

SERIES OF SEVEN LECTURES

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Retired, University of Arizona

Unifying theme: Isotope Geochemistry

**Progression: Economic Geology to Isotope
Hydrology**

LIGHT STABLE ISOTOPE STUDIES OF PORPHYRY COPPER DEPOSITS

Lecture prepared for a short course for
mining industry geologists

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Plan:

- 1. Review of light stable isotopes**
- 2. O and H isotopes: origin of hydrothermal water? Multiple fluids?**
- 3. S isotopes: Origin of sulfur? Multiple sources?**

Review of work done in last 40-50 years

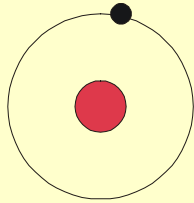
Homework:

Read

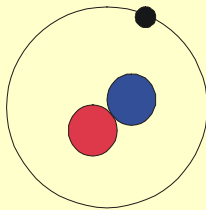
Bowman et al. 1987, Econ. Geol.

Write an outline of the major points in the paper.

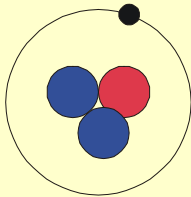
Isotopes of Hydrogen



Hydrogen-1 (protium)



Hydrogen-2 (deuterium)



Hydrogen-3 (tritium)

Radioactive > helium + electron

Half-life about 12.5 years

Isotopes of O and S

O-16 8 p, 8 n

O-17 8 p, 9 n

O-18 8 p, 10 n

S-32 16 p, 16 n

S-33 16 p, 17 n

S-34 16 p, 18 n

S-36 16 p, 20 n

Isotopes of O and S

O-16 8 p, 8 n

O-17 8 p, 9 n

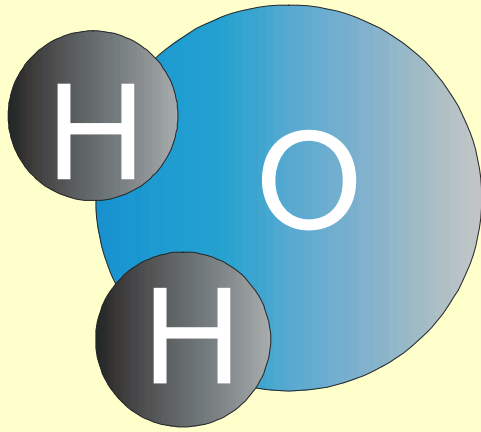
O-18 8 p, 10 n

S-32 16 p, 16 n

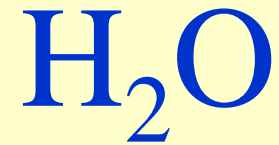
S-33 16 p, 17 n

S-34 16 p, 18 n

S-36 16 p, 20 n



The Water Molecule



Abundance of Isotopes

10,000 water molecules:

19,996 atoms of H-1 **4 H-2 (deuterium)**

9975 O-16 **4 O-17** **21 O-18**

Tritium: 1 to 10 in 10^{18} atoms of H
(same order as distance, sun to nearest star, cm)

Notation

- For the stable isotopes, we measure isotope ratios

$$R = D/H, \text{ } ^{18}\text{O}/^{16}\text{O} \text{ etc.}$$

- $\delta = \left\{ \left(R_{\text{sample}} / R_{\text{std}} \right) - 1 \right\} \times 1000 \text{ ‰ (per mil)}$
- Higher δ - value implies more of heavy isotope
- Standards: VSMOW Vienna Standard Mean Ocean Water, CDT Canyon Diablo Troilite
- $\delta (\text{standard}) = 0 \text{ ‰}$

Equilibrium fractionation of isotopes

- Example: quartz and water at equilibrium
- O Isotope ratio in quartz is not the same as ratio in water
- $\Delta^{18}\text{O} (\text{qtz-water}) = \delta^{18}\text{O} (\text{qtz}) - \delta^{18}\text{O} (\text{water})$
is constant at a particular temperature, and varies predictably with temperature.

Disequilibrium fractionation of isotopes (kinetic)

- Example: bacterial reduction of sulfate to H_2S
- $^{34}\text{SO}_4^{2-} \longrightarrow \text{H}_2^{34}\text{S}$, rate constant k_1
 $^{32}\text{SO}_4^{2-} \longrightarrow \text{H}_2^{32}\text{S}$, rate constant k_2
- $k_2 > k_1$, i.e. “32” reaction goes faster
- If sulfate is partially reduced, $\delta^{34}\text{S}(\text{H}_2\text{S}) < \delta^{34}\text{S}(\text{SO}_4)$

Equilibrium fractionation of O isotopes

$$1000 \ln \alpha = \Delta^{18}\text{O}$$

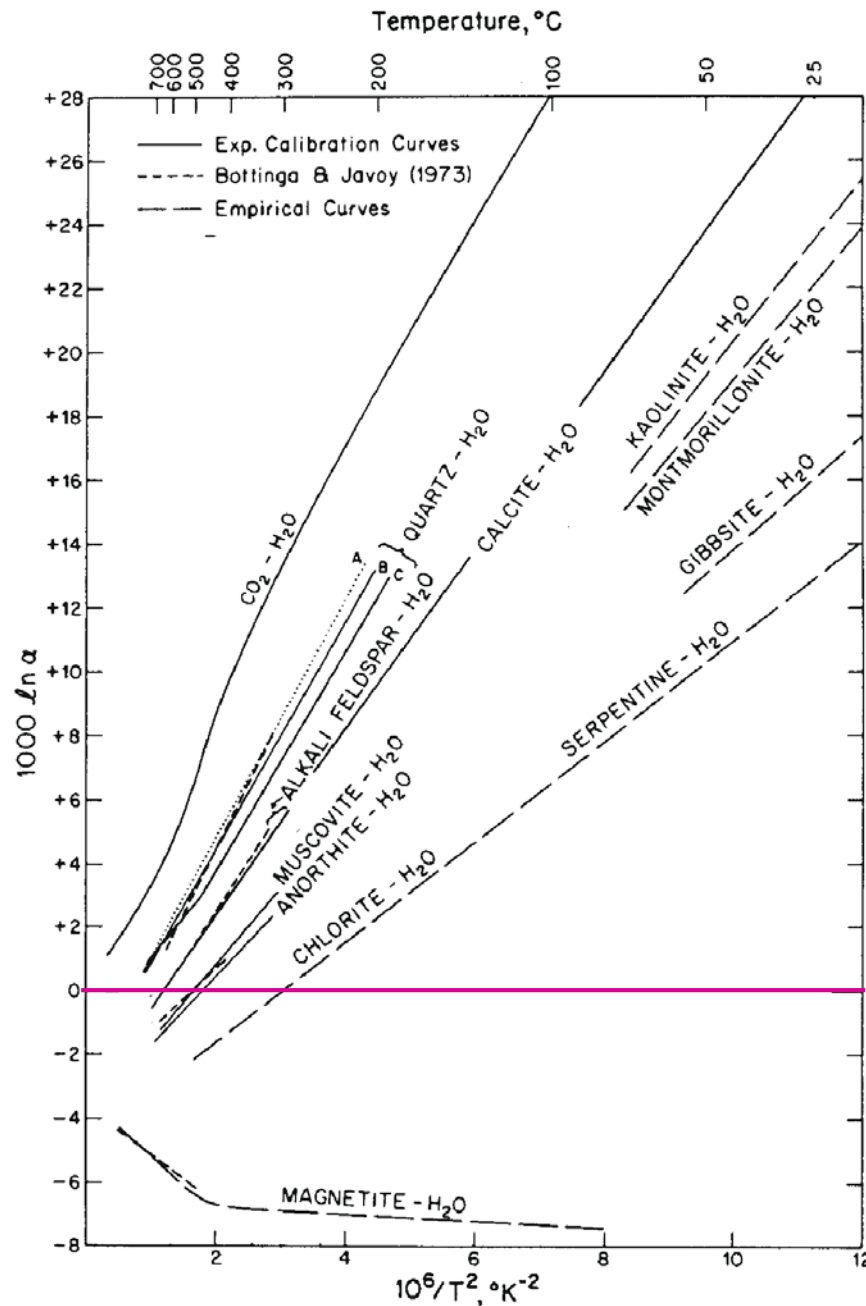


Fig. 6.1 Experimentally determined equilibrium oxygen isotope fractionation curves for various mineral- H_2O systems, all based on using $\alpha = 1.0412$ for calcite- H_2O instead of 1.0407: calcite- H_2O (O'Neil et al., 1969); quartz- H_2O (the dotted curve A is based on the quartz-

Ohmoto and Rye, 1979

Equilibrium fractionation of H isotopes

$$1000 \ln \alpha = \Delta D$$

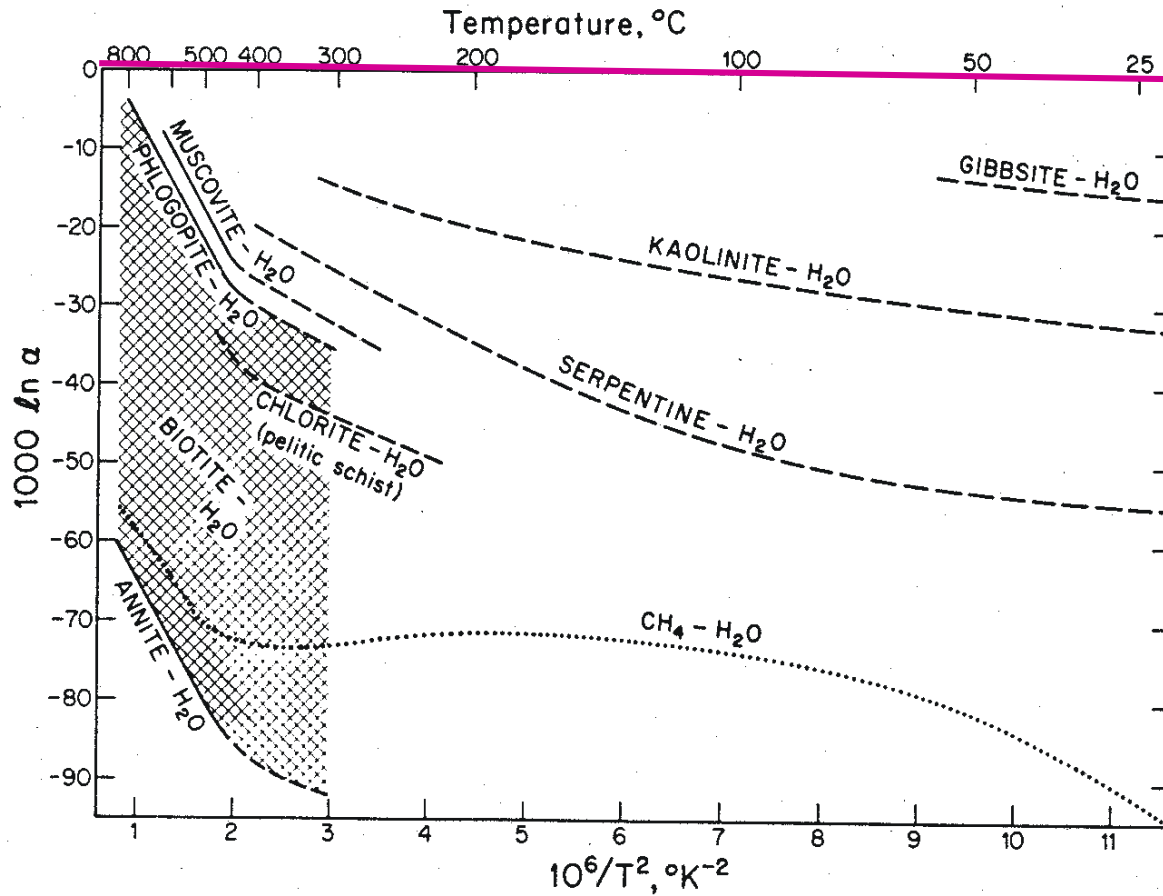


Fig. 6.2 Equilibrium hydrogen isotope fractionation curves for various mineral-H₂O systems. The solid lines represent data by Suzuoki and Epstein (1976). The dashed lines are empirical extrapolations based on natural assemblages (Savin and Epstein, 1970a; Lawrence and Taylor, 1971; Wenner and Taylor, 1973). The dotted line is the calculated CH₄-H₂O curve of Bottinga (1969). Note that below the critical point of H₂O, the curves are all based on values for *liquid* water.

