

GRANITES, VOLATILE SOLUBILITY & TRACKING THE FORMATION OF MAGMATIC FLUIDS

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Magmatic fluids have an important role in carrying metals from a source region to ultimate deposition and preservation in an ore deposit. Magmatic fluids are typically dominated by H₂O, and generally they are supercritical; that is, they exist at conditions greater than the critical point (374 °C and ~220 bars for pure H₂O). Magmatic fluids may also contain other low-density molecules or "volatiles" such as Cl, other halides, H₂S, SO₂, CO₂, CH₄, N-compounds, and B. In this workshop we summarize aspects of volatile solubility, the initial volatile content of a melt, and the onset of fluid formation.

Water and granite magmas

Water is the most abundant volatile component in silicate rocks and it is highly soluble in granitic melts. For example, at 700 MPa (7 kbar) a granitic melt may dissolve up to 14 wt. % H₂O (Tuttle & Bowen, 1958). Water solubility is primarily dependent on pressure (Tuttle & Bowen, 1958) and therefore the granitic melt can dissolve increasingly less H₂O as it moves to lower pressures.

When water-saturated minimum-temperature haplogranite (albite-orthoclase-quartz) melts move to lower pressure, they crystallize because of the negative slope of the water-saturated solidus in P-T space. Upon crystallization, the H₂O that was dissolved in these melts exsolves as a fluid phase:

Magma with dissolved H₂O → Crystals + H₂O (fluid phase)

In the case of a haplogranite melt, the crystals are quartz, albite and orthoclase, but in nature other minerals are present, including hydrous minerals that take up H₂O.

A conundrum in the literature has been that since water-saturated magmas crystallize upon decompression then they should be trapped deep in the crust! However, we observe shallow level granites and volcanoes that are saturated in magmatic volatiles. This problem is solved if the granitic melt is initially water-undersaturated because such melts may move to higher levels in the crust without crystallizing due to the positive slope of the water-undersaturated solidus. When water-undersaturated granite magmas are intruded to high levels in the crust (typically ~50 MPa; 0.5 kbar) they become water-saturated and exsolve a supercritical fluid phase:

Water-undersaturated melt with some dissolved H₂O (high pressure & low volume) →

Drier melt, but water-saturated + H₂O fluid (low pressure & high volume)

Miarolitic cavities, essentially holes where well-terminated crystals have grown in contact with the fluid phase, allow us to track the process of volatile exsolution and fluid formation. Large miarolitic cavities occur in granites intruded to pressures <100 MPa (<1 kbar) based on stratigraphy. At 100 MPa granite can dissolve 3.5 – 4 wt% H₂O (Johannes & Holtz, 1996, p. 63) and hence it is suggested that typical granite melt contains ~3 wt. % H₂O.

In some cases, miarolitic cavities are connected in a three-dimensional network, indicating that the partly solidified magma was permeable to (potentially ore-bearing) fluids when the cavities formed (Candela & Blevin, 1996).

Other volatile species in granite magmas

Although H₂O is generally the most abundant volatile phase in magmatic fluids, other volatiles have a significant role in transporting and depositing metals. Since other volatiles have lower solubility than H₂O in granitic melts they may be major contributors to the initial

fluid phase. Furthermore, one volatile may affect the solubility of another and therefore onset of fluid phase exsolution is a function of the partial pressures of all of the volatiles in the system.

Halides

Chlorine is an important ligand in ore systems and likely complexes with metals such as Mo and Cu. Chlorine is most soluble in peralkaline melts, followed by peraluminous melts (Carroll & Webster, 1994). Solubility is also dependent on pressure and H₂O content (Webster, 1997). For instance, a haplogranite with 0% H₂O dissolves ~0.28 wt. % Cl at 200 MPa (2 kbar) and dissolves ~0.23 wt. % Cl at 50 MPa (0.5 kbar). In contrast, a haplogranite with ~3 wt.% H₂O dissolves ~0.26 wt. % Cl at 200 MPa and dissolves ~0 wt. % Cl at 50 MPa. Because Cl is not very soluble in granitic melts, it partitions into the vapor phase and only a small amount of Cl is required to produce a volatile phase. It is notable that is relatively easy to produce a fluid in the H₂O-Cl system without a dramatic depressurization or crystallization, relative to the H₂O-only system. For example, at 200 MPa, 800 °C a fluid phase may exsolve with only 1-3 wt.% H₂O and 0.24-0.26 wt. % Cl in the melt, but if Cl is absent then an excess of ~5 wt. % H₂O is required to produce a fluid phase.

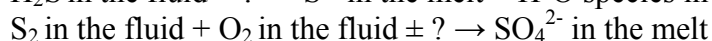
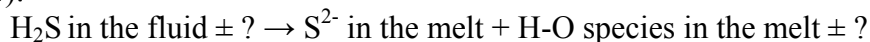
Fluorine may also be abundant in granitic systems although it prefers to be in the melt than the fluid phase. Nonetheless, F has two important roles in ore deposits. First, F-rich melts dissolve more H₂O and Cl than F-poor melts, hence, the F-rich melts will exsolve a fluid phase at shallower pressures, all other factors kept equal (Webster, 1997). Second, F has a role in hydrothermal alteration.

Br and I, although low in abundance, may have a role in metal transport because they partition strongly into the fluid phase (Bureau et al., 2000) and Br-bearing salts are found in fluid inclusions from some ore deposits (e.g., Kamenetsky et al., 2002).

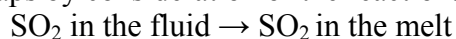
Sulfur species

Sulfur is another important ligand in ore systems, but its behaviour is complicated in melts and fluids because it changes speciation, primarily as a function of oxygen fugacity (fO_2). In the fluid, the dominant sulfur species are H₂S at fO_2 s lower than ~2.2 log units below the nickel-nickel oxide buffer (<~NNO-2.2) and SO₂ at higher oxygen fugacities (Carroll & Webster, 1994). In granitic melts, at fO_2 <~NNO+0.3, S²⁻ dominates, whereas at higher fO_2 , SO₄²⁻ (S⁶⁺) is assumed to be present in the melt phase (Carroll & Webster, 1994).

The disconnect between the change in speciation in the fluid phase (~NNO-2.2) and the melt phase (~NNO+0.3) is poorly understood, but it would be helpful to understand to better predict S speciation in ore-forming processes. Proposed reasons include involvement of species in the fluid phase such as H₂S, S₂, O₂, SO₃, and species in the melt such as O²⁻, H₂O, OH-, FeO, and CaO and can be summarized by reactions of the form (modified after Carroll & Webster, 1994):



One problem with these existing reactions is that SO₄²⁻ (S⁶⁺) is assumed to be the oxidized sulfur species in the melt phase, but in most cases specific analyses have not been made for other species (Carroll & Rutherford, 1988; Nagashima et al., 1972; Paris et al., 2001). Recent work indicates that S⁴⁺ (as SO₃²⁻ or SO₂) occurs in significant concentrations in silicate glasses (Métrich et al., 2002; M.E. Fleet pers. comm.). In our opinion, the sulfur solubility models need to be modified to account for the presence of S²⁻, S⁶⁺ and S⁴⁺ species in the melt, perhaps by consideration of the reaction:



As well as affecting the sulfur speciation, oxygen fugacity also affects the quantity of sulfur-bearing fluid that may form and consequently the sulfur fugacity of that fluid. In dacitic melts at moderate oxygen fugacity (NNO to NNO+1), the formation of an H₂S-bearing magmatic fluid phase is not favored because sulfur diffusivity is low and sulfur goes into sulfide "sinks" (fluid-melt partition coefficient ~1, at ~225 MPa, ~780 °C; Scaillet et al., 1998). In dacitic melts at higher oxygen fugacity (NNO+1.4 to NNO+2.6), sulfur partitions preferentially into a SO₂-rich fluid phase (fluid-melt partition coefficient ~1000, at ~225 MPa, ~780 °C; Scaillet et al., 1998).

In terms of metal transport, these data indicate that very oxidized (>NNO+1.4) conditions are more favorable for production of a S-rich fluid phase. This finding is in agreement with the observations that Cu, Au and Mo are likely transported as S-complexes in the fluid and/or vapor phase (e.g. Audétat et al., 1998) and porphyry Cu-Au-Mo deposits are associated with oxidized granites (e.g., Blevin & Chappell, 1992; Burnham & Ohmoto, 1980).

CO₂

CO₂ is not very soluble in granitic melts where it dissolves as molecular CO₂ species. The solubility increases with decreasing (Si + Al) content and increasing Ca content and accordingly CO₂ is more soluble in intermediate melts where both molecular CO₂ and CO₃²⁻ species are present (King & Holloway, 2002). As a result, granitic suites that are high in Ca (more mafic I-type suites) are the best source rocks for ore deposits with CO₂-rich fluids such as intrusion-related gold deposits (Baker, 2002; Lowenstern, 2001).

