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W.T. Holser: GEOLOGY AND GEOCHEMISTRY OF SULFIDE AND SULFATE DEPOSITION

Sulfide deposition is dominated by the bacterial reduction of marine sulfate to HS^- , which is then sequestered as Fe_{1-x}S , and eventually reacts with another sulfur source to be permanently deposited as pyrite, FeS_2 . That shallow and shelf marine sites are more important than the deep sea is shown by the fact that the flux rate from the shallow marine zones is 5.5×10^{11} moles per year whereas that from the deep ocean sediments is about 0.7×10^{11} moles per year (Holser, 1975). Sulfate deposition is dominated by the geological accidents leading to evaporite formation that deposit gypsum/anhydrite, halite, and potash facies minerals (potassium minerals, primarily carnallite and sylvite), in that order. The special conditions of high net evaporation and semi-isolation (but not complete isolation) from sea water input and reflux occur only sporadically in geological time, but when they do occur they fill up any pre-formed basins with these evaporite minerals at a catastrophically high depositional rate.

The isotope ratio of sulfur in sea water, as recorded in the "age curve" of sulfate in evaporite rocks, provides a running account of the relative importance of sulfide (heavier sulfate isotopes) and sulfate (lighter isotopes) in the world reservoirs. Comparison of sulfur and carbon (in carbonate) isotope age curves reflects the balance of oxidation and reduction in these two global cycles.

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EVAPORATION SEQUENCE

NAME	SALT	CONCENTRATION OF SEA WATER WHEN SALT PRECIPITATES
Anhydrite	Calcium sulfate CaSO_4	3-4 times
Gypsum	Calcium sulfate, 2 waters $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	3-4 times
Salt	NaCl	10 times
Potash facies	Potassium chloride KCl	60-70 times
	Magnesium sulfate MgSO_4	
	Potassium magnesium chloride $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$	
	Tachyhydrite Magnesium calcium chloride $\text{MgCaCl}_2 \cdot \text{H}_2\text{O}$	

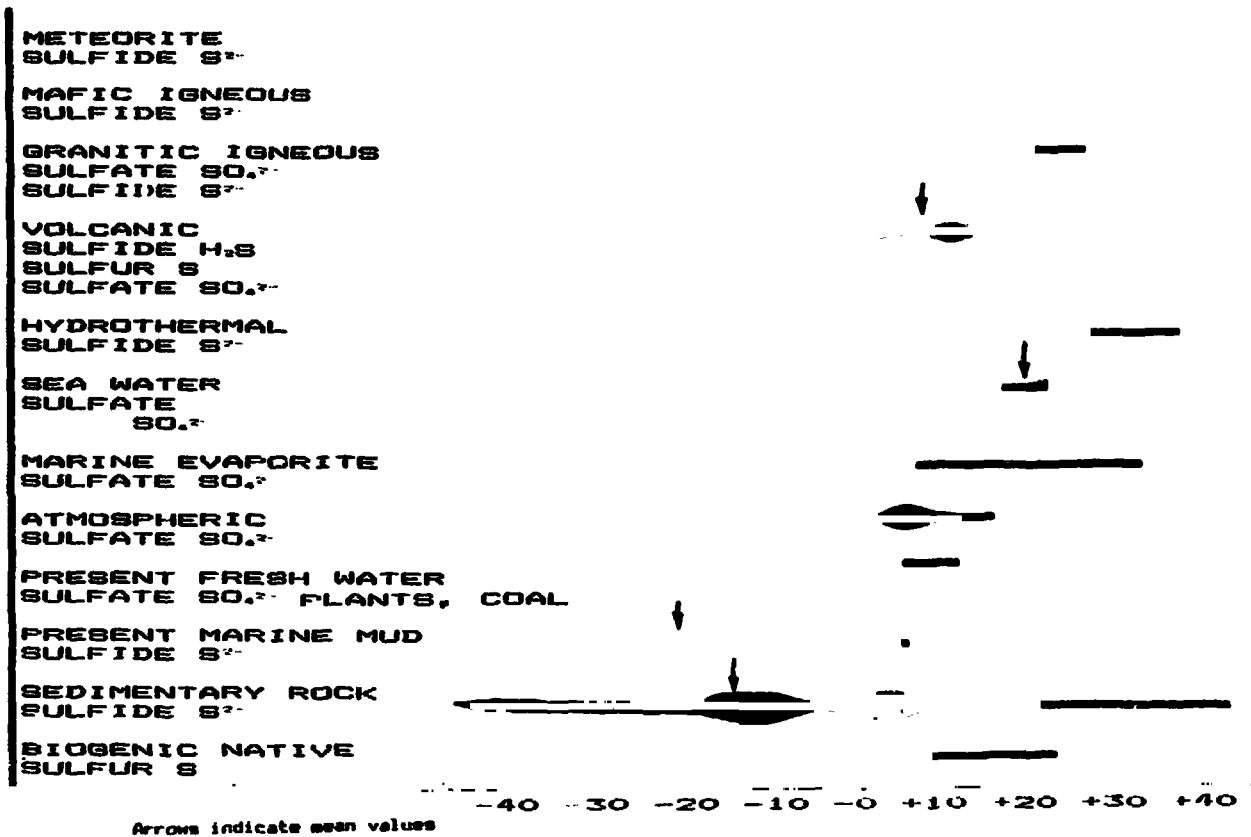
(In nature, tachyhydrite is found in the evaporation sequence whereas in the lab bischoffite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) is produced at a concentration of about 70 times

