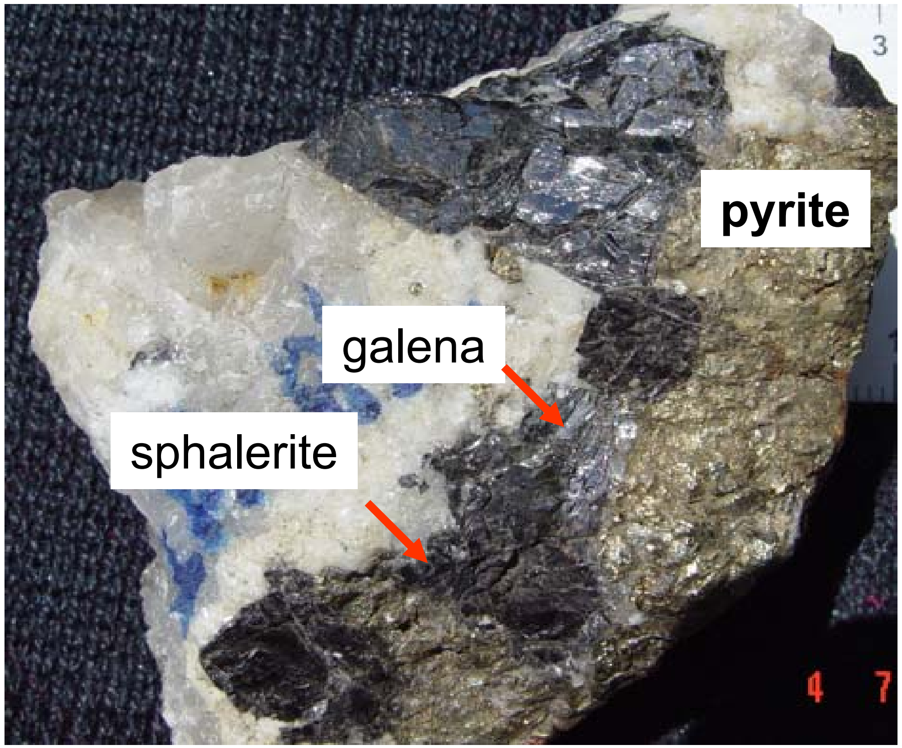


FIGURE 21.3 Fractionation of sulfur isotopes among cogenetic mineral pairs as a function of temperature, based on calculated values of isotope equilibrium constants by Sakai (1968).

^{34}S-Me: čvrstoća veze opada u nizu Py>Sph>Chp>Gn

To je razlog frakcionacije ukoliko se taložе iz iste H_2S otopine (kogenetski minerali)



Geotermometrija

- Najpouzdaniji par su sfalerit – galenit
- Pirit – galenit je najosjetljiviji par, ali rijetko u
-prirodi dolazi "kogenetski"

$$\Delta^{34}S_{AB} = A \times 10^{6} * T^{-2}$$

A - konstanta

$$\Delta^{34}S_{AB} = \delta^{34}S_{A} - \delta^{34}S_{B}$$

Table 21.2 **Isotope Fractionation of Sulfur Among Coexisting Sulfide Minerals in Isotopic Equilibrium with an External Sulfur Reservoir**[a]