Isotope data available

- $\delta^{18}\text{O}$ quartz, phyllosilicates, anhydrite
- δD phyllosilicates, fluid inclusions
- $\delta^{34}\text{S}$ sulfides, anhydrite, alunite
- $\delta^{37}\text{Cl}$ fluid inclusions, biotite

O and H isotopes in PCDS

What is the origin of hydrothermal water?

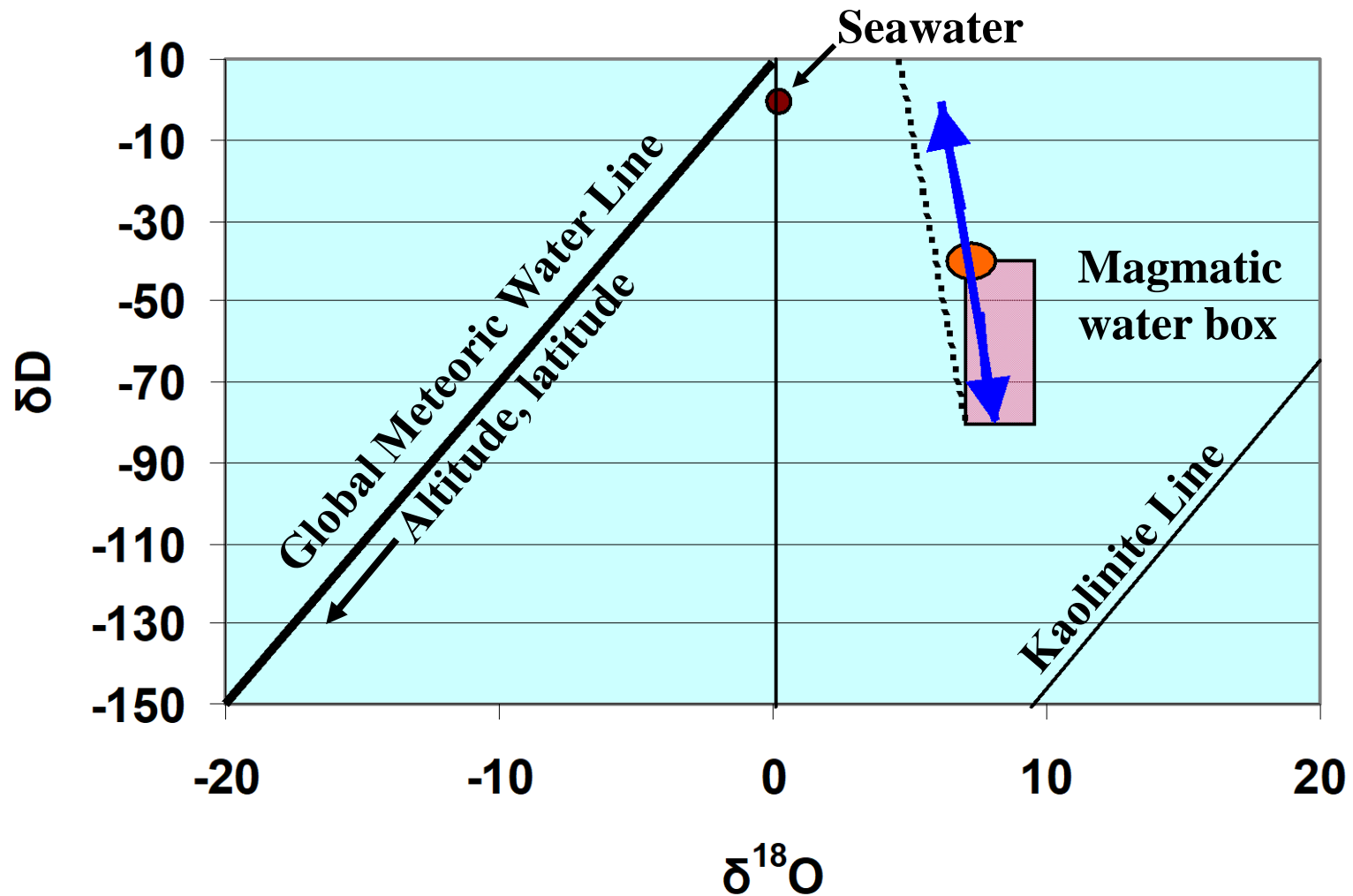
Method:

Measure δD and $\delta^{18}O$ in OH-bearing minerals, anhydrite, quartz, fluid inclusions

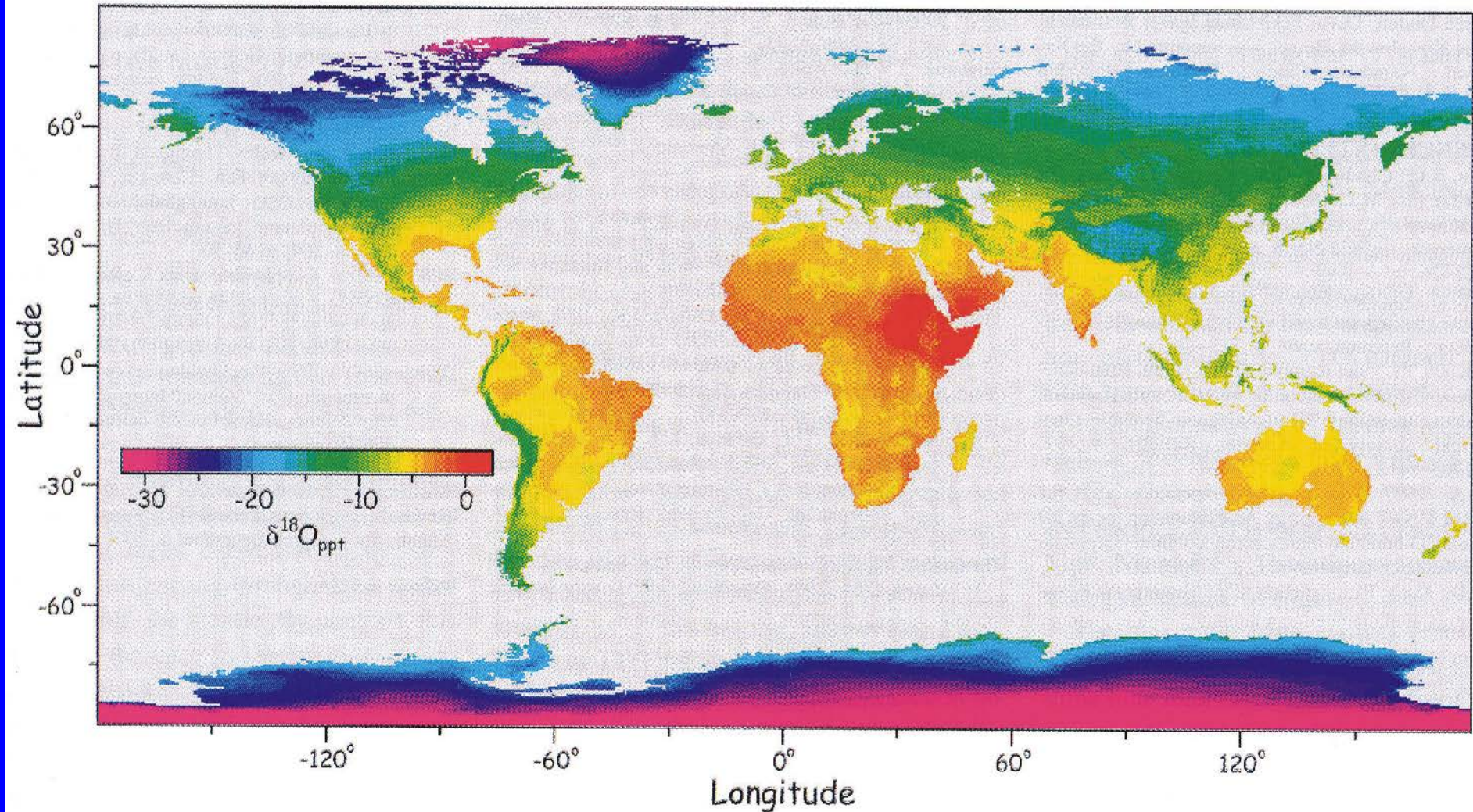
Calculate δD and $\delta^{18}O$ of coexisting water