MAJOR MINERALS OF THE POTASH FACIES ("BITTERNS")

Sylvite KCl
Carnallite KMgCl_3
Kieserite
Kainite
Schönite

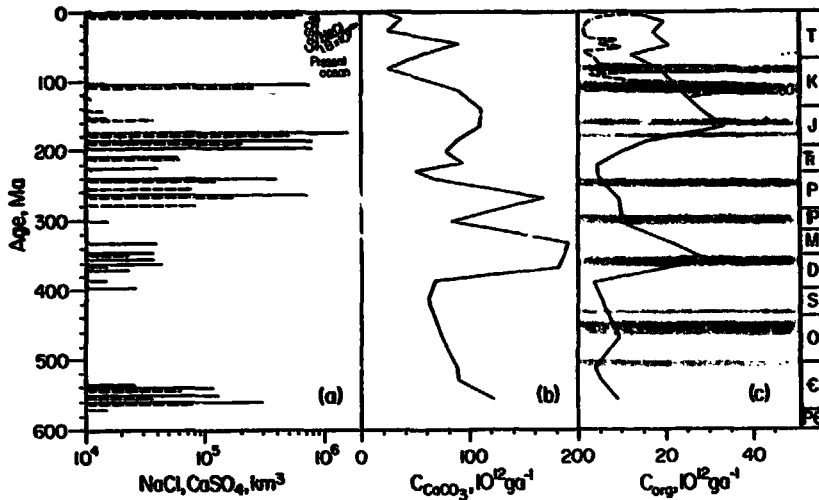
Figure I-15. As sea water evaporates salts come out of solution in this determined sequence.

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SUMMARY OF SULFUR ISOTOPE
FRACTIONATION DATA
 δS^{34}

Figure I-16. Summary of literature values. Delta 34S in natural samples varies from over -40 to over +40 depending on several factors, including its source. The width of the black bars approximate the distribution of the values.



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Figure I-17. Phanerozoic marine evaporites and carbon deposition. (a) NaCl and CaSO₄ in marine evaporites, scaled logarithmically; content in the present ocean is also shown. Data from Zharkov for Cambrian through Pennsylvanian time, and from Holser et al. for the Permian through the Cenozoic. (b) Rate of deposition of C_{carb} (c) Rate of deposition of C_{org}. Solid lines in (b) and (c) are carbon in sediments present today on the continents, aggregated to epochs; dashed line in (c) is based mainly on deep-sea cores and aggregated by stages or substages (2). Shaded areas in (c) are times of recognized anoxic events. Note that the scale in (c) is expanded relative to (b).

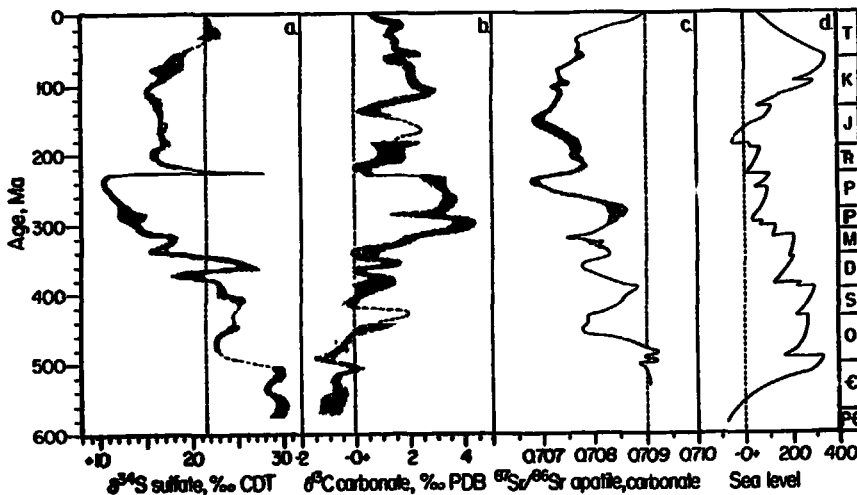


Figure I-18. Age curves of (a) sulfur isotopes in evaporite sulfate; (b) carbon isotopes in carbonate; (c) strontium isotopes in carbonate and in fossil apatite; and (d) sea level. Shading gives range of uncertainty; dashed lines, lack of data.

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