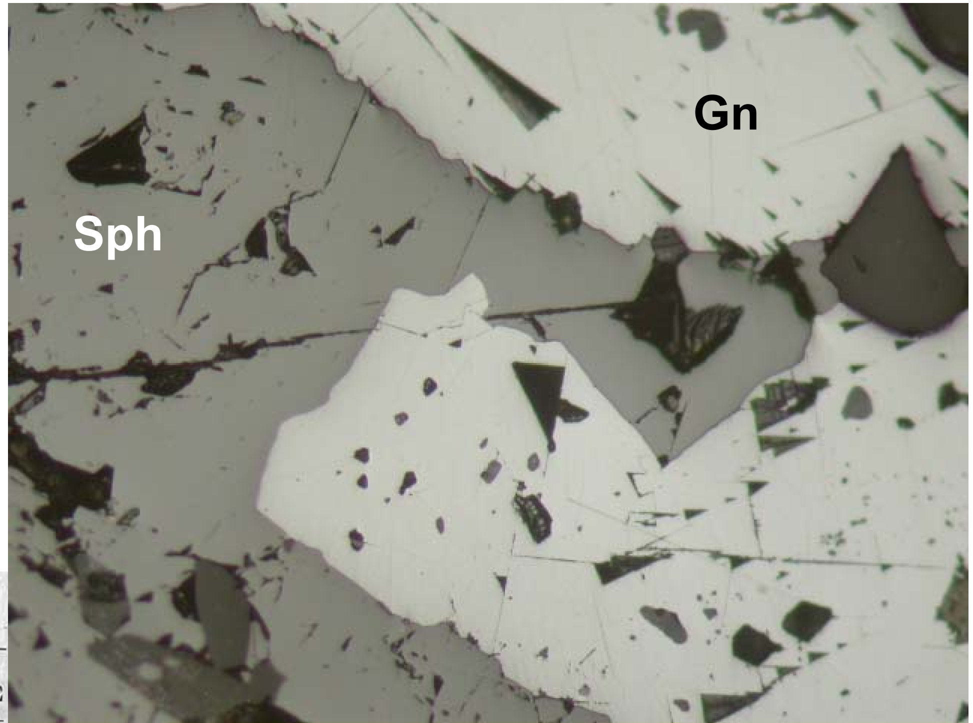
MINERAL PAIR	A	TEMPERATURE RANGE, °C	REFERENCE
Pyrite-galena	1.319	27–527	1
	~0.9	340–690	2
	1.10	250–600	3
Sphalerite-galena	0.963	27–527	1
	~0.62	340–690	2
	$\sim 0.66 \times 10^{6} T^{-2} - 0.1$		2 by 4
	0.80	250–600	3
	0.70	275–600	4
	~0.78	0–1000	5
Pyrite-sphalerite	0.356	27–527	1
	~0.26	340–690	2
	0.30	250–600	3
Chalcopyrite-galena	0.65	250–600	3
Pyrite-chalcopyrite	0.45	250–600	3
Pyrite-pyrrhotite	0.30	250–600	3
Sphalerite-chalcopyrite	0.15	250–600	3
Pyrrhotite-chalcopyrite	0.15	250–600	3
Sphalerite-pyrrhotite	~0	250–600	3

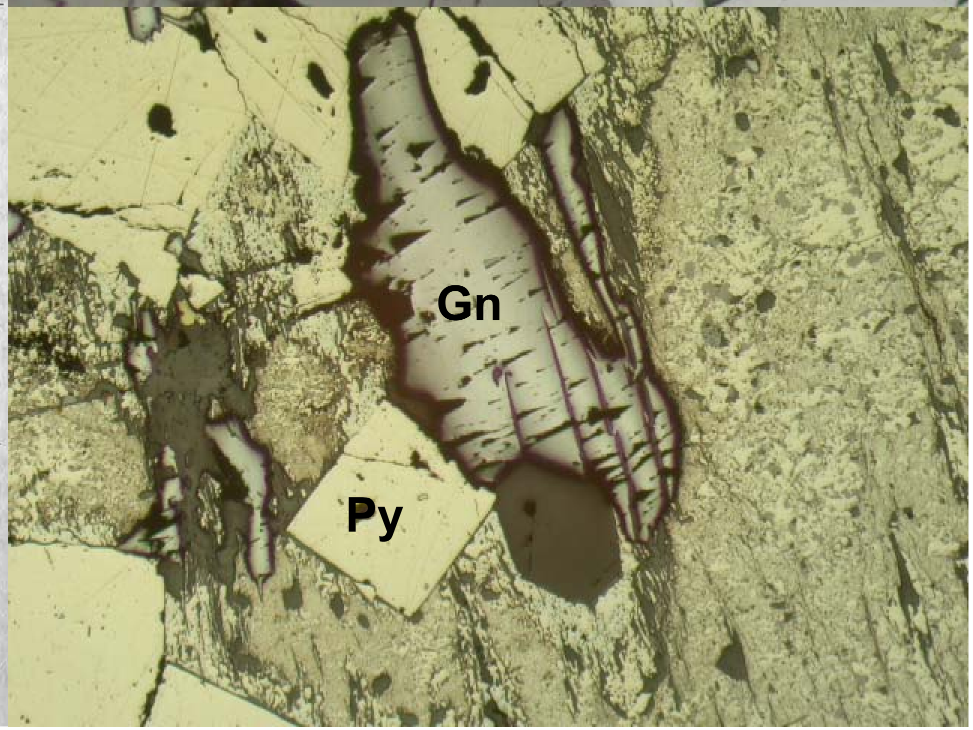
1. Sakai, 1968
2. Grootenboer and Schwarcz, 1969
3. Kajiwara and Krouse, 1971
4. Czamanske and Rye, 1974
5. Groves et al., 1970, quoting Hulston

