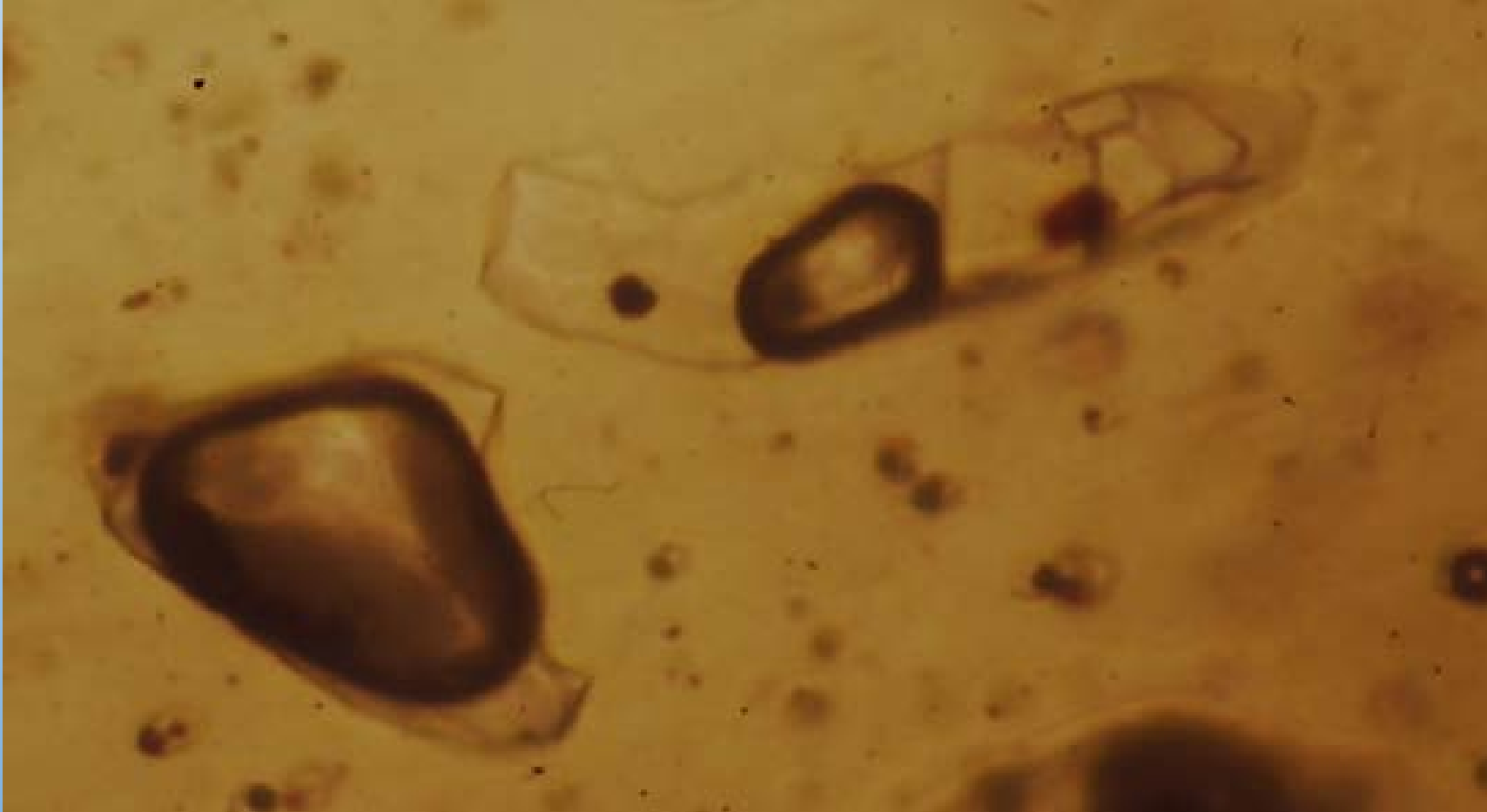


Stable Cl isotopes in porphyry copper deposits – opportunity for further research?