Extra data needed: Mineral-water fractionation curves; temperatures of formation

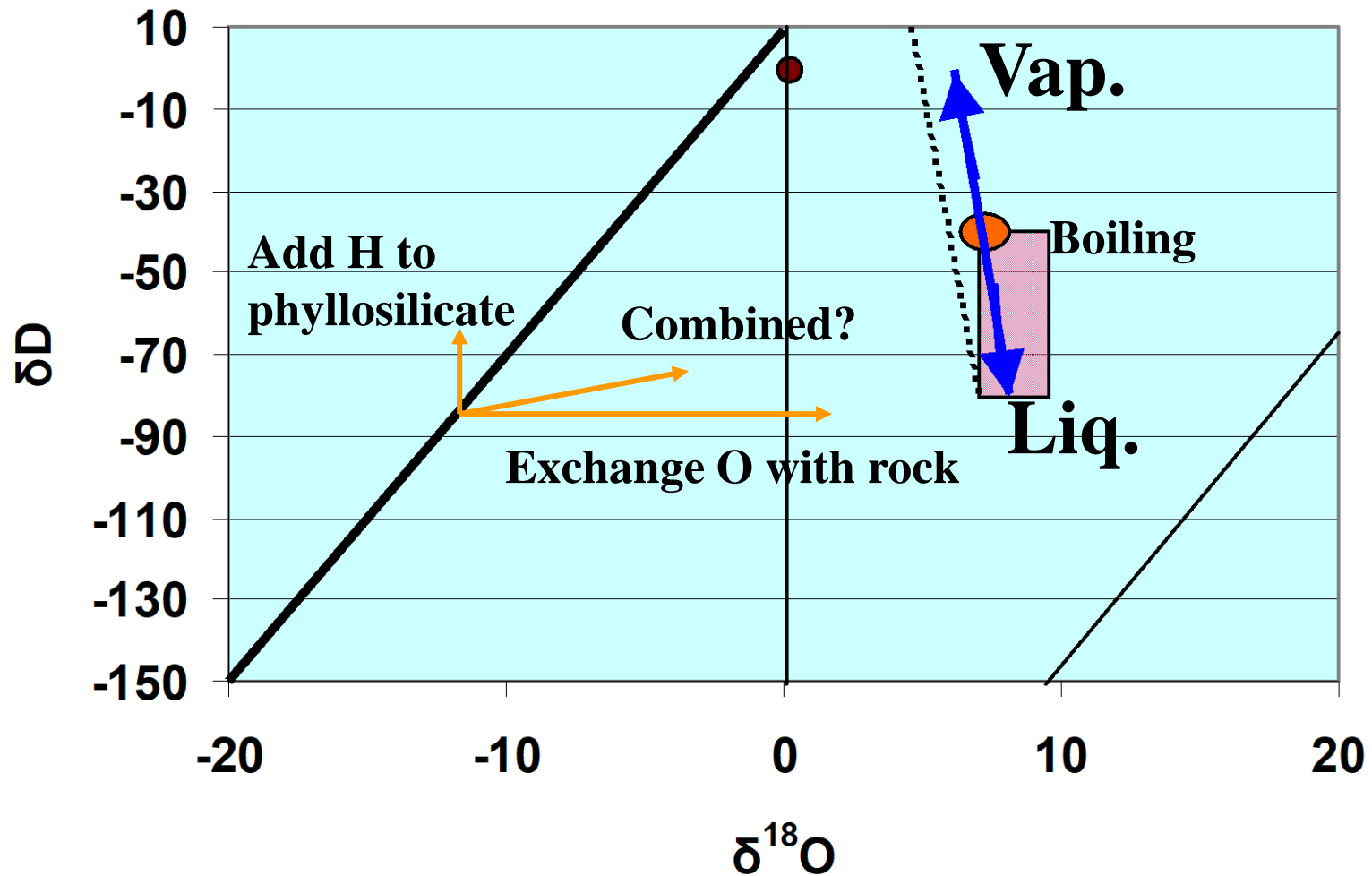
δD vs. $\delta^{18}O$ plot



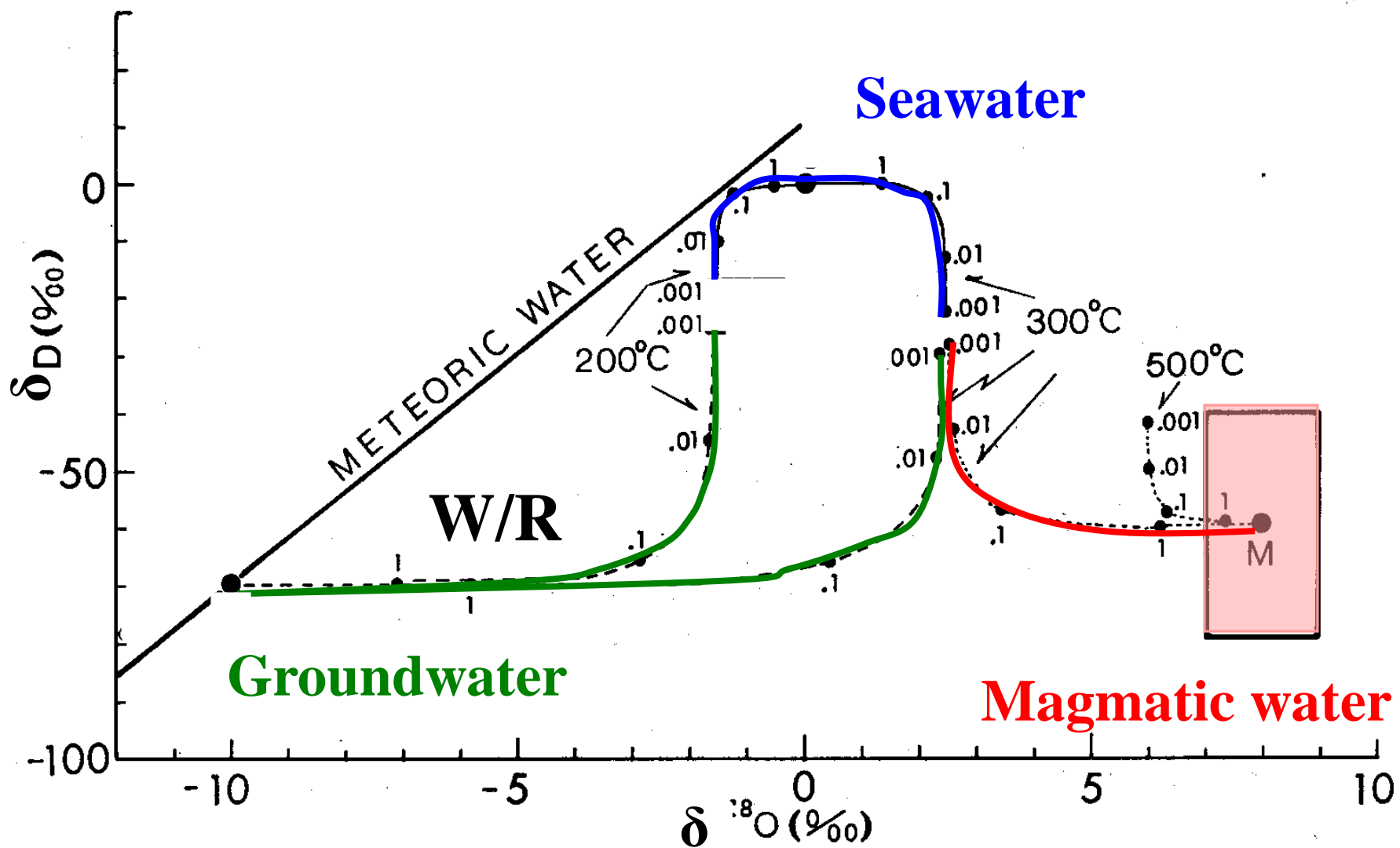
Latitude + altitude + continental effects