[a] The temperature dependence of $\Delta^{34}S$ values of mineral pairs is expressed as:

$$\Delta^{34}S = A \times 10^{6}/T^{2}$$

where $\Delta^{34}S$ is the difference between $\delta^{34}S$ values of two coexisting minerals, A is a constant and T is the absolute temperature.





$H_2S_{(aq)} \leftrightarrow H^+ + HS^-$

$HS^- \leftrightarrow H^+ + S^{2-}$

$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$

$KSO_4^- \leftrightarrow K^+ + SO_4^{2-}$

$NaSO_4^- \leftrightarrow Na^+ + SO_4^{2-}$

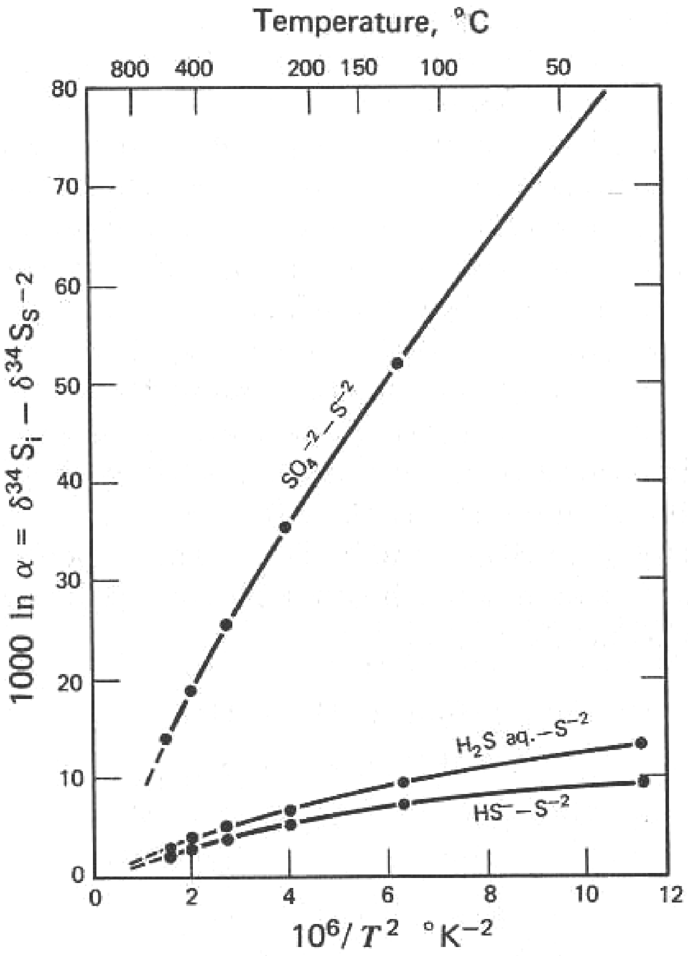
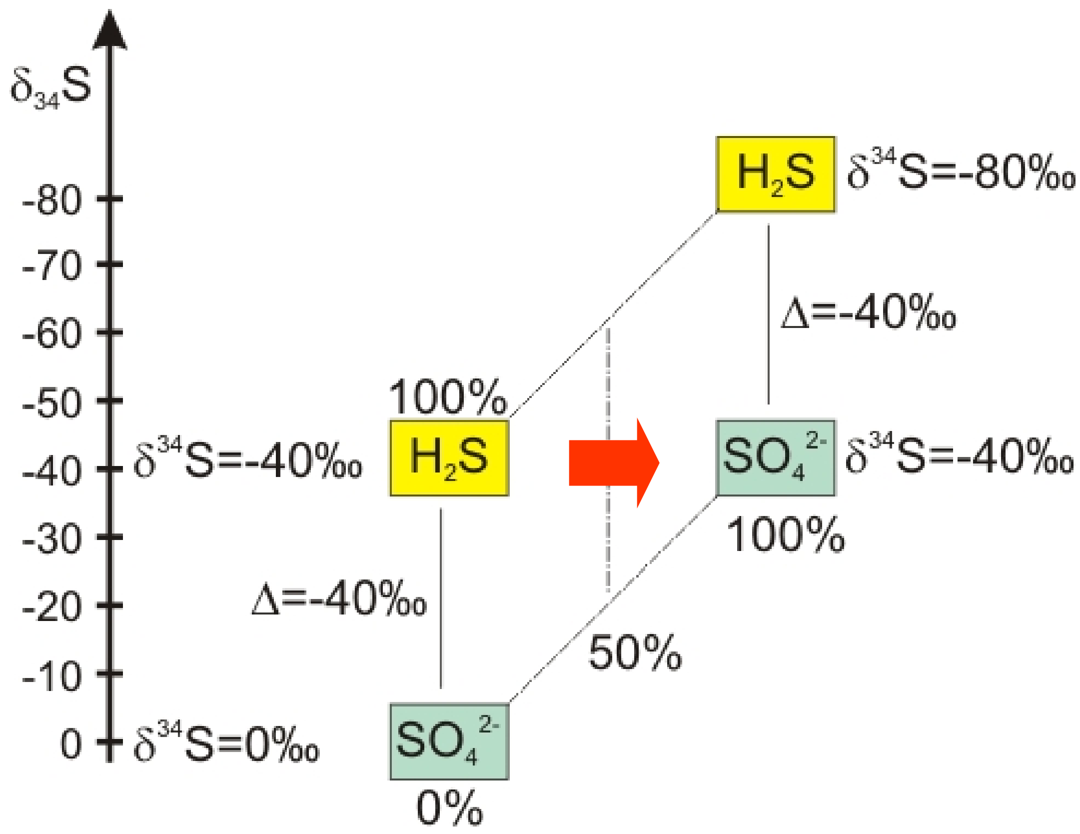