Like H₂O, CO₂ solubility increases with pressure. Since CO₂ is more volatile than H₂O, it behaves like Cl and degasses at greater depth and may make up the initial magmatic volatile phase (assuming that other more volatile species are absent). During closed-system decompression, CO₂ contents in a granitic melt will initially decrease when a CO₂-rich, H₂O-poor fluid evolves and as a result the H₂O content of the melt will remain relatively constant (Holloway, 1976). At shallower depths (1-4 km) much of the CO₂ will have degassed and CO₂-poor, H₂O-rich fluids will evolve, resulting in decreasing concentrations of both CO₂ and H₂O in the melt. Some intrusion-related gold systems and porphyry Mo deposits, show the predicted evolution of magmatic fluids from CO₂- to H₂O-rich with decreasing pressure (Baker, 2002; Lowenstern, 1994).

In intermediate systems, the situation is slightly different than felsic systems because CO₃²⁻ is present and H₂O enhances CO₂ solubility; for example, CO₂ solubility in the melt increases by 0.06 wt.% per wt.% of H₂O (1 GPa (10 kbar) and 1350 °C, King & Holloway, 2002). Hence, relative to more felsic systems the total quantity of CO₂ in the fluid would be greater for a given pressure, temperature and H₂O content.

While it is not known whether C-O-species are effective ligands for ore metals in hydrothermal fluids (summary in Lowenstern, 2001), CO₂ readily forms a vapor and for this reason it may cause a hydrothermal fluid to unmix to a vapor and a hydrosaline brine (Joyce & Holloway, 1993). The presence of a CO₂-bearing vapor phase may also incorporate other species that might act as ligands for metals in the vapor phase (Lowenstern, 2001).

Summary and fate of high temperature fluids

Ore deposits in granites are often related to exsolved magmatic fluids that may form during decompression or crystallization. While these fluids are commonly dominated by H₂O, other species such as the halides, sulfur species and CO₂ may partition into the fluid early and aid metal transport. It is possible to infer the presence of a fluid phase by features such as miarolitic cavities that may represent an interconnected fluid network. The evolution of the fluid phase may be tracked using solubility data and analyses of melt inclusions and fluid inclusions.

When the supercritical fluid rapidly cools below the critical P and T to a hydrothermal solution, the concentrations of the fluid species will change dependent on temperature. The fluid composition will be a function of the initial bulk composition, buffering reactions, extent of interaction with the wall rock and organic molecules, input of new hydrothermal or meteoric fluids, unmixing and boiling, changes in the local conduit conditions and other factors (e.g., Thompson, 1995).

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& TRACKING THE FORMATION OF
MAGMATIC FLUIDS**

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&
Allan J.R. White (VIEPS, Melbourne)**

IMPORTANCE OF WATER AND OTHER VOLATILES IN GRANITE MAGMAS

Magmatic fluids have an important role in carrying metals from a source region to ultimate deposition and preservation in an ore deposit.

Magmatic fluids are typically dominated by H₂O, thus they normally exist at temperatures greater than the critical point (361°C for pure water).

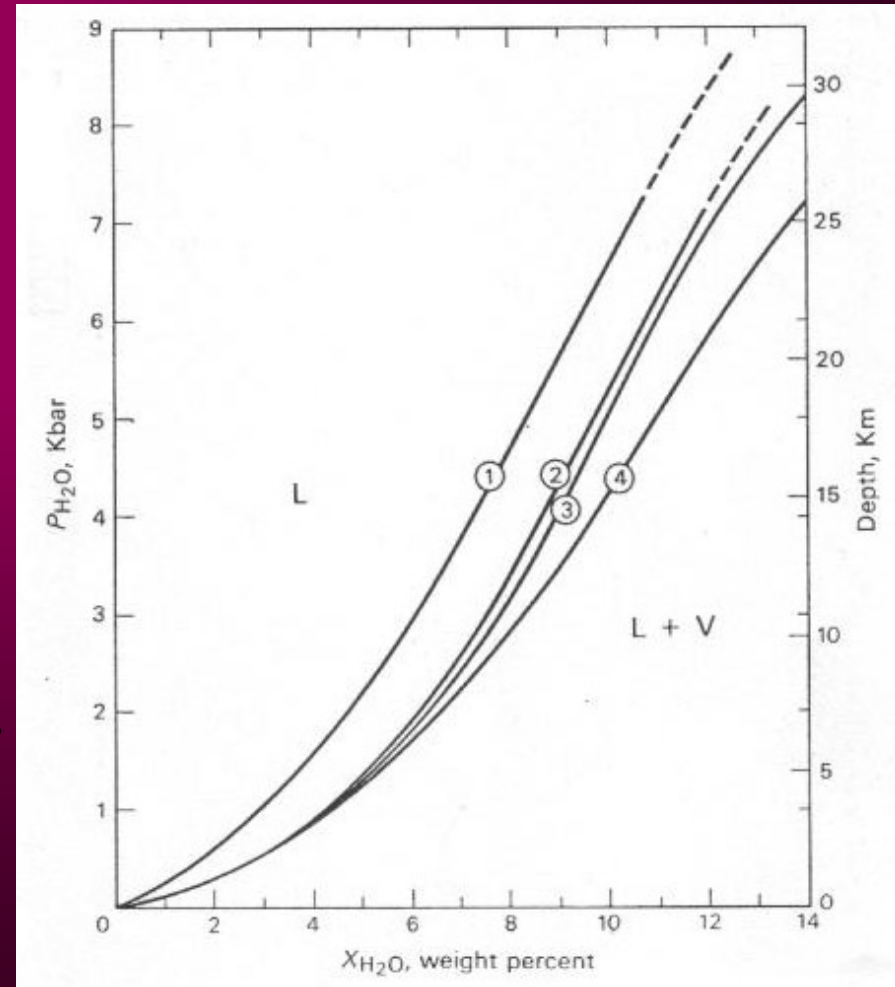
These fluids may also contain other low-density molecules or "volatiles" such as CO₂, CH₄, N-compounds, H₂S, SO₂, HCl and other halides and B.

SOLUBILITY IN GRANITE MELTS

- Solubility is high e.g. at 700MPa (7Kb) granite melt may dissolve 14wt% H₂O (Tuttle & Bowen 1958).
- So long as temperature is above the liquidus, temperature has little effect on solubility. Solubility is primarily dependent on pressure (Tuttle & Bowen 1958).
- Hamilton et al. (1964) showed that solubility of H₂O is very similar in granite, albite, basalt and andesite melts.

SOLUBILITY IN GRANITE MELTS

Solubility of H₂O in melts of basalt at 1000°C (1), andesite at 1100°C (2), albite 700 – 850°C (3) and Li pegmatite (fractionated granite) at 600 – 720°C (4). After Hamilton et al. (1964).

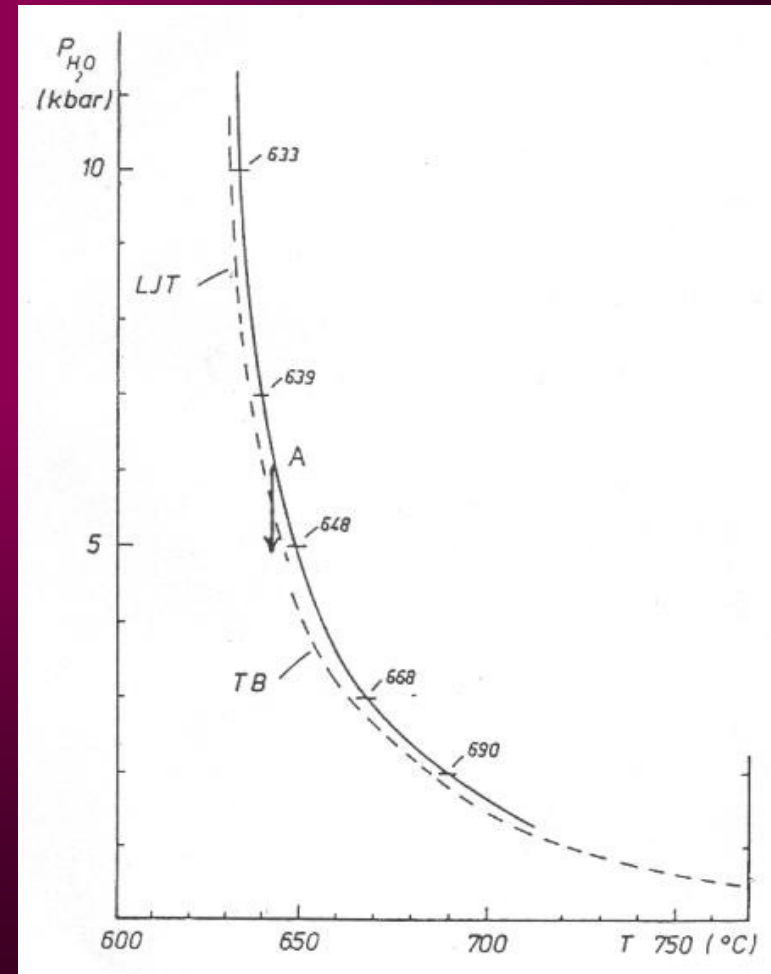


SATURATED HAPLOGRANITE SOLIDUS

After Johannes (1984)
(full line).

Dashed line Tuttle &
Bowen (1958) and
Luth, Jahns and Tuttle
(1964).