δD vs. $\delta^{18}O$ plot

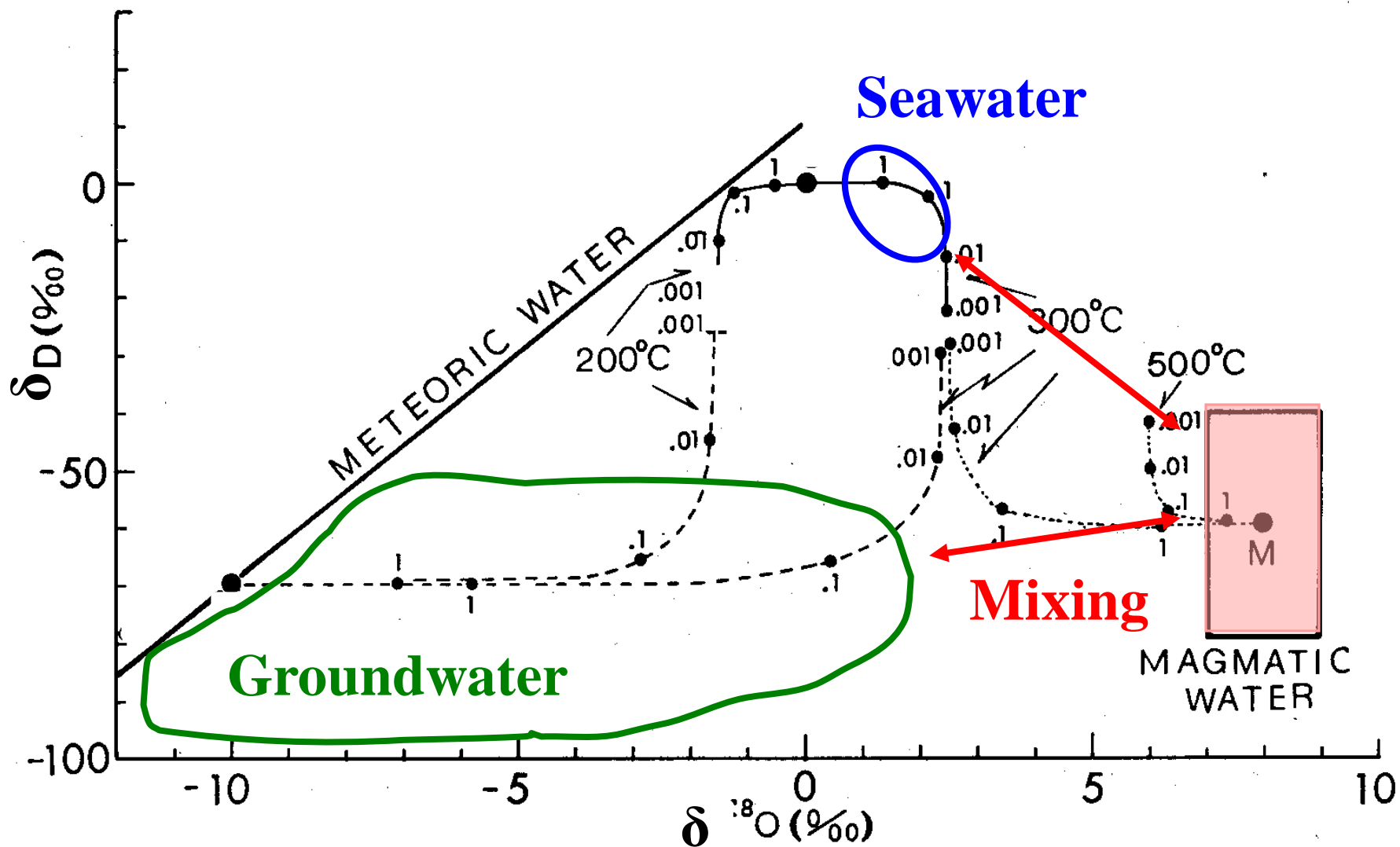


Boiling trend from Harris and Golding, *Geology*, 2002



**ISOTOPE EXCHANGE WITH VOLCANIC
ROCK, O: +8 ‰ H -70‰**

Ohmoto and Rye, *Econ. Geol.*, 1974



**ISOTOPES IN GROUNDWATER AND SEAWATER
AFTER CIRCULATING THROUGH VOLCANIC
ROCK, 300° C**

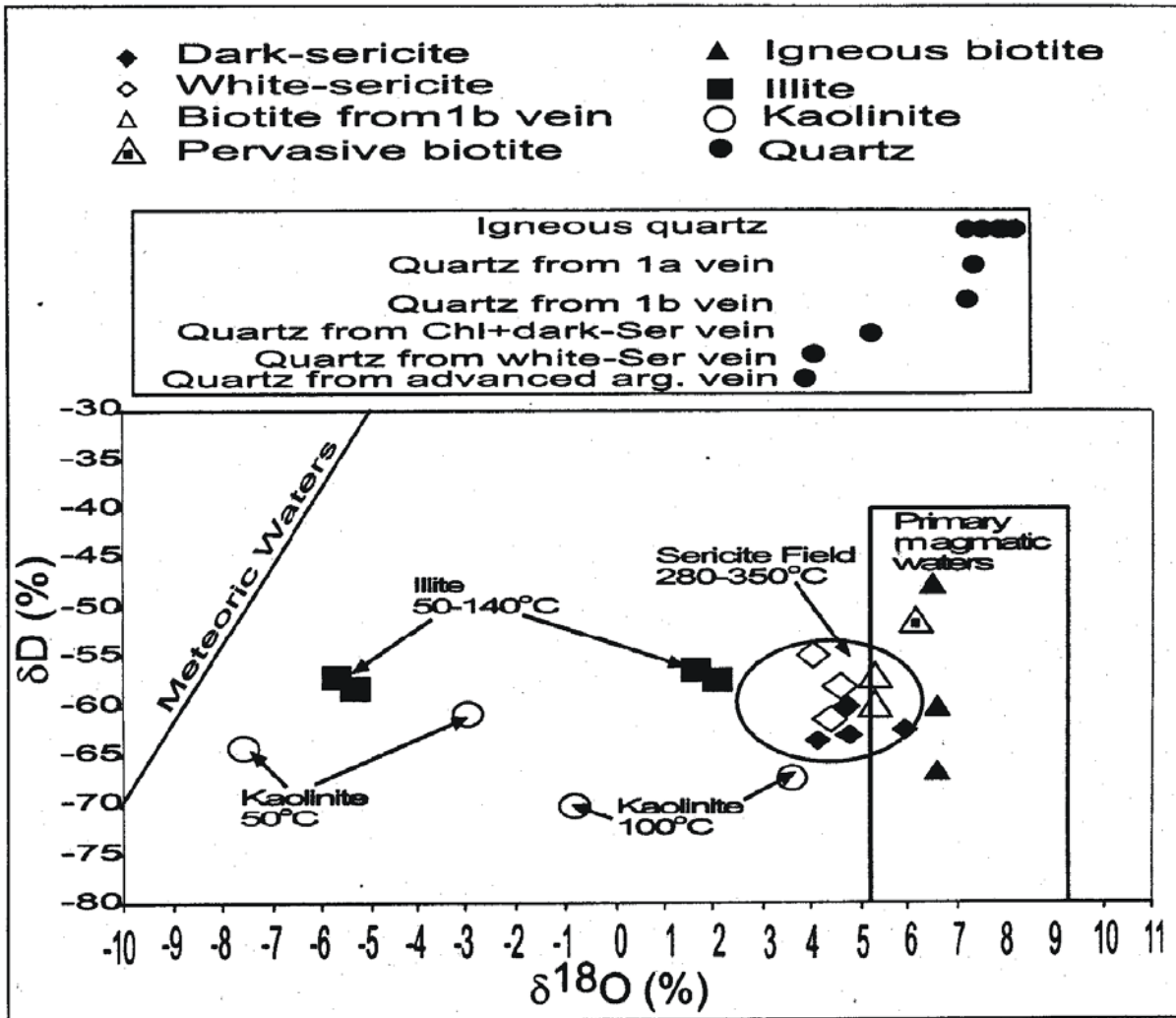


Fig. 43: δD (%) versus $\delta^{18}O$ (%) diagram for the calculated isotopic composition of H_2O in equilibrium with the alteration minerals over the range of temperatures measured in fluid inclusions. Also given are the oxygen isotope compositions of H_2O in equilibrium with igneous and hydrothermal quartz. Meteoric and primary magmatic water values from Taylor (1979).

Valley Copper, BC

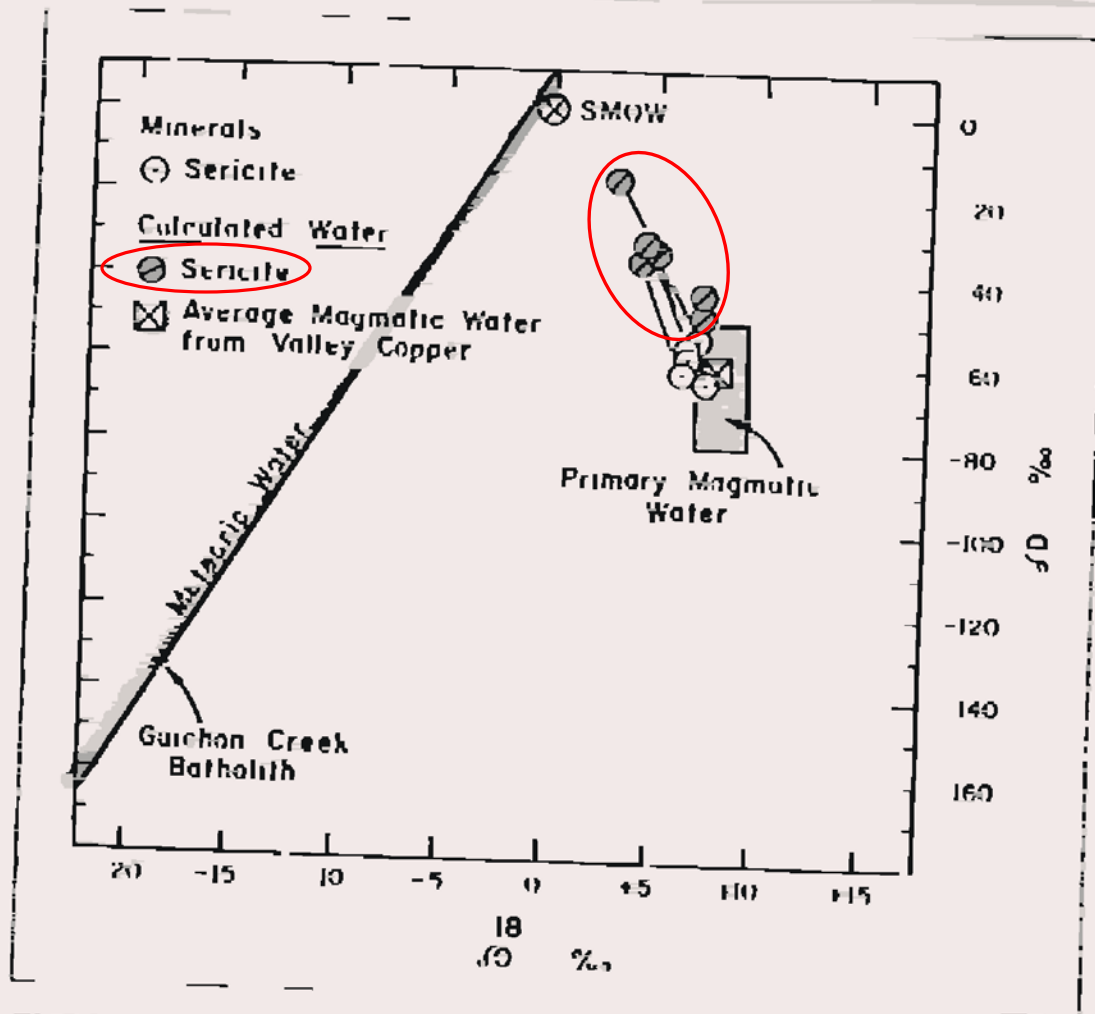


FIGURE 25—Diagram showing probable degree of mixing of seawater (SMOW) and magmatic waters during the formation of the Valley Copper deposit.