Chris Eastoe

Retired, University of Arizona

Why Cl isotopes?



Plan:

1. Physics of porphyry copper deposit formation

Fluid inclusion evidence

Behavior of Cl

2. Review of stable Cl isotope studies

3. Suggestions for future work

**Panguna,
Bougainville
Island,
Papua New
Guinea**



**Bingham
Canyon,
Utah,
USA**

Literature – Physics of PCD formation

Economic Geology
Vol. 73, 1978, pp. 721-748

A Fluid Inclusion Study of the Panguna Porphyry Copper Deposit, Bougainville, Papua New Guinea

C. J. EASTOE

Abstract

Copper mineralization at Panguna took place at a pressure of 200 to 300 bars and at temperatures between 350° and 700°C or higher. Cu, Fe sulfides, quartz, anhydrite, and hematite were deposited by dense, boiling, salt-rich liquids of magmatic origin. The composition of the salt-rich liquids (those which nucleated both KCl and NaCl in fluid inclusions) in terms of the system NaCl-KCl-H₂O varied between 76 percent salts (60% NaCl, 16% KCl) and 46 percent salts (30% NaCl, 16% KCl) by weight. Other liquids, apparently more dilute, nucleated only NaCl. The salt-rich liquids also contained Fe, Ca, and SO₄ and minor quantities of Mg, Cu, Mn, and Zn. A Cu concentration of 1,900 ppm has been estimated in one liquid. The atomic K/Na ratios of salt-

Economic Geology
Vol. 77, 1982, pp. 127-153

Physics and Chemistry of the Hydrothermal System at the Panguna Porphyry Copper Deposit, Bougainville, Papua New Guinea

C. J. EASTOE

Geology Department, University of Tasmania, Box 252C, G. P. O. Hobart, Tasmania 7001, Australia

Abstract

Various hydrothermal processes have been suggested as important in the formation of porphyry coppers, e.g., orthomagmatic evolution of salt-rich liquid, condensation of salt-rich liquid from magmatic vapor, convection of ground water driven by magmatic heat, and boiling of ground water. A fluid inclusion study based on detailed two-dimensional sampling indicates that all of these processes may have contributed to the evolution of the Panguna deposit, but that the copper was deposited mainly by salt-rich liquid expelled directly from the magma. Significant salt-rich liquid may also have condensed from a vapor plume.

ECONOMIC GEOLOGY

AND THE

BULLETIN OF THE SOCIETY OF ECONOMIC GEOLOGISTS

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No. 1

Magmatic Vapor Plumes and Ground-Water Interaction in Porphyry Copper Emplacement

R. W. HENLEY AND ALEX McNABB

Abstract

Porphyry copper deposits, all showing similar geological characteristics, occur in Tertiary and older orogenic-volcanic belts around the world. Recent isotope and fluid inclusion studies have shown that in a number of deposits the development of the characteristic ore alteration pattern, at some stage, involved the interaction of meteoric ground waters with saline fluids evolved from a magma. A fluid dynamic model is proposed for porphyry copper emplacement which focuses on the interaction of a buoyant

Reprinted from
Economic Geology
Vol. 66, 1971, pp. 98-120

Fluid Inclusion Studies on the Porphyry-Type Ore Deposits at Bingham, Utah, Butte, Montana, and Climax, Colorado¹

EDWIN ROEDDER

Literature: Stable Cl isotopes in PCDs

Geochimica et Cosmochimica Acta Vol. 56, pp. 4247–4255
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Stable chlorine isotopes in hydrothermal processes

C. J. EASTOE and J. M. GUILBERT

Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA

Miner Deposita (2009) 44:837–848
DOI 10.1007/s00126-009-0248-0

ARTICLE

Cl/Br ratios and stable chlorine isotope analysis of magmatic–hydrothermal fluid inclusions from Butte, Montana and Bingham Canyon, Utah

Taras Nahnybida • Sarah A. Gleeson • Brian G. Rusk •
Len I. Wassenaar

Bougainville