Note melt at A
(saturated) must
solidify as soon as it
begins to move
upwards.

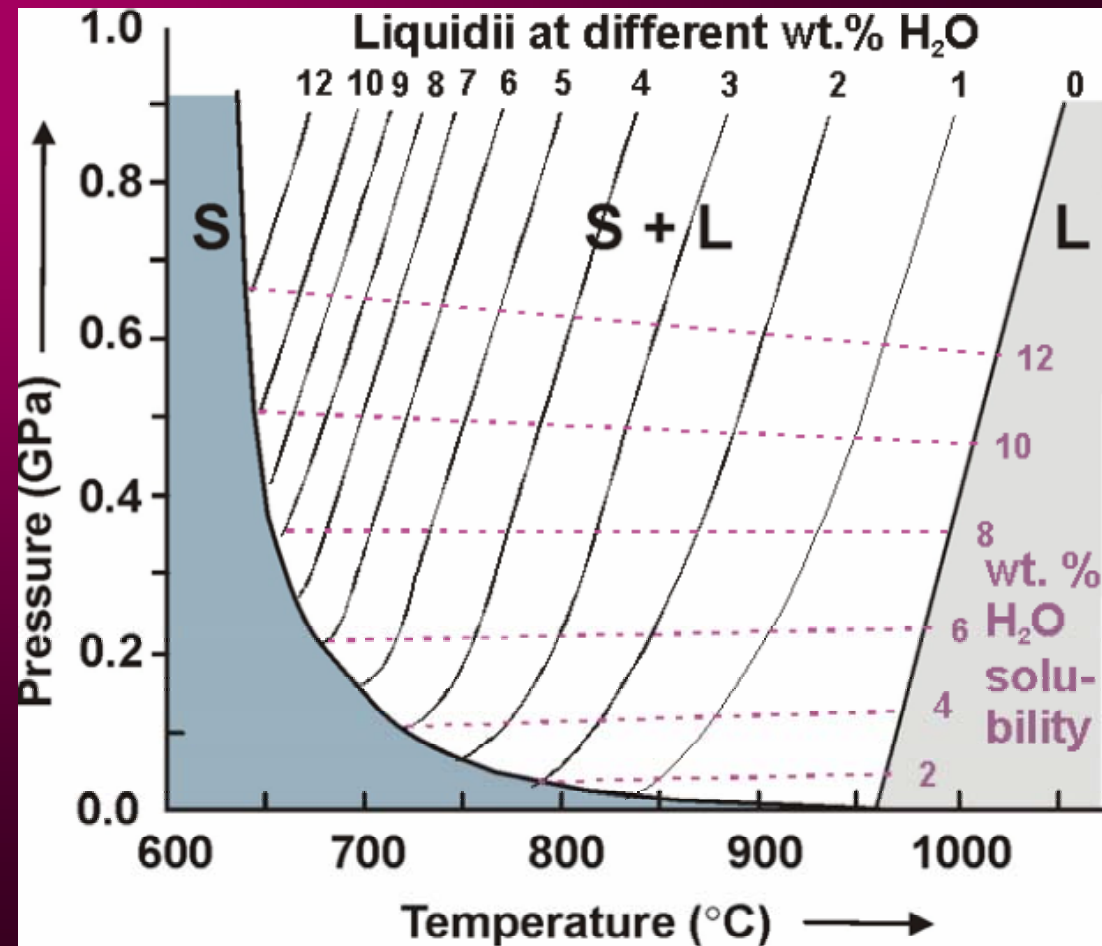


UNDERSATURATED GRANITE MELTS

Granite-vapor system

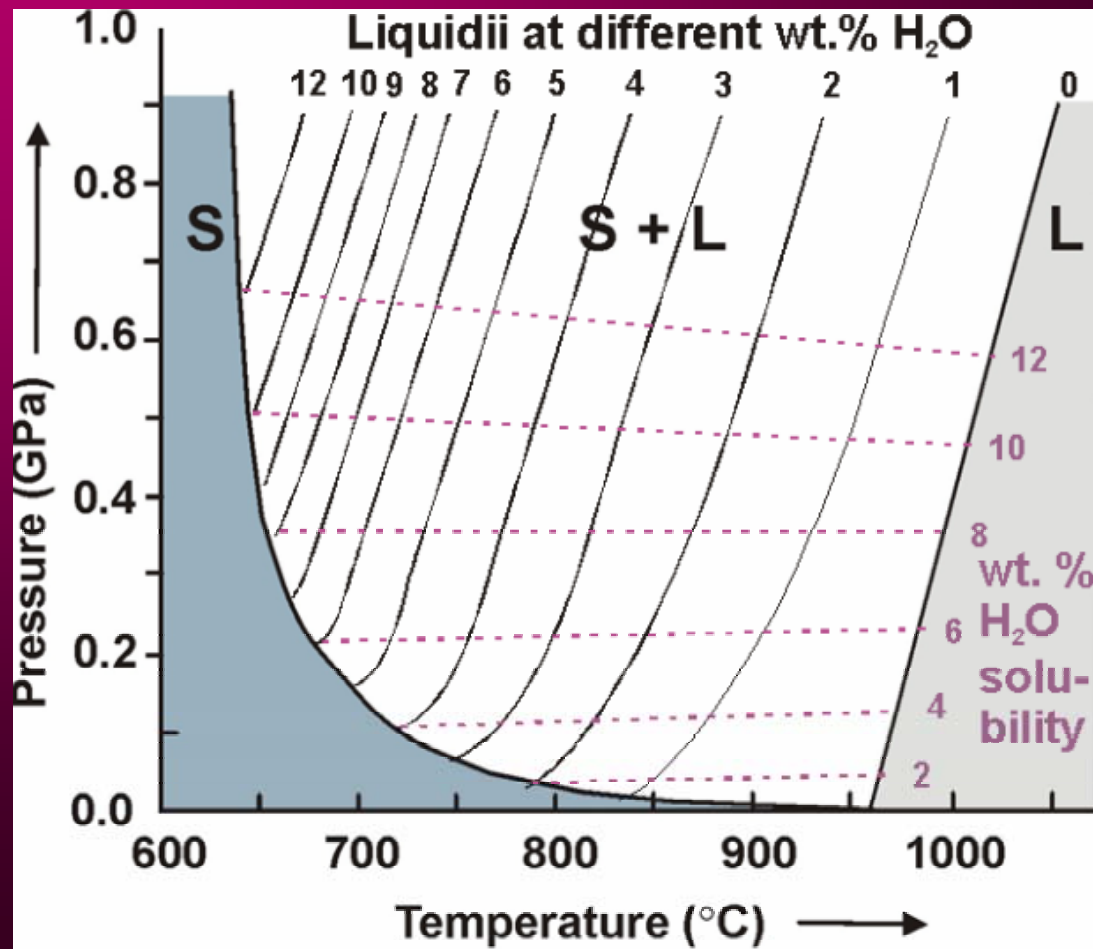
Granite melt at 200 MPa (2 Kb) could contain 6wt% H₂O if saturated but if it contains only 3wt% H₂O at this pressure (at 800 degrees C) it will be strongly underaturated.

This granite will undergo decompression boiling at about 50MPa (500 bars).



UNDERSATURATED GRANITE MELTS

Granite-vapor system



HOW MUCH H₂O IS THERE IN A TYPICAL GRANITE MELT ?

H₂O must be appreciable because intrusion temperatures are commonly near 850°C but the dry liquidus is above 1100°C and it is H₂O that lowers the liquidus.

There are many estimates based on questionable assumptions (see Clemens, 1984, *Lithos* 17 pp 273-287). His best estimate is between 3 and 5 Wt% H₂O.

I use miarolitic cavities which are leaked bubbles of supercritical fluid produced by decompression boiling. Large miarolitic cavities occur in granites intruded to pressures < 100 MPa (1000 bars) based on stratigraphy. At 100 MPa granite can dissolve 3.5 – 4 Wt% H₂O (Johannes & Holtz 1996 p 63).

MIAROLITIC CAVITIES

These are holes or gas cavities occurring in granites. Perfect crystals of quartz and feldspars project into the cavity as shown in below.

20 mm



MIAROLITIC CAVITIES

When filled by secondary minerals such as chlorite, these are more difficult to recognise but commonly marioles occur within small pod "pegmatites" as shown: these are easily recognised.



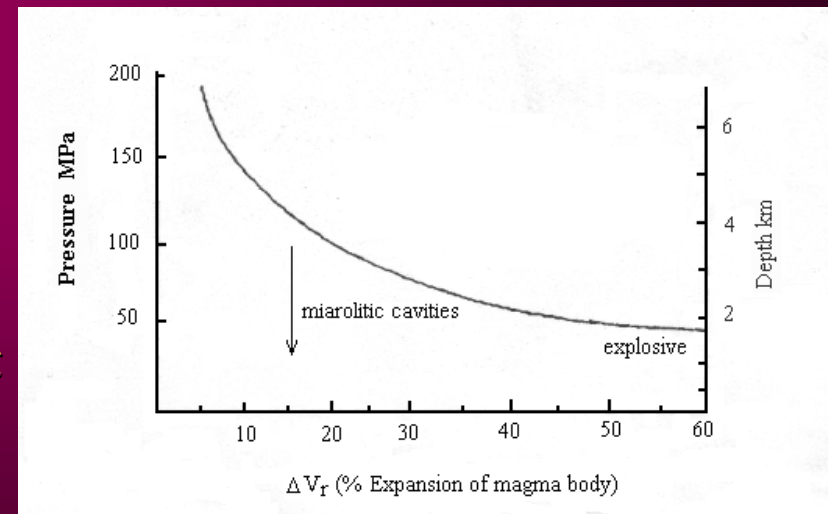
MIAROLITIC CAVITIES

Volume change ΔV_r for the reaction:



This shows that large miarolitic cavities are most likely at pressures < 100 MPa.