Osatenko and Jones,
1976

Bingham Canyon

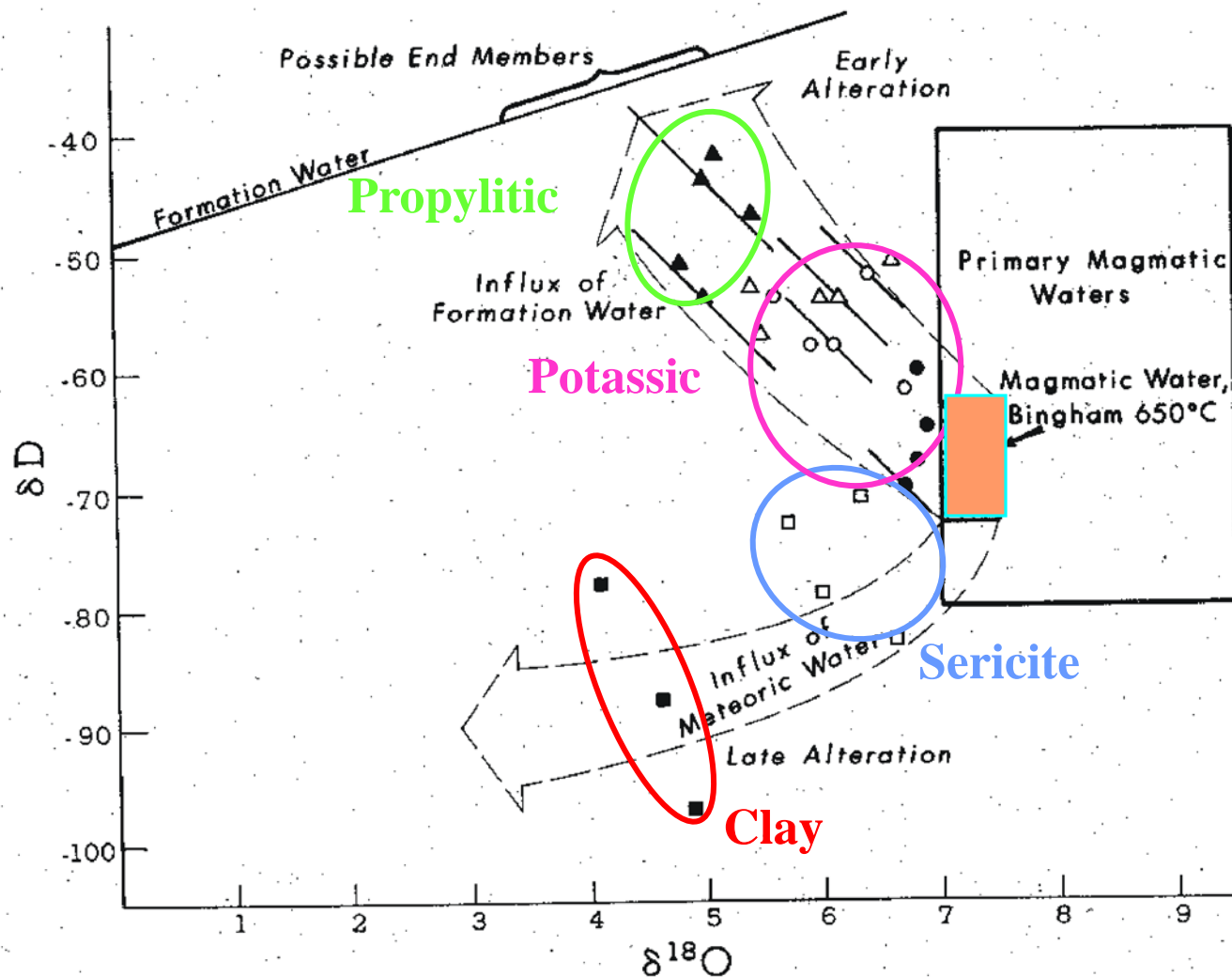
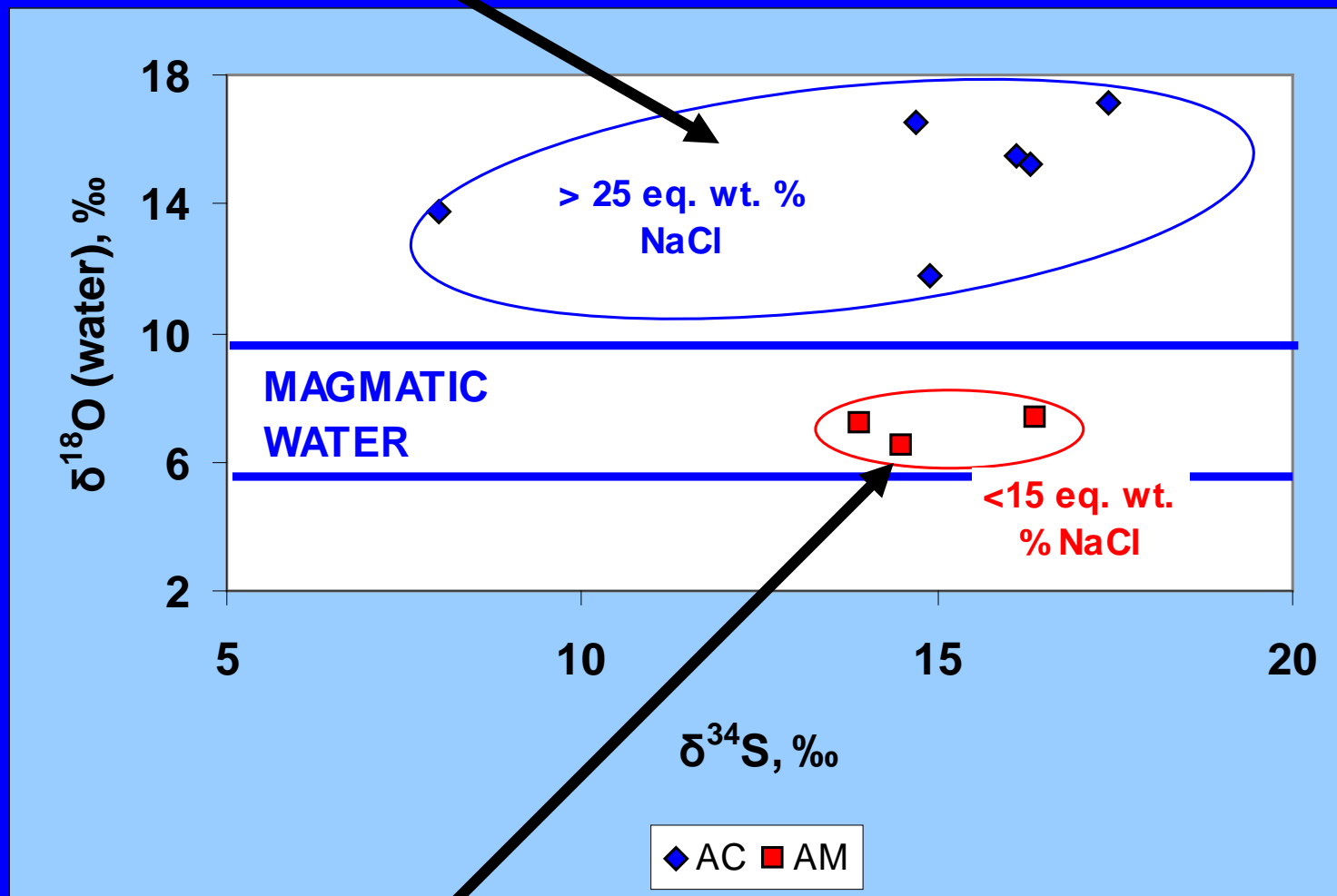


FIG. 15. Plot of calculated δD and $\delta^{18}O$ of water in exchange equilibrium with hydrothermally altered rock in the Bingham porphyry system.

Bowman et al., 1987

Mineral Park AZ -- anhydrite

Anhydrite + chalcopyrite; $\delta^{18}\text{O}$ (water) ~ 16 per mil



Anhydrite + molybdenite; $\delta^{18}\text{O}$ (water) ~ 7 per mil

Lang et al., 1989

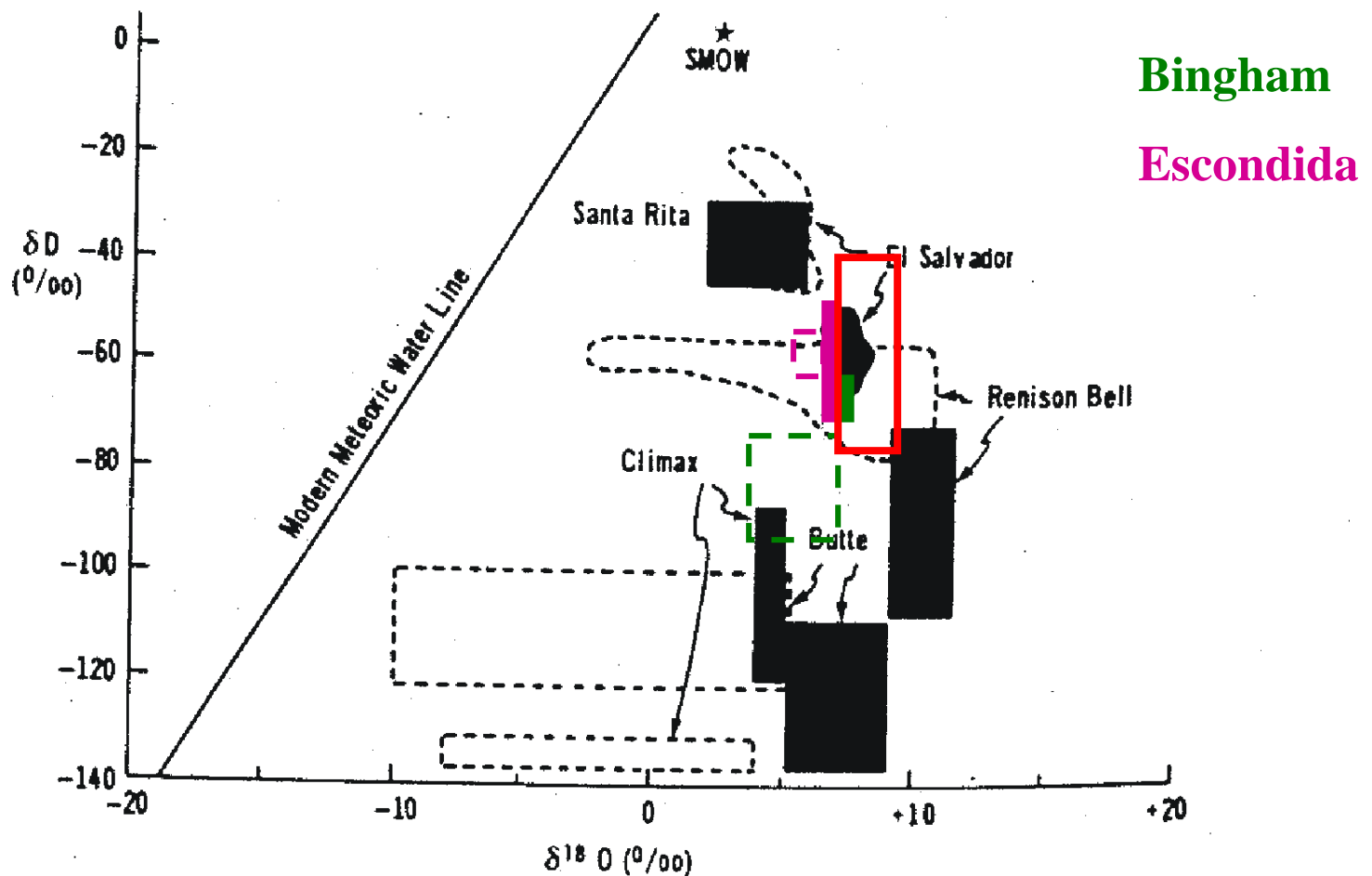


Figure 28. δD - $\delta^{18}O$ characteristics of ore-forming fluids for selected deposits associated with porphyries. Shaded areas = early fluids, dotted areas = later fluids. Data from Sheppard et al. (1969, 1971, 1976), Sheppard and Taylor (1974), Hall et al. (1974), and Patterson et al. (1981).

S isotopes in PCDs

Questions

- Origin of sulfur – magmatic or external?
- Hypogene evolution of sulfur – oxidation/reduction?
- Supergene evolution of sulfur – bacterial reduction?
- Temperature of mineralization -- cf. fluid inclusions

Much more complicated than O and H isotopes!!

Method:

Measure $\delta^{34}\text{S}$ in sulfides, anhydrite, alunite

Compare variations with spatial, temporal distribution of samples

Calculate $\delta^{34}\text{S}$ of ore fluids

Compare different deposits

S isotope fractionation

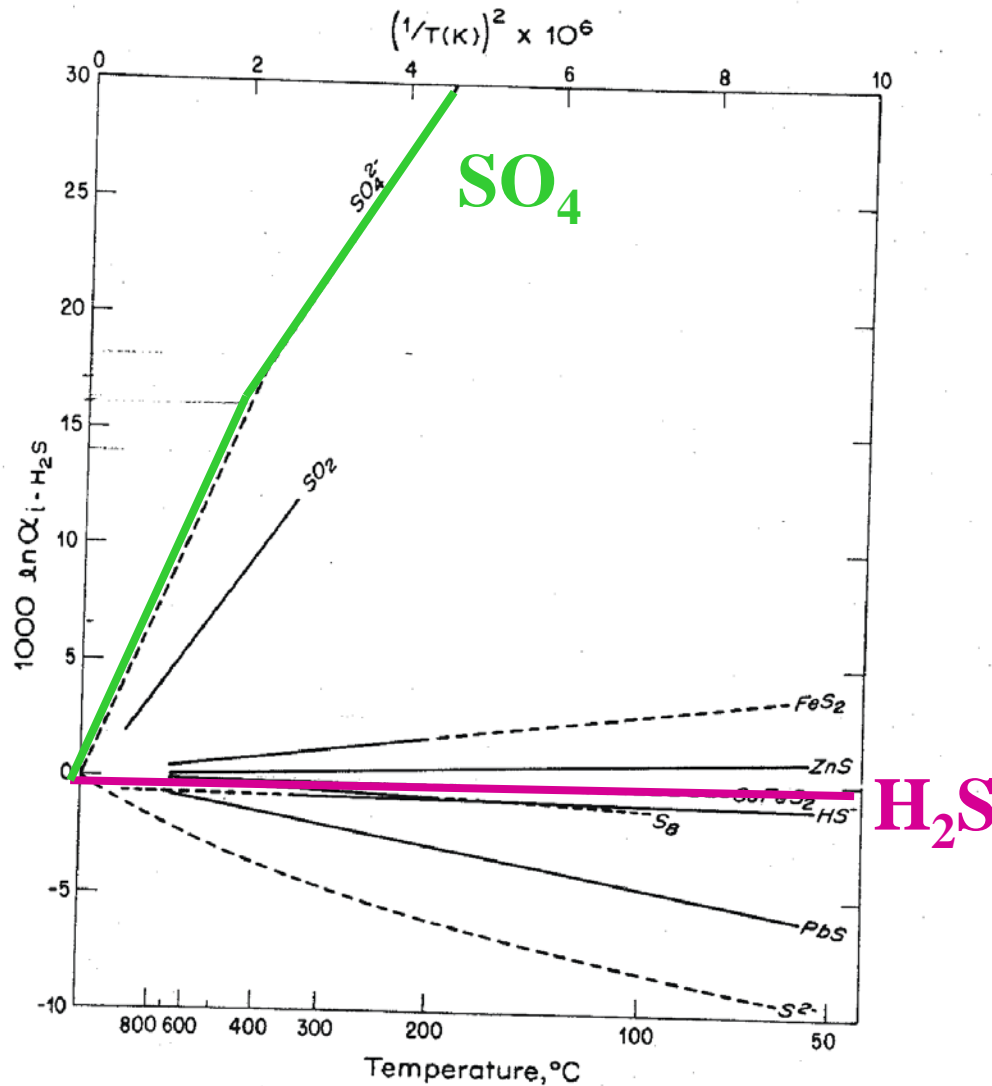


Fig. 10.3 Equilibrium isotopic fractionation factors among sulfur compounds relative to H_2S . Solid lines—experimentally determined. Dashed lines—extrapolated or theoretically calculated.

$$1000 \ln \alpha = \Delta^{34}S$$

Ohmoto and Rye, 1979

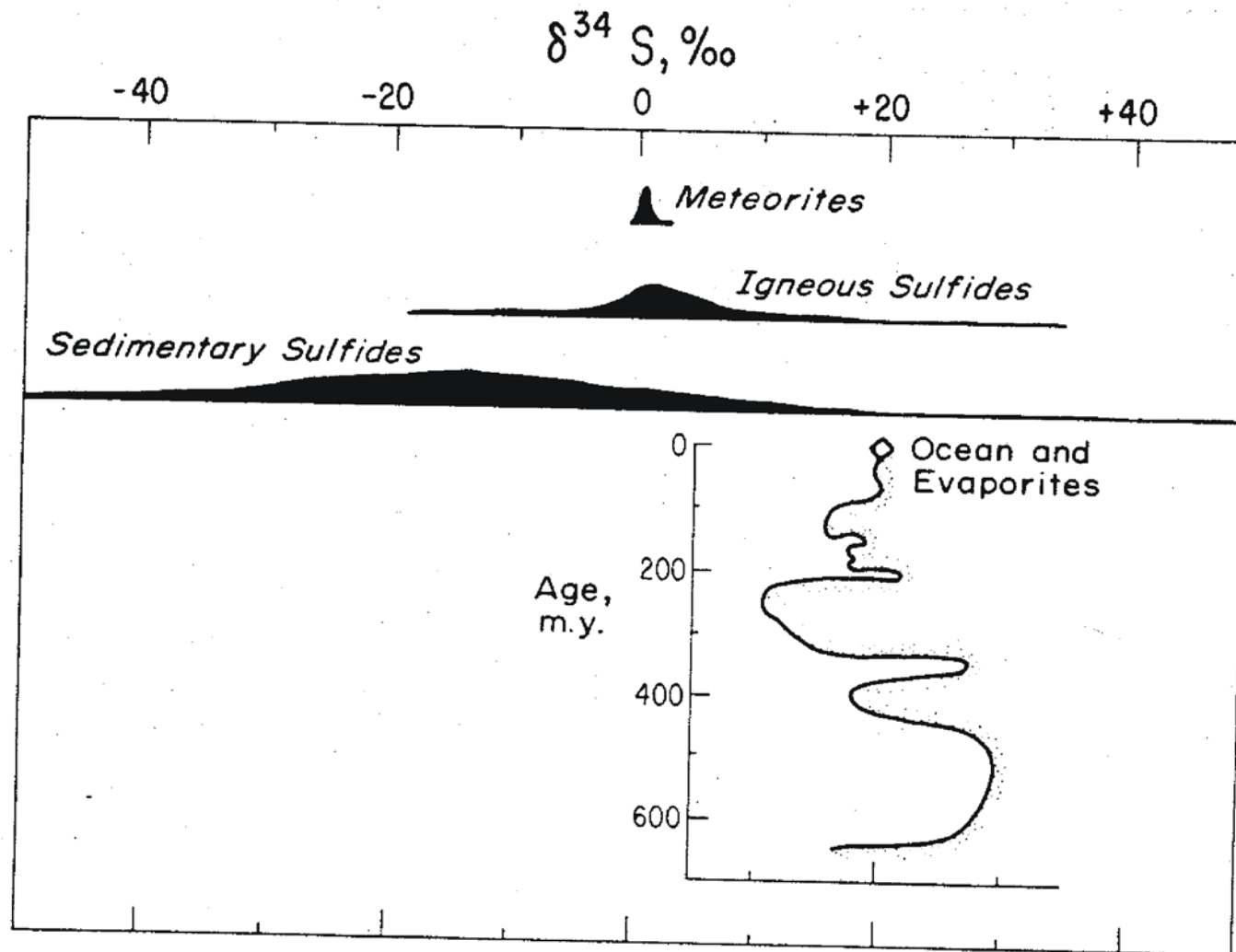


Fig. 10.1 Sulfur isotopic variation in nature.

EVOLUTION OF SULFUR IN MAGMATIC SYSTEMS

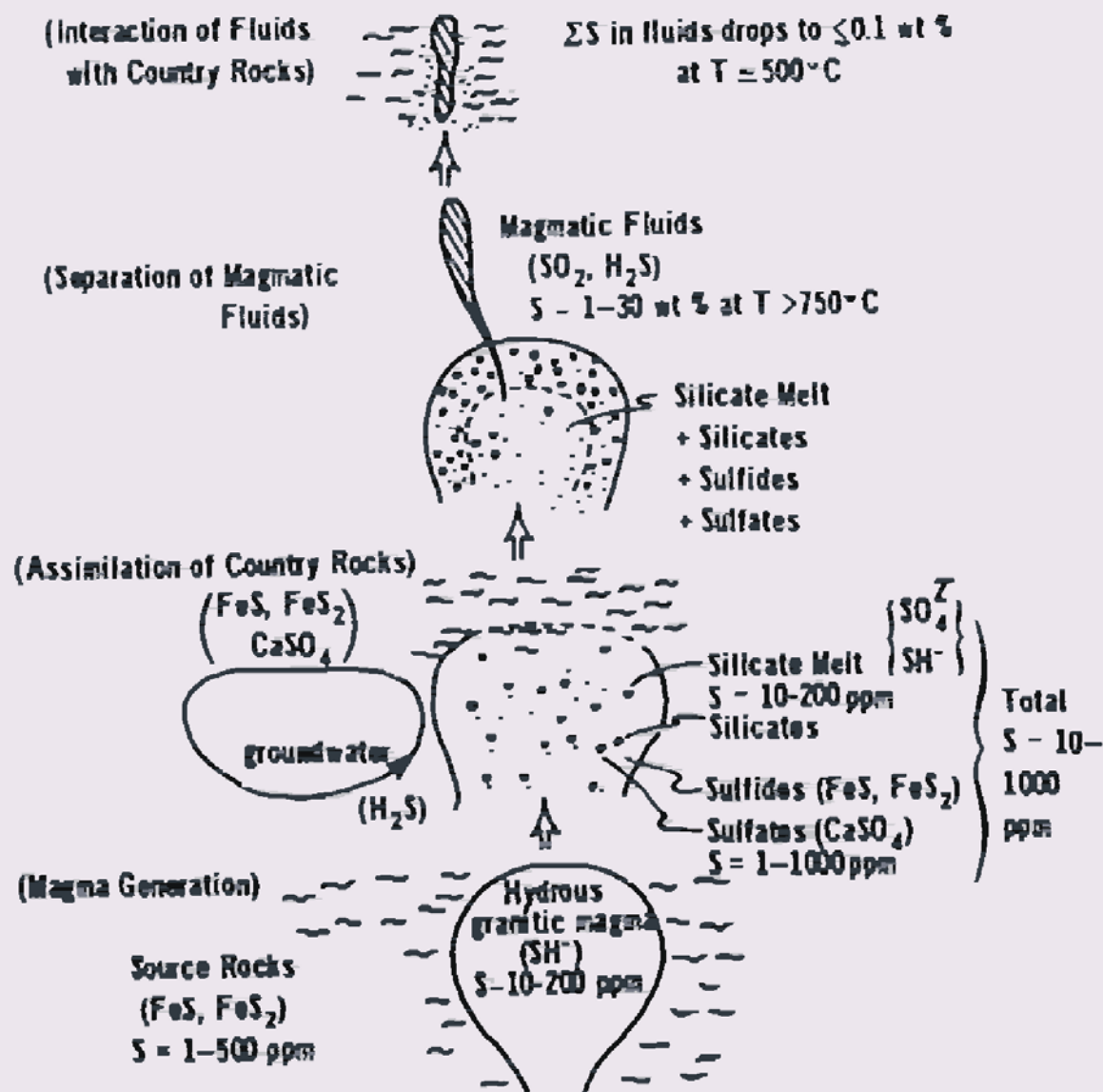
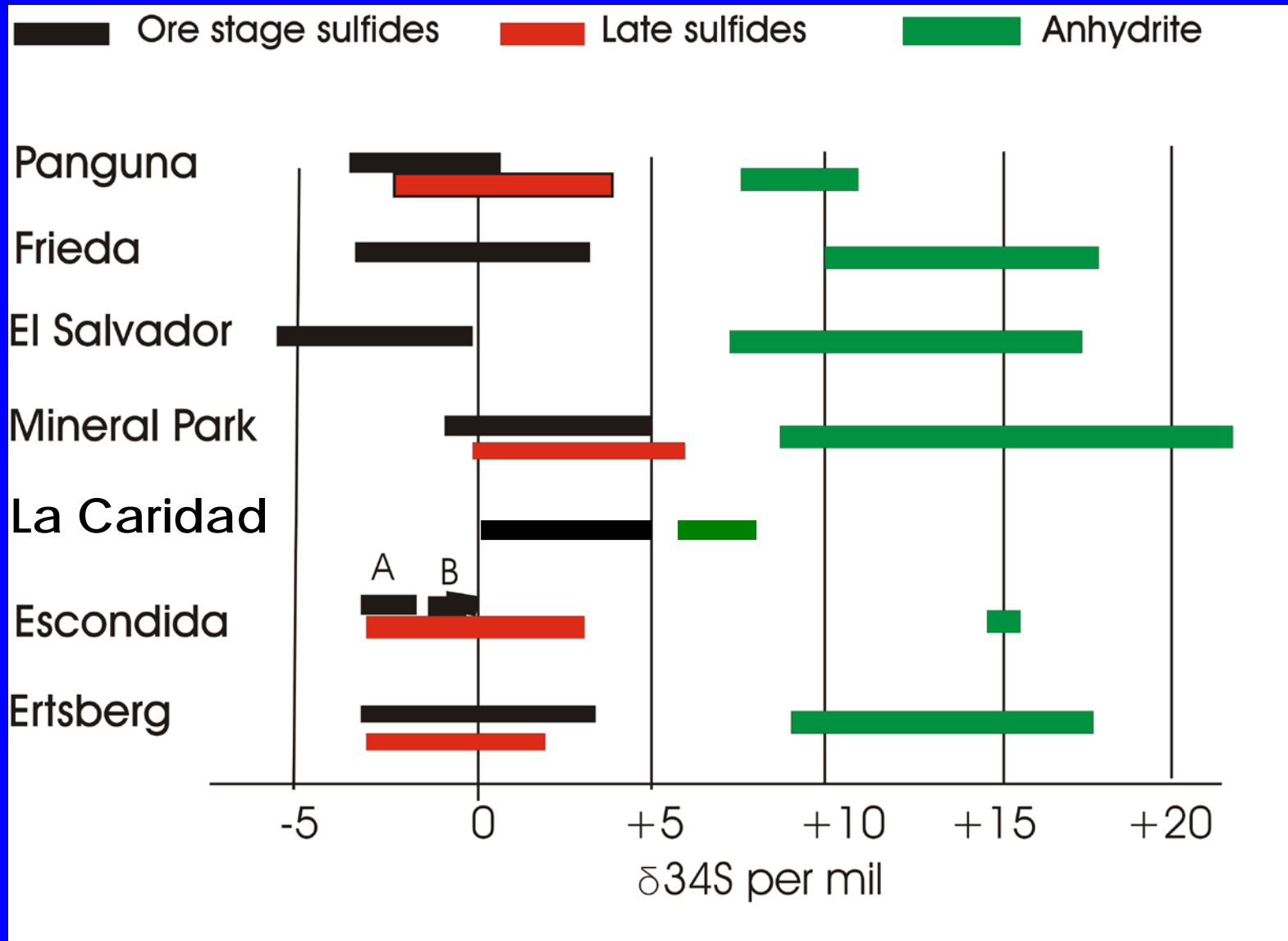