FIGURE 21.4 Fractionation of sulfur isotopes among SO_4^{-2}, H_2S (aq), HS^-, and S^{-2} as a function of the temperature. Note that SO_4^{-2} is strongly enriched in ^{34}S relative to S^{-2} and that the enrichment increases with decreasing temperature. Fractionation of sulfur isotopes among H_2S (aq) and HS^- is less pronounced but these ions clearly prefer ^{34}S over ^{32}S compared to the sulfide ion. These fractionation factors were calculated by Sakai (1968) from ratios of reduced partition coefficients.

$$\Delta^{34}S_{SO4/H2S} = 1000\ln\alpha_{SO4/H2S} \approx A \times 10^6 * T^{-2}$$



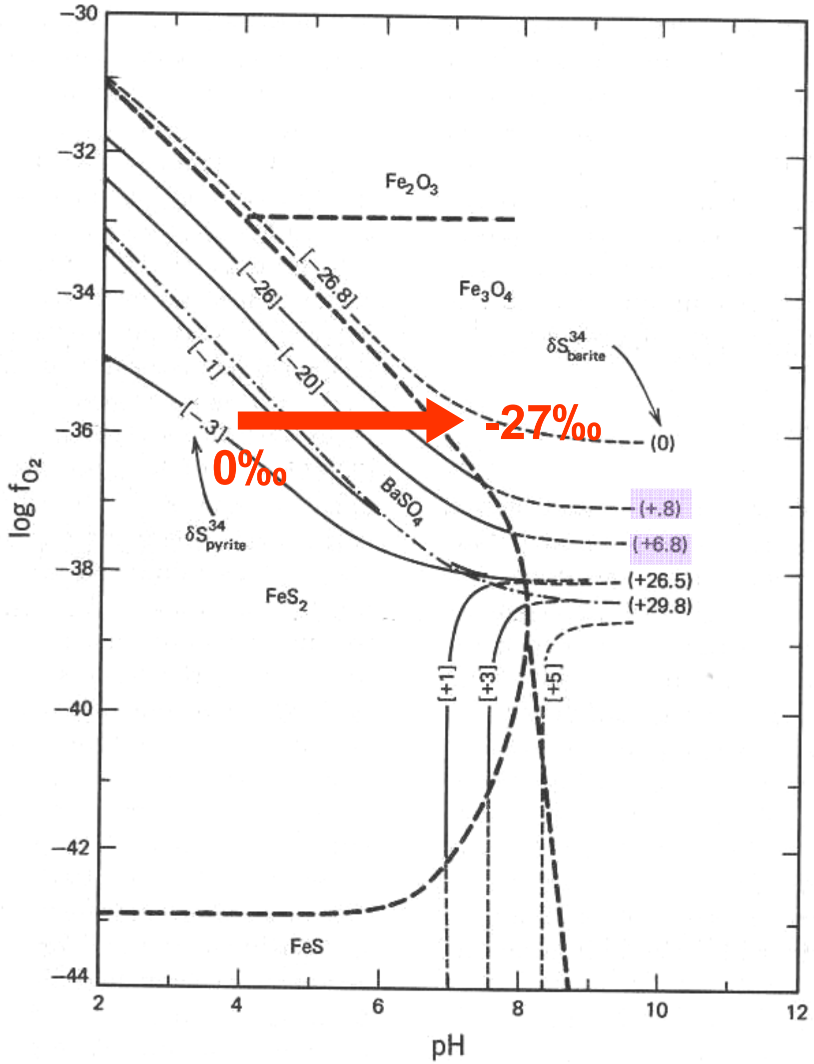
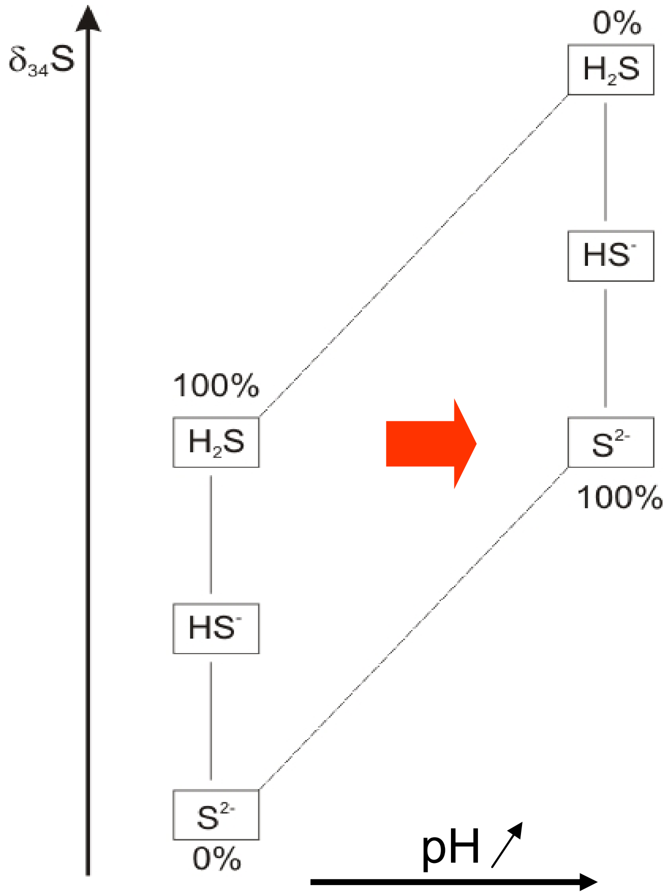


FIGURE 21.5 Isotopic composition of sulfur in pyrite and barite in the system Fe-S-O as a function of pH and the fugacity of oxygen. Square brackets indicate $\delta^{34}S$ of pyrite; round brackets denote $\delta^{34}S$ of barite. Note that $\delta^{34}S$ of pyrite varies widely depending on the fugacity of oxygen and the pH of the solution. The $\delta^{34}S$ of the total sulfur in the system is equal to zero per mil. The Fe-S-O mineral boundaries represent a total sulfur content of 0.1 moles S/kg H_2O, T = 250°C, ionic strength = 1.0. The dash-dot line is the barite soluble/insoluble boundary ($m_{Ba^{+2}} \times m_{\Sigma S} = 10^{-4}$). (Adapted from Figure 5 (p. 559) of Ohmoto, H., Economic Geology, vol. 67, No. 5, 551–578, 1972 with permission for the use of the diagram from H. Ohmoto.)



$$K = \frac{pO_2 \cdot [H_2S]}{[SO_4^{2-}] \cdot [H^+]^2}$$

$$pO_2 = K \cdot \frac{[SO_4^{2-}] \cdot [H^+]^2}{[H_2S]}$$

$$\frac{[SO_4^{2-}]}{[H_2S]} = \frac{pO_2}{[H^+]^2} \cdot K$$