Data from Burnham & Ohmoto (1980: Mining Geol. Special Issue 8, 1-11)



HOW MUCH H₂O IS THERE IN A TYPICAL GRANITE MELT ?

FROM MIAROLITIC CAVITY DATA
NORMAL BATHOLITHIC GRANITE MELTS
CONTAIN ABOUT 3 WT % H₂O.

Naney's (1983 *Amer.J. Sci* 283, 993-1033) experiments showed that early hornblende crystallisation in granites requires about 4wt% H₂O. This is consistent with the above because hornblende is considered to be relatively late in most hornblende granites.

NOTE: A granite magma with only 33% melt (near the critical melt fraction) could contain no more than 1% H₂O to produce cavities near surface.

PEGMATITE MELT

Pegmatites are fractionated H₂O- rich granite melts. They are probably saturated.

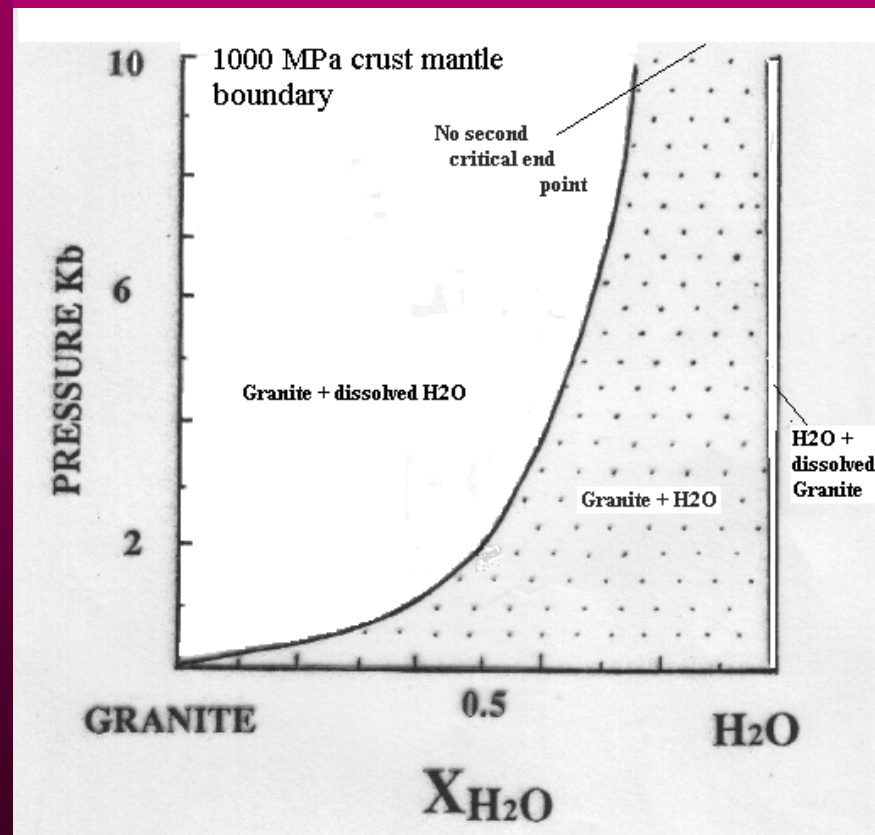
Some (e.g. Clarke, 1992, *Granitoid Rocks*, Chapman & Hall) say pegmatites are products of the vapour or fluid.

However:-

Note 1. The very low amount of granite dissolved in the fluid and

2. There is no second critical end-point at crustal pressures.

Data on granite in H₂O from Burnham (1967 In Barnes, *Geochemistry of Hydrothermal Ore Deposits*, Holt Rinehart & Winston, NY)



PRIMARY HYDROTHERMAL SOLUTIONS

Evolution of primary fluid phase

When undersaturated granite magmas are intruded to high levels in the crust they become saturated and exsolve a fluid phase at high temperatures.

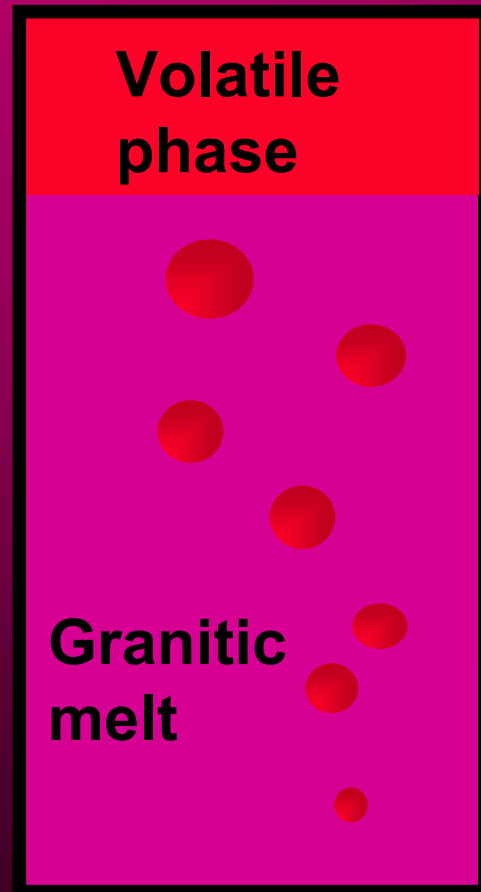
This is above the critical temperature and pressure and hence are referred to as “supercritical fluids”.

This commonly occurs at about 50 MPa. The supercritical fluid rapidly cools below the critical P and T to a hydrothermal solution.

In addition to H₂O, magmatic fluids may also contain other low-density molecules or "volatiles"

For example:

- Cl, I, Br
- sulfur species: H₂S, SO₂
- CO₂, CH₄
- N-compounds
- B
- Mo



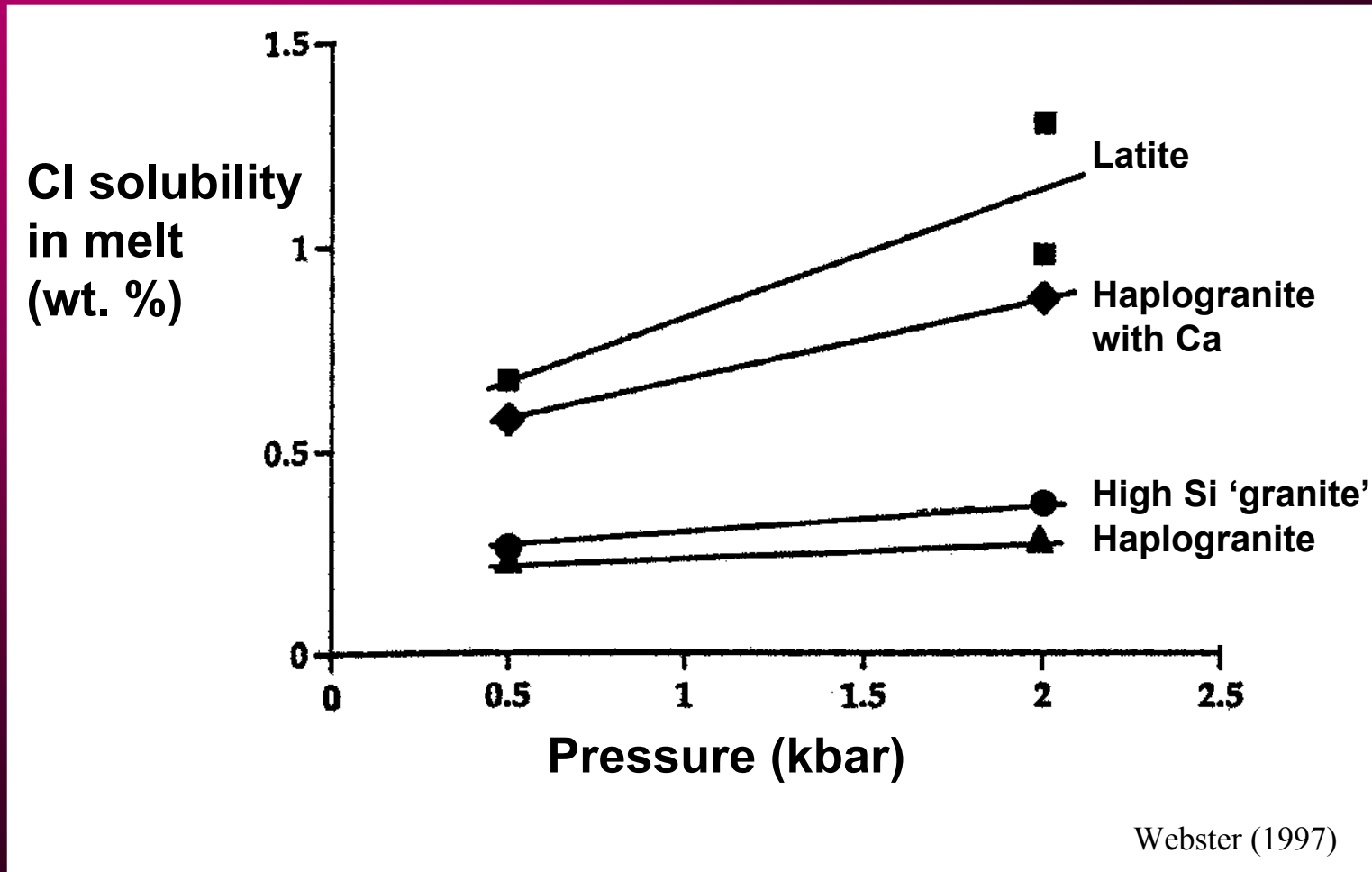
**Solubility =
max. amount
that can dissolve**