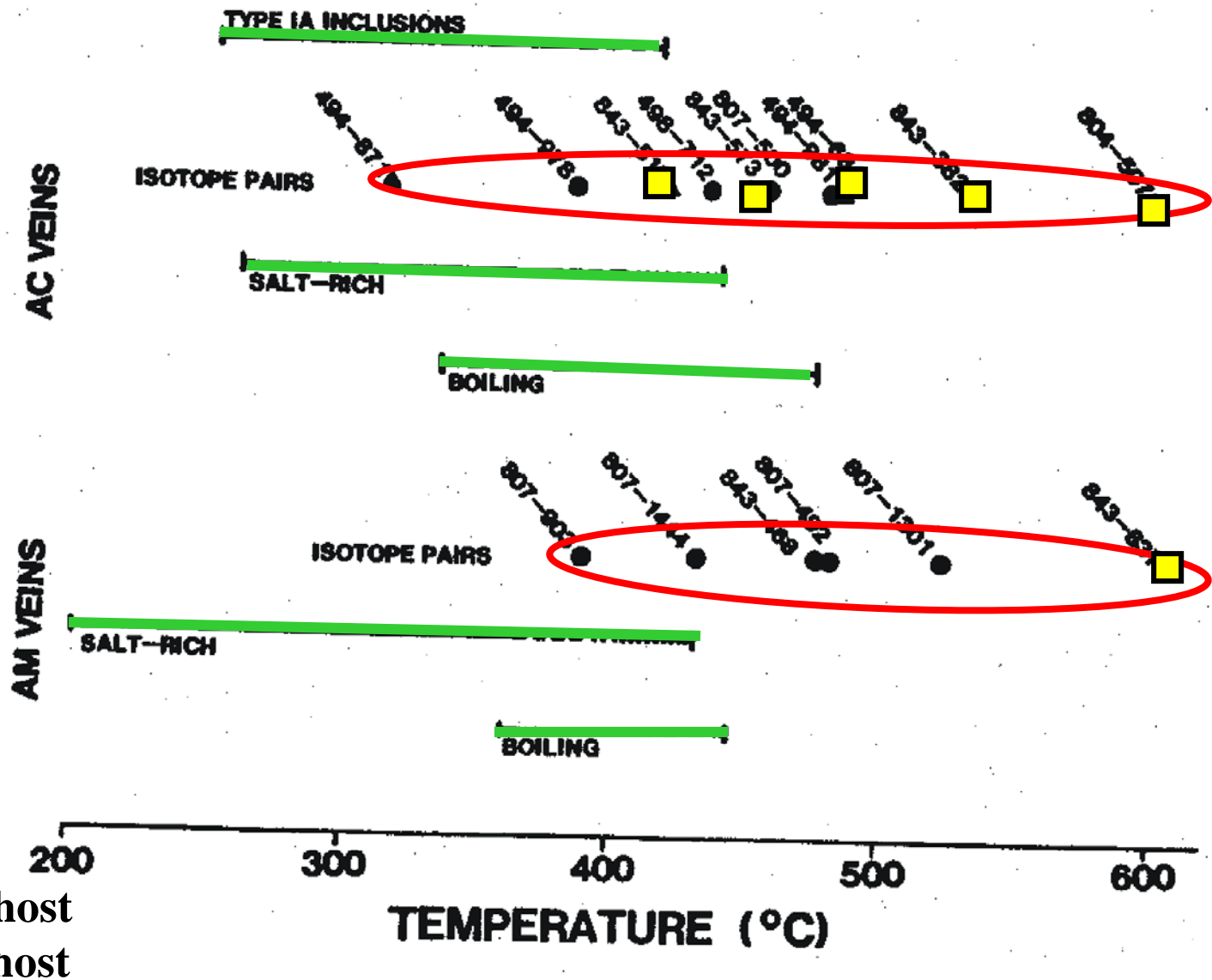
Figure 25. Model for origin and evolution of sulfur in igneous systems (see text).

Hypogene

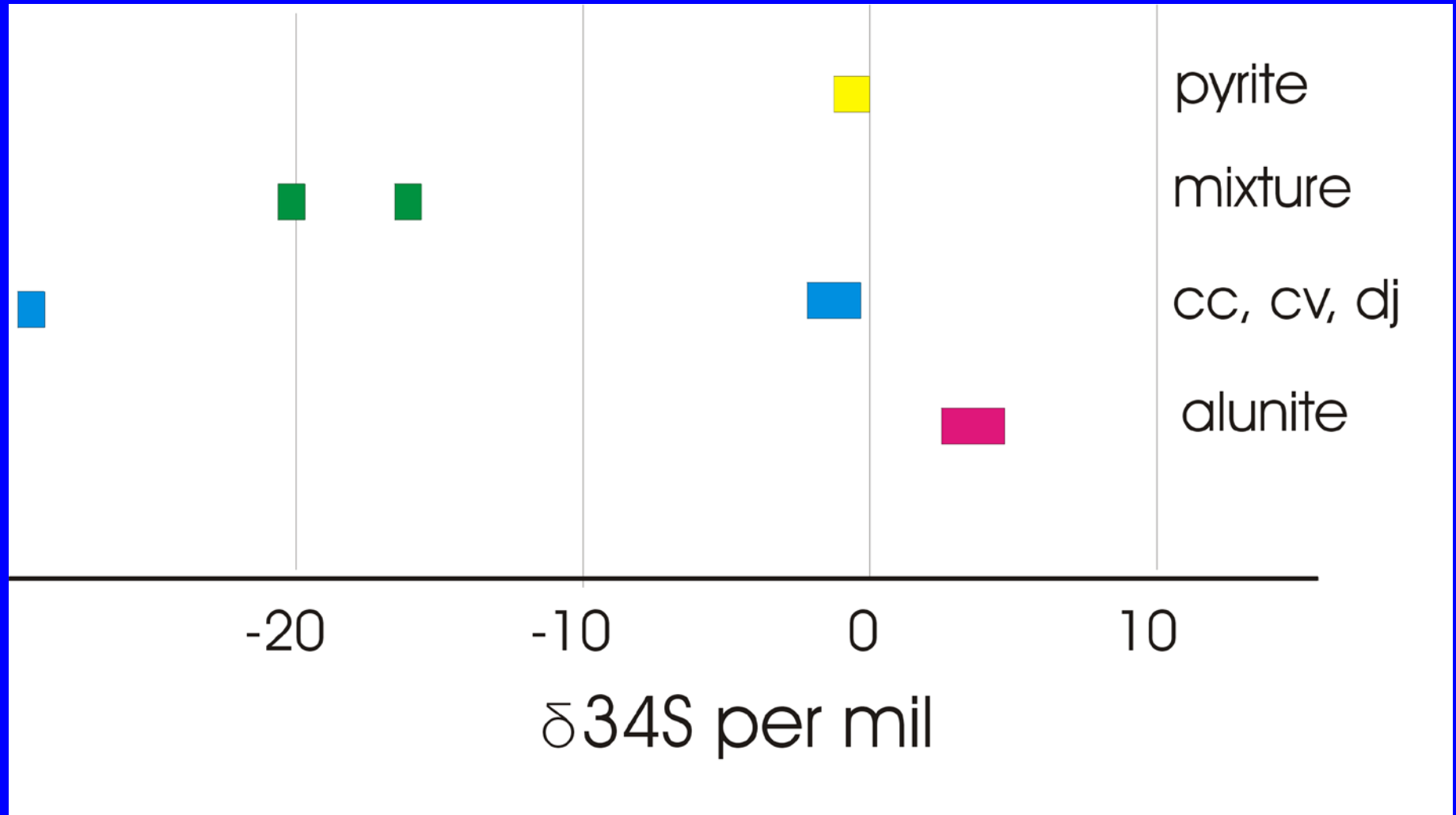


Eastoe, 1983; Field and Gustafson, 1976; Lang et al., 1989; Padilla, 2003; Porter, 2004