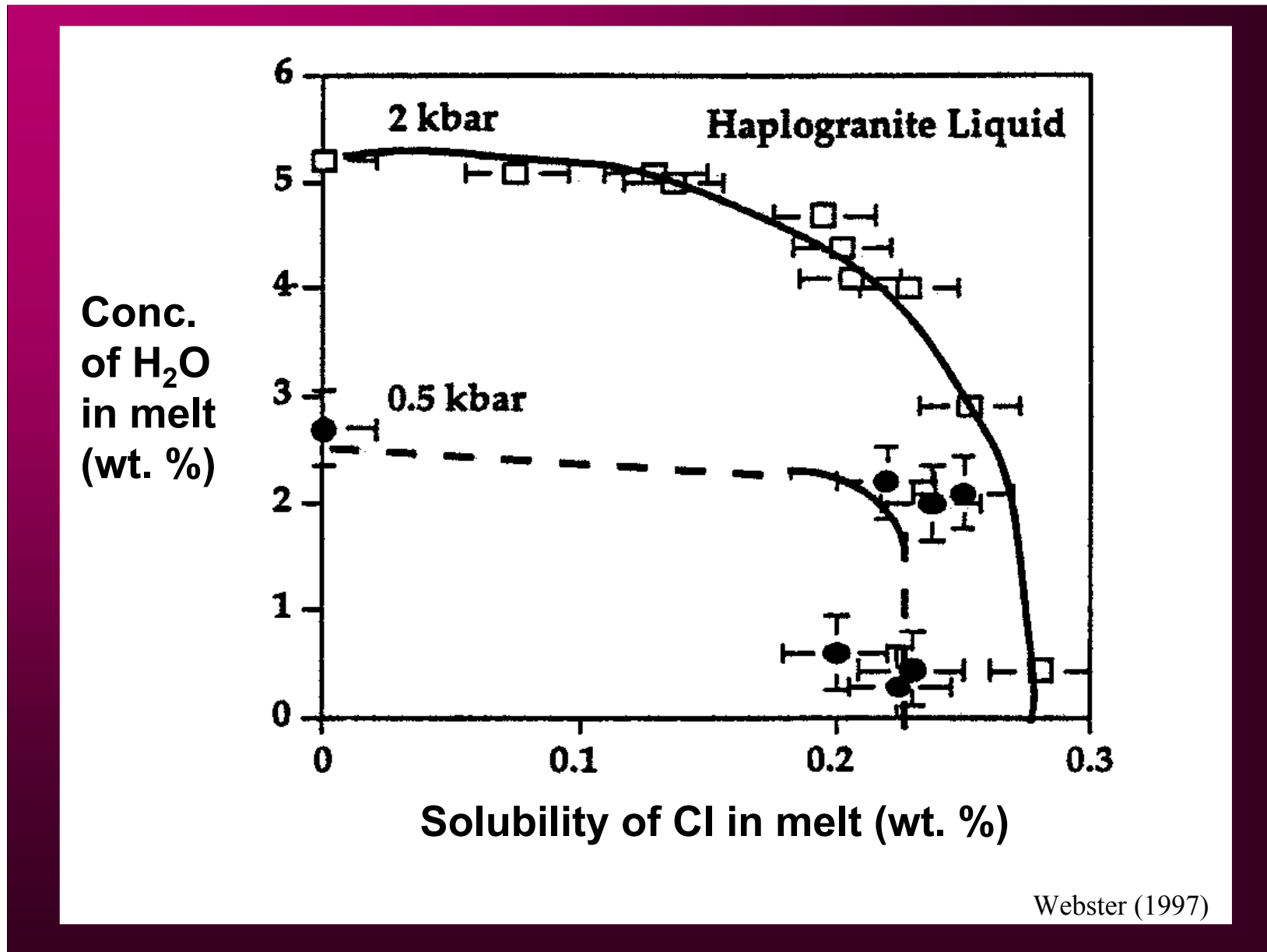
Since other volatiles have lower solubility than H₂O in granitic melts they may be major contributors to the initial fluid phase

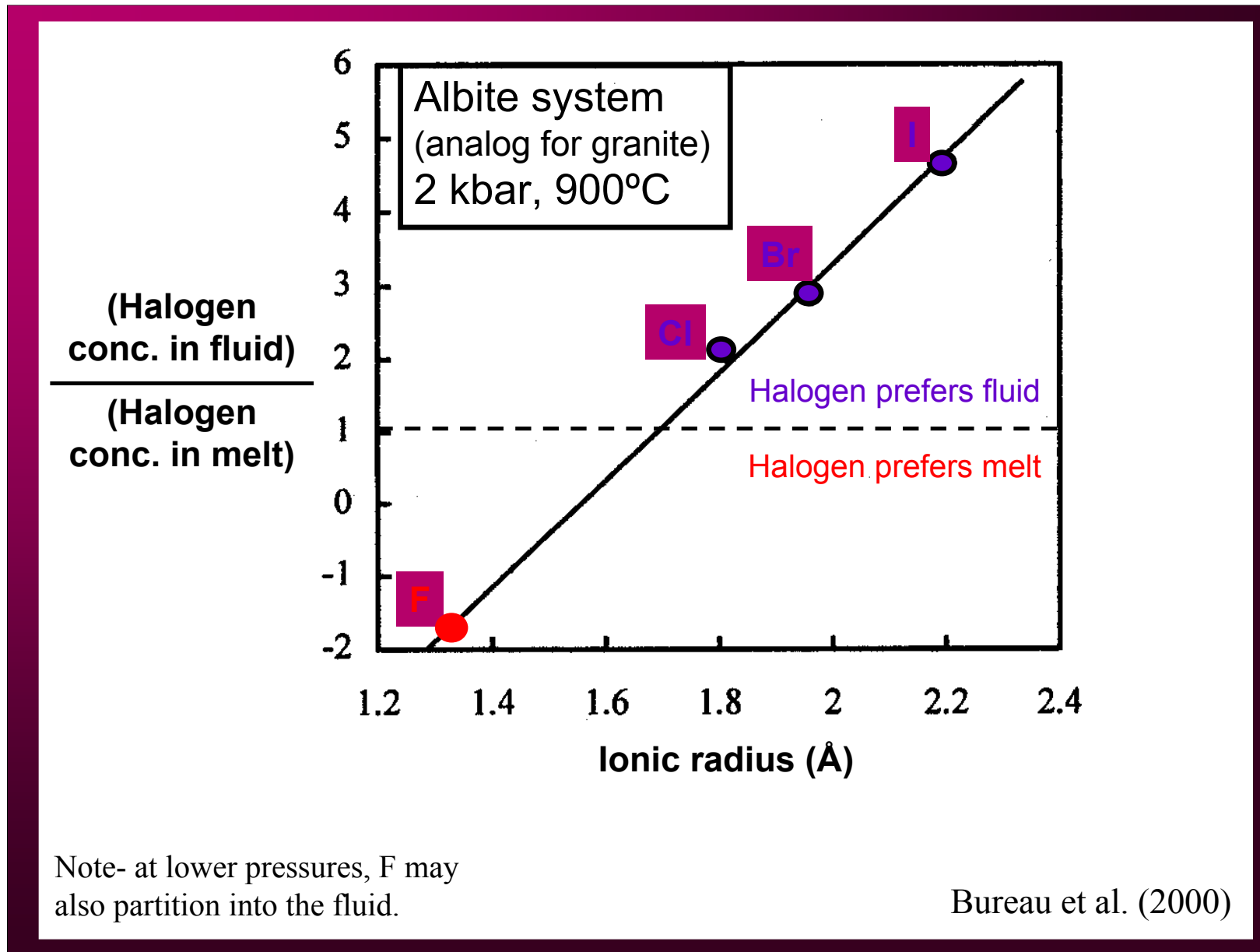
Halogens in granites

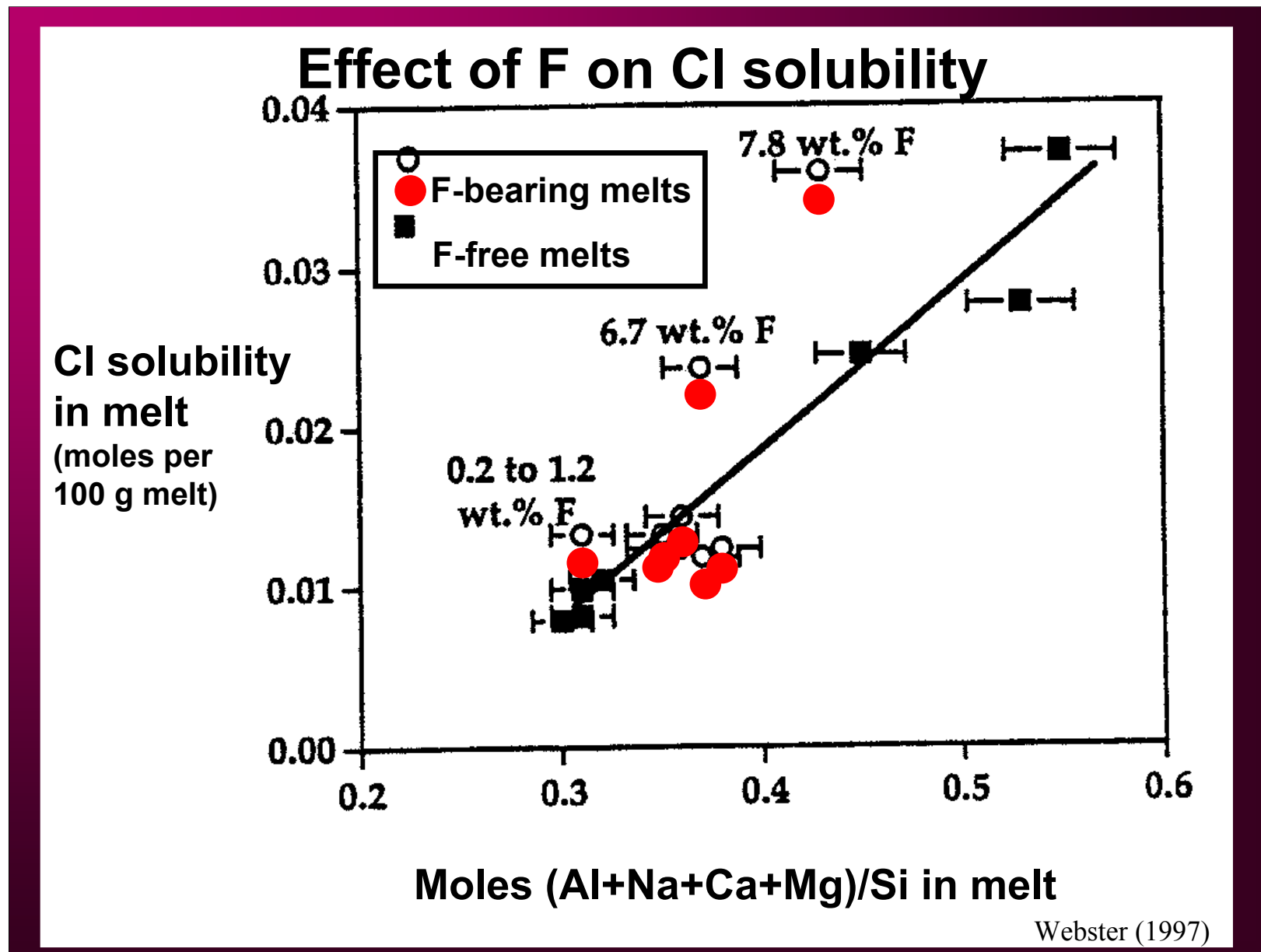
- Chlorine is the most abundant halogen, followed by fluorine. Bromine & iodine are minor constituents.
- Chlorine is very insoluble in granite melts so it forms a fluid phase readily
- Chloride species are important in metal transport
(e.g. Cu, Mo)