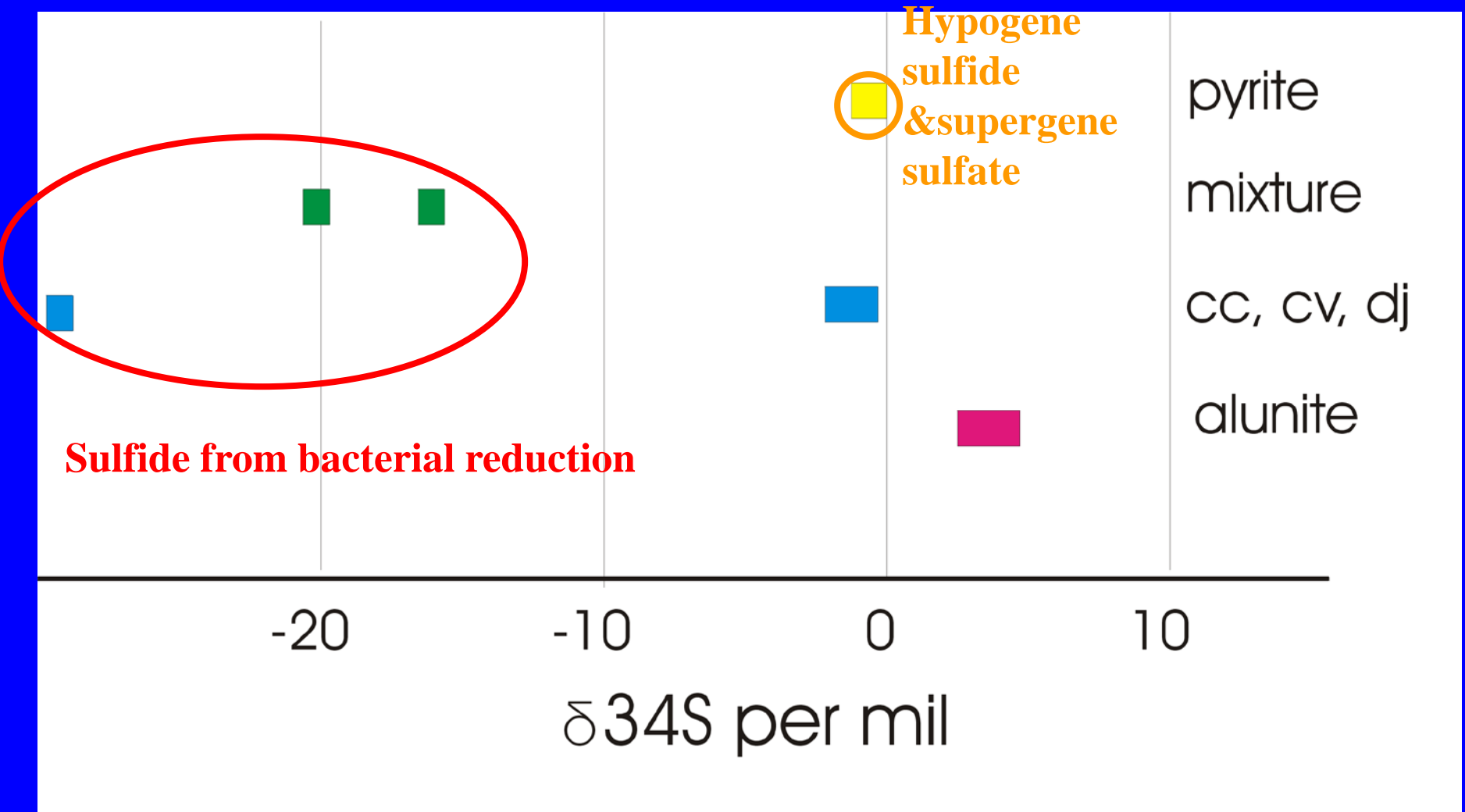
Mineral Park – anhydrite-sulfide pairs



Supergene -- Morenci



Supergene -- Morenci



Escondida Alunite

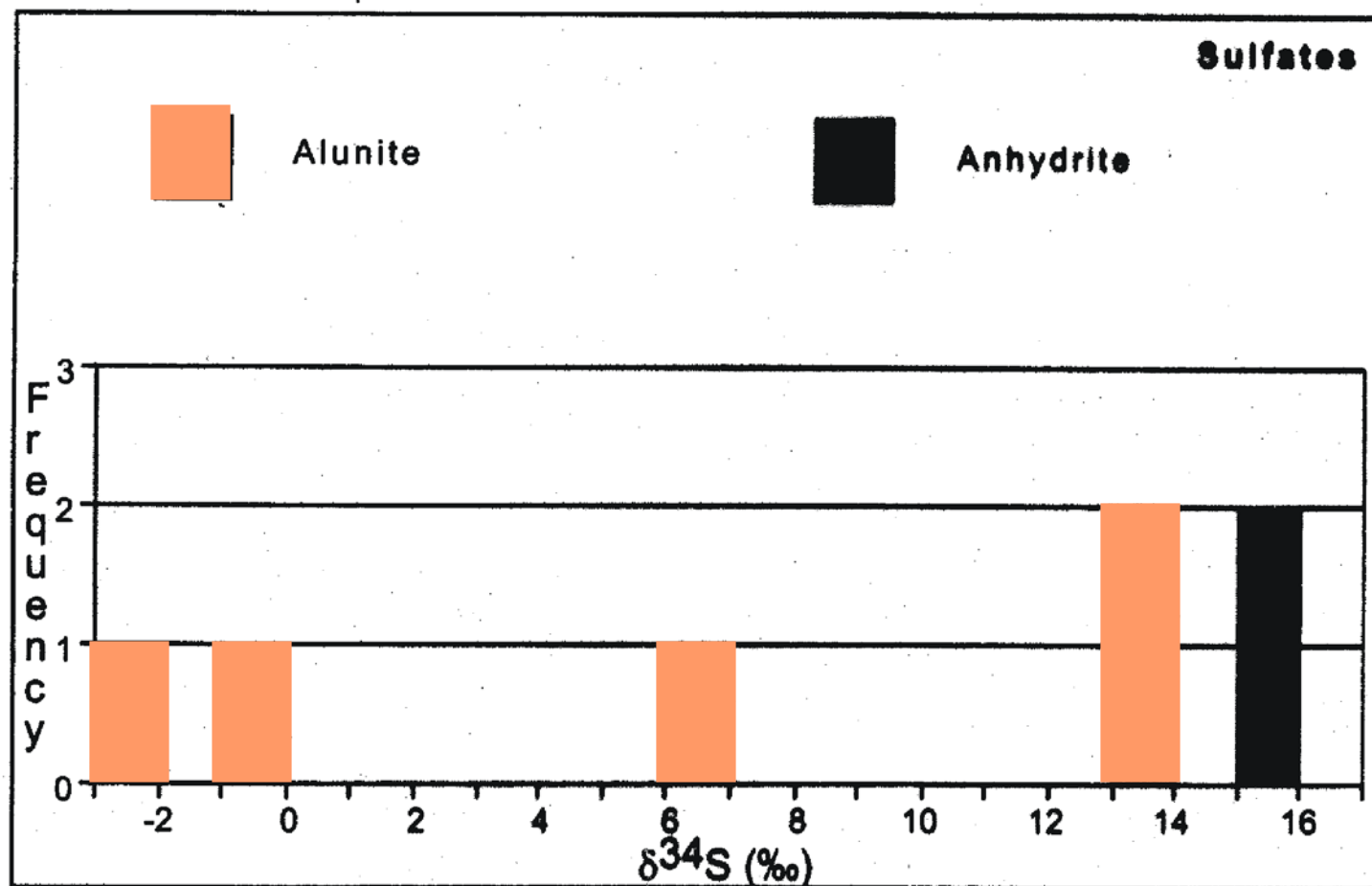
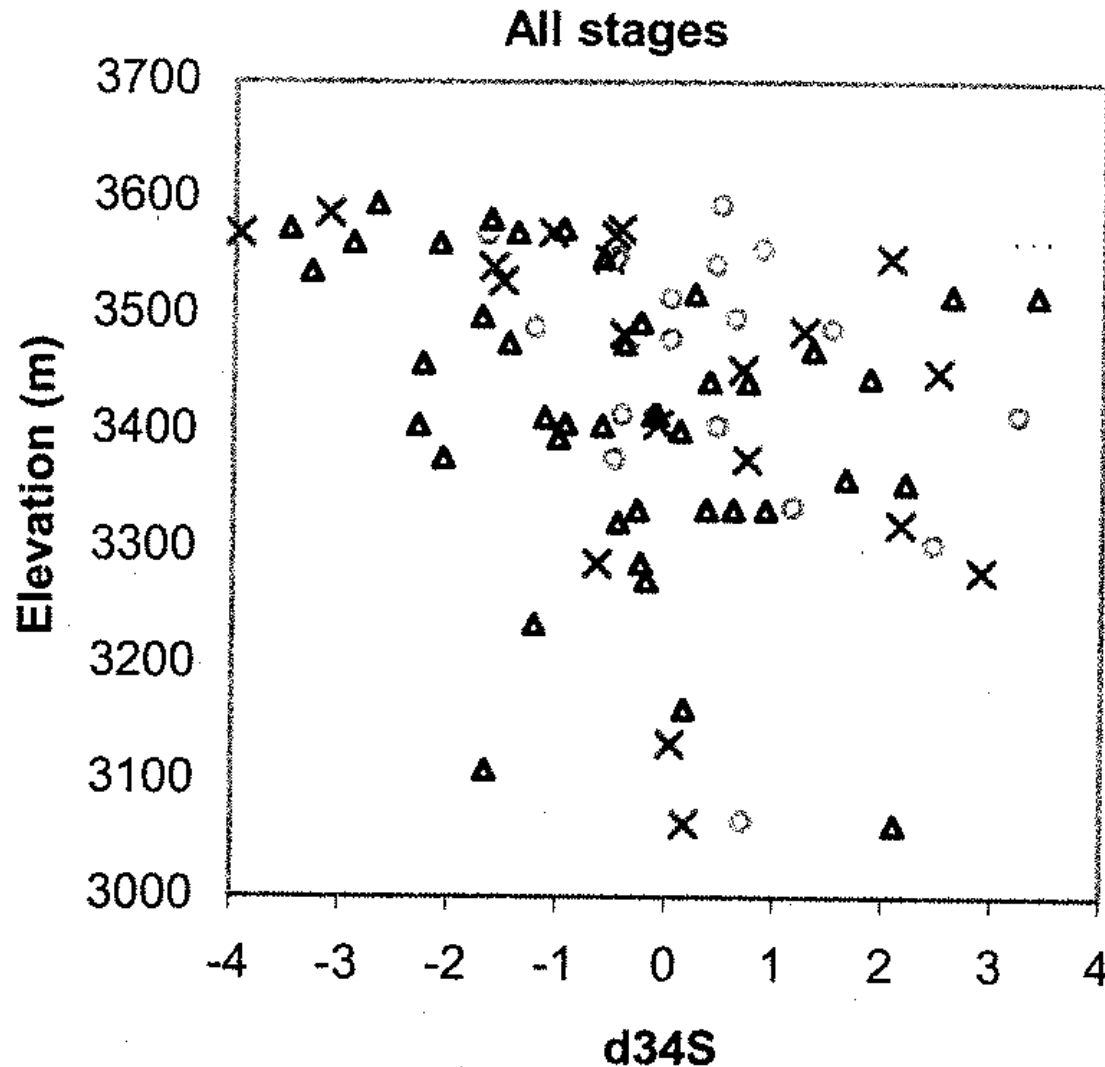


Fig 42: Histogram of $\delta^{34}\text{S}$ (‰) values of sulfates from the different hydrothermal stages of the Escondida deposit. For mineral abbreviations see Appendix E.

Ertsberg -- sulfides



Vein stages:

I x cpy, bn, anh;
biotite and Kspar stable

II o qtz, bn, cpy, anh;
sericite stable

III T qtz, py, cpy, gn,
sp, cal; sericite stable

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