Cl solubility for H₂O-poor silicate melts



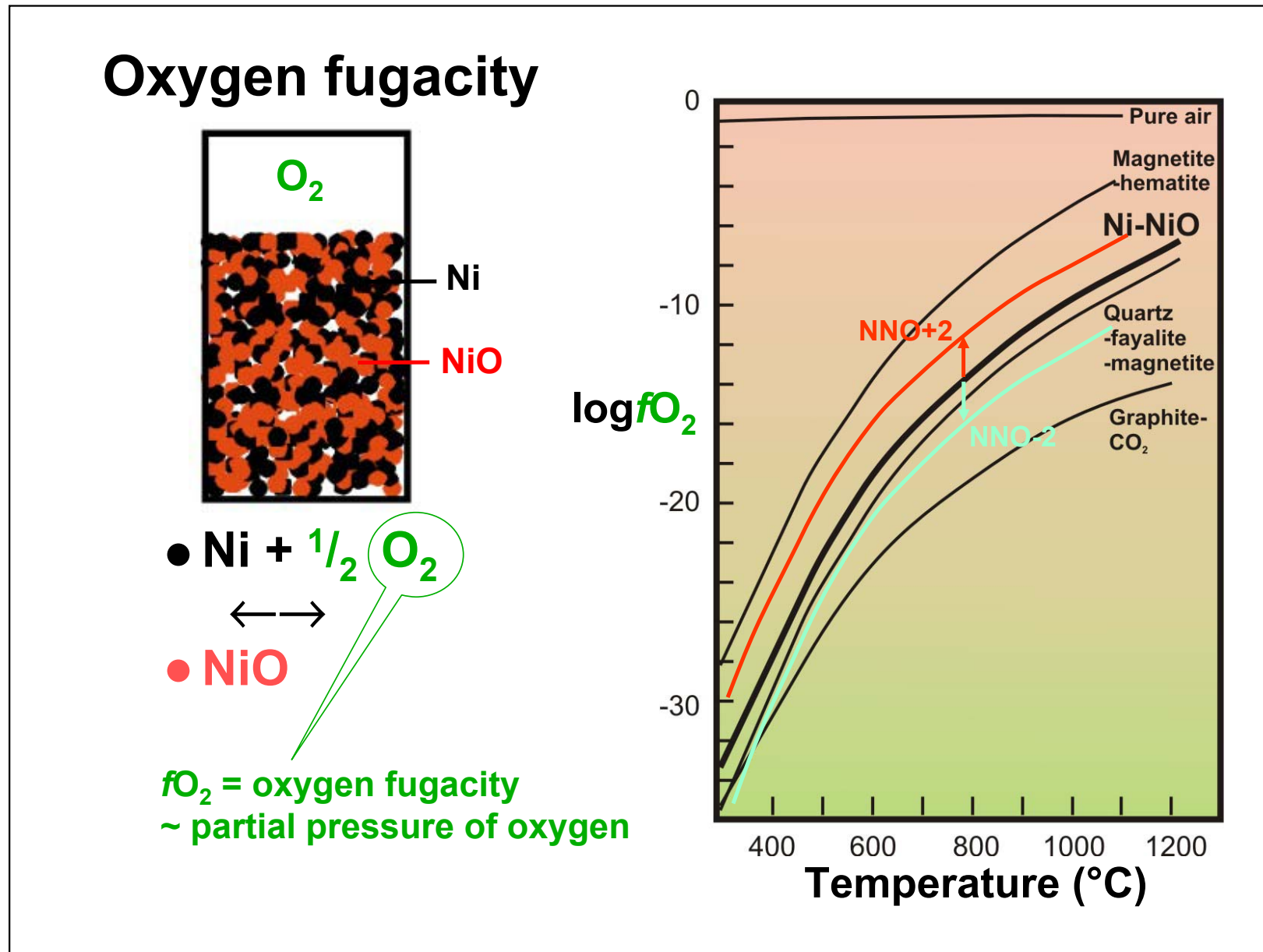


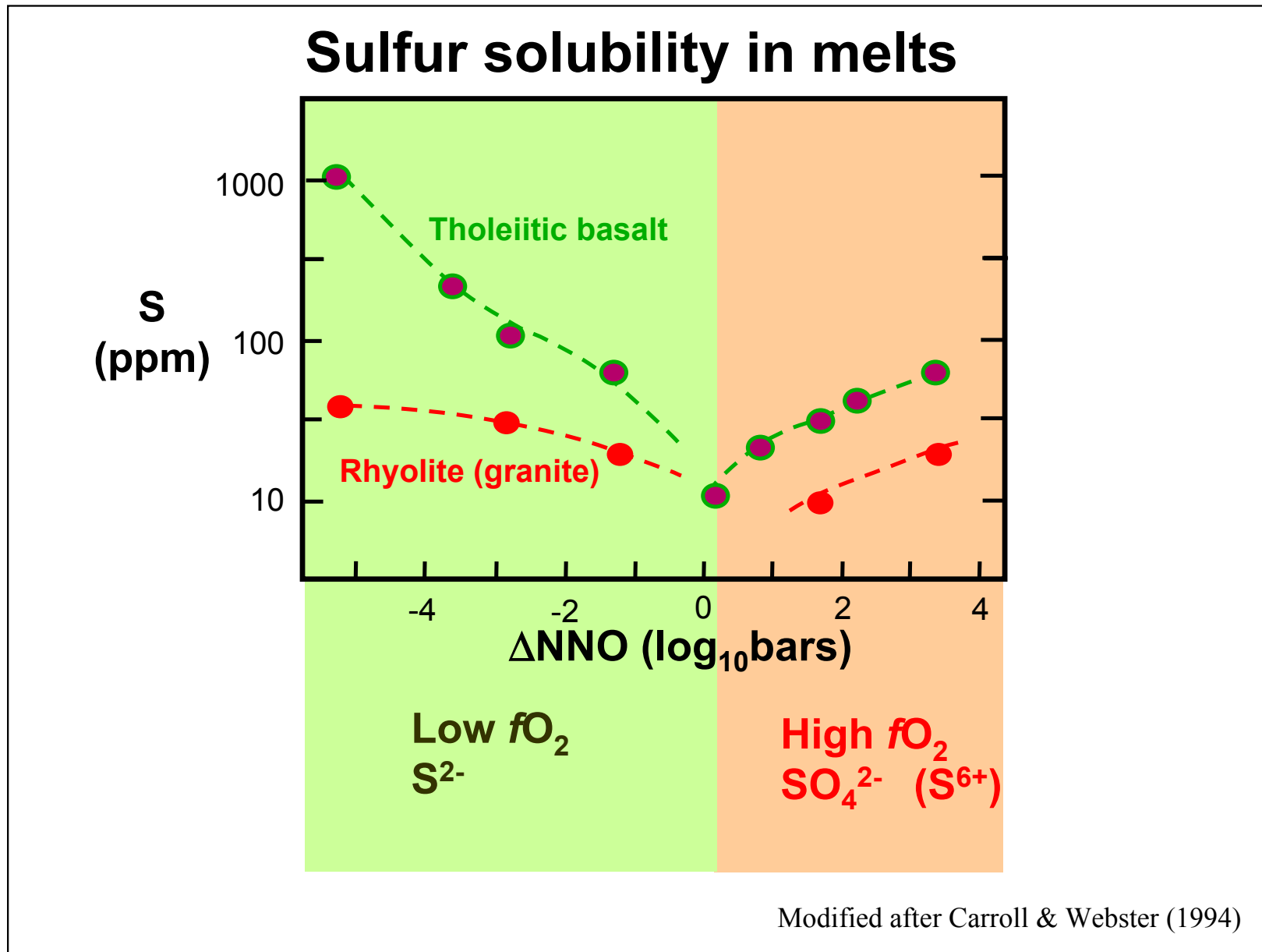


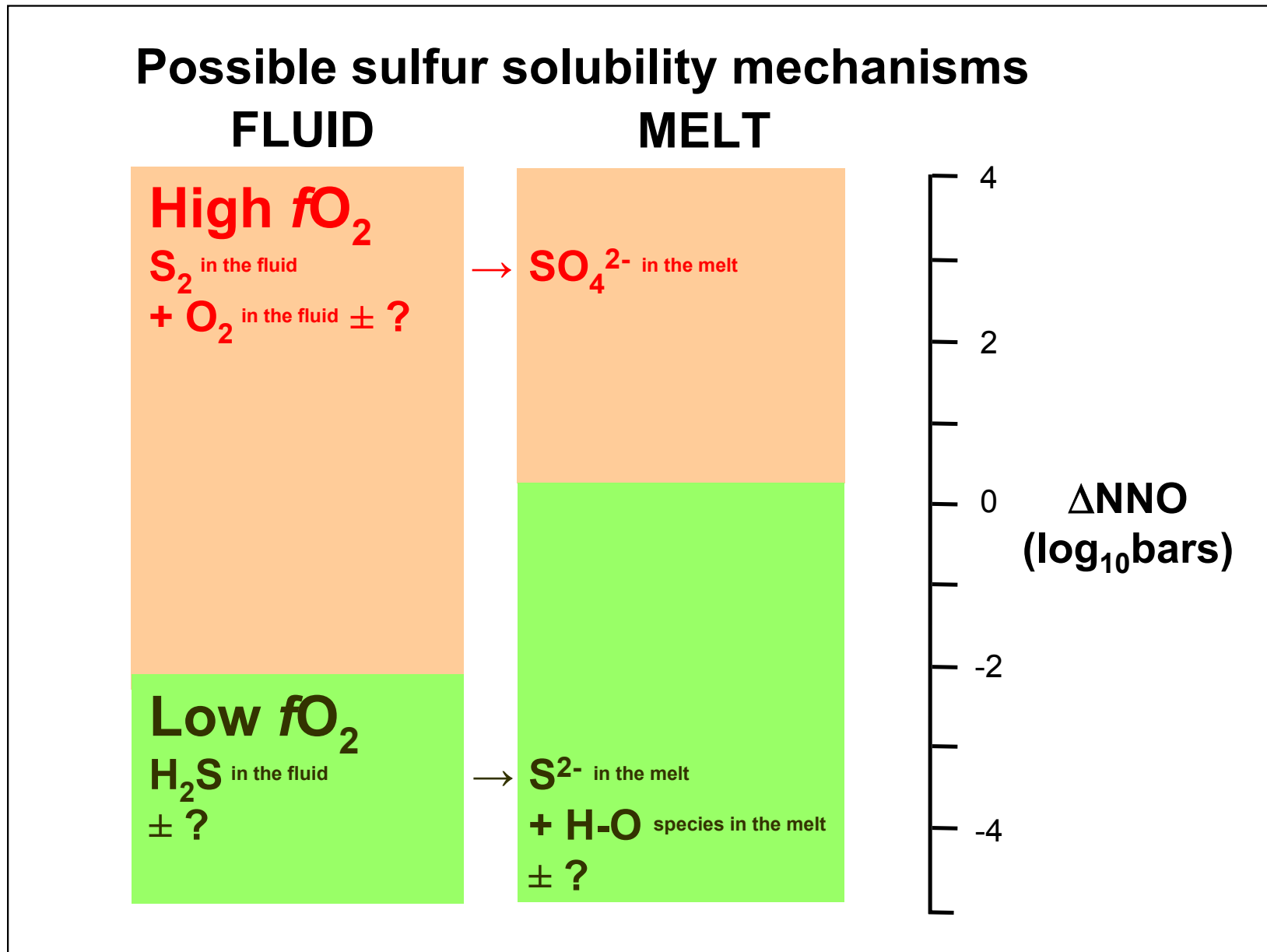


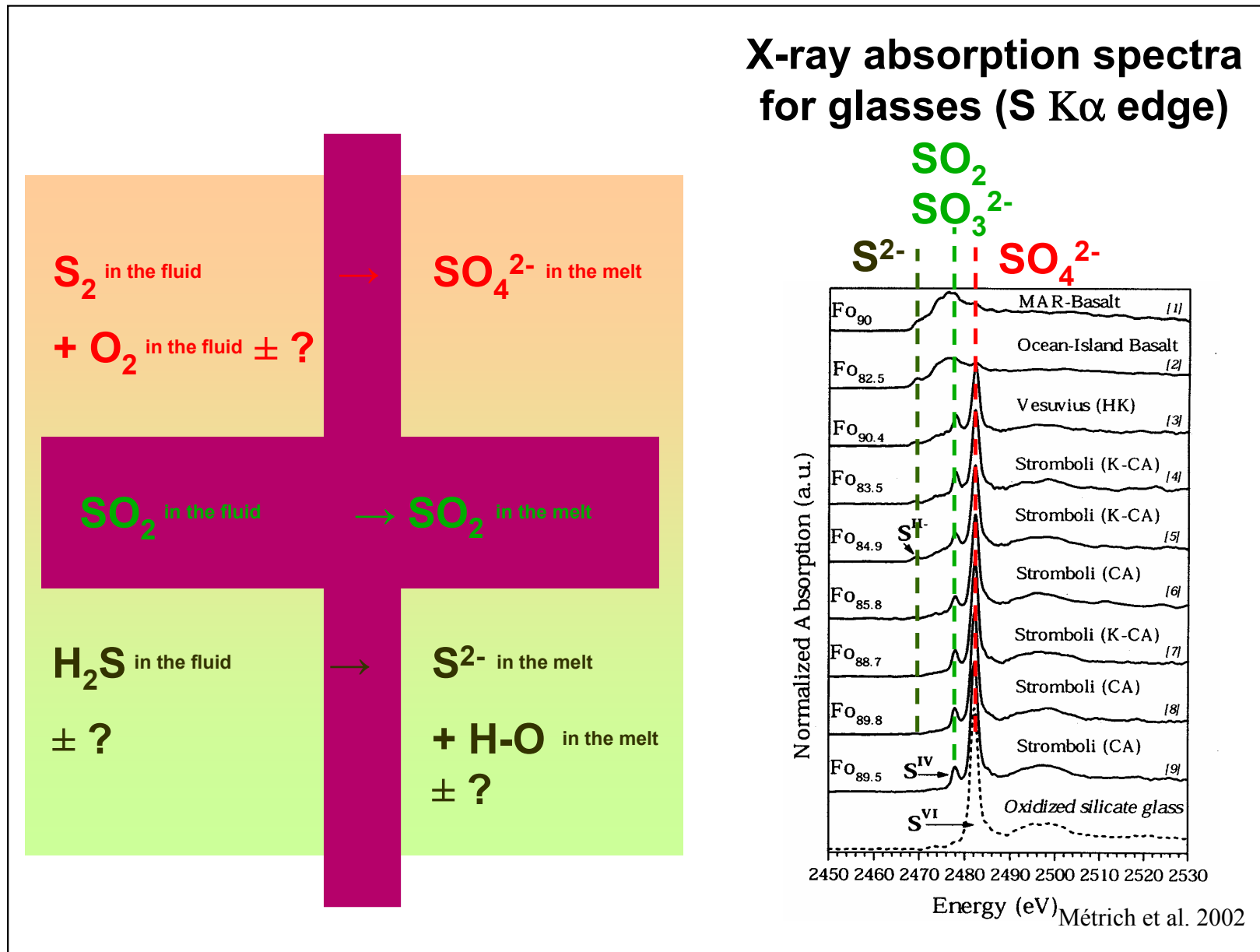
Sulfur in granites

- Sulfur is quite insoluble in granite melts so it, like Cl, forms a fluid phase readily
- Sulfur species are thought to be important in metal transport
- Sulfur speciation (e.g., H_2S vs. SO_2) depends on oxygen fugacity









Sulfur & ore deposits

In dacites, rel. high fO_2 conditions produce more fluid

- SO_2 fluid/melt ~ 1000
- H_2S fluid/melt ~ 1 (Scaillet et al., 1998)

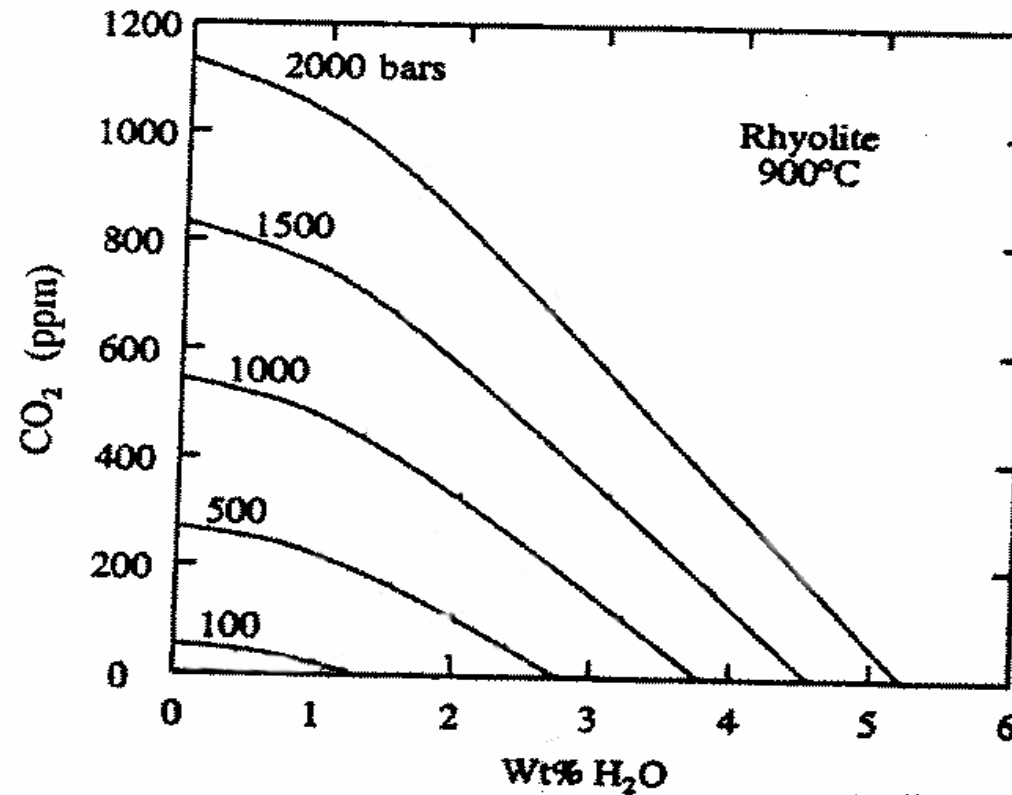
This is likely why many Cu, Mo deposits are oxidized

CO₂ in melts

- In granites, CO₂ is not very soluble
- It is not known whether C-O species carry significant quantities of metals or not (except perhaps U)
- Diorites (Ca-rich, mod. SiO₂ rocks) dissolve more CO₂ than granites
 - In granites, CO₂ solubility is not affected by H₂O
 - In diorites, CO₂ solubility increases with increasing H₂O

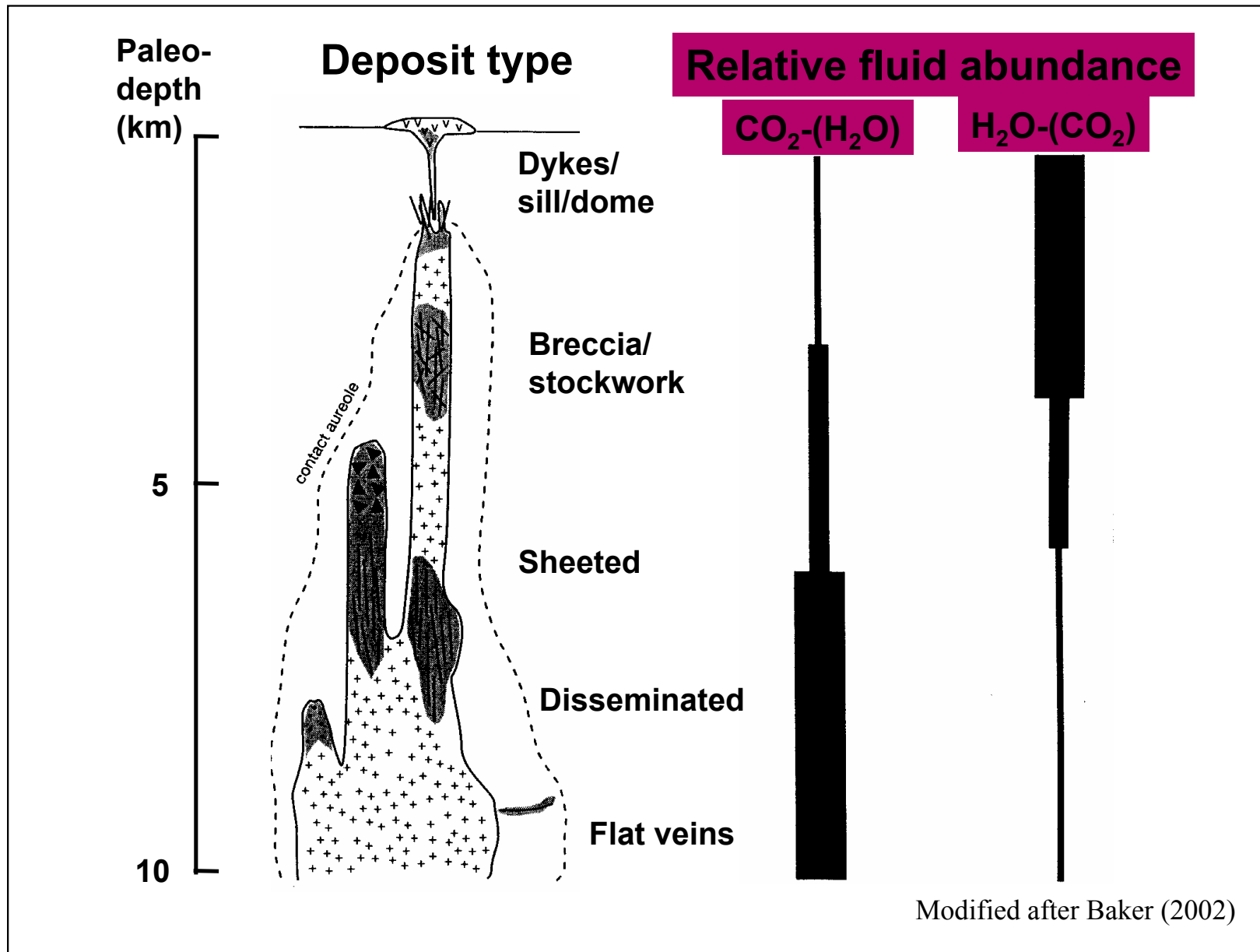
Lowenstern (2001)
King & Holloway (2002)

**During decompression in C-O-H systems
CO₂ degases first followed by H₂O**



(Holloway and Blank, 1994)

Two-volatile solubility diagrams can be a useful way of examining volatile data. These diagrams predict the maximum amount of a volatile expected in a melt at a given pressure. Thus, the diagrams can be used to model open- and closed-system decompressional degassing (first boiling), isobaric fluid-saturated crystallization and fluid-absent crystallization trends. CO₂-H₂O solubility diagram for CO₂ and H₂O in rhyolite at 900 °C as a function of pressure and fluid composition (Holloway and Blank, 1994)



Modified after Baker (2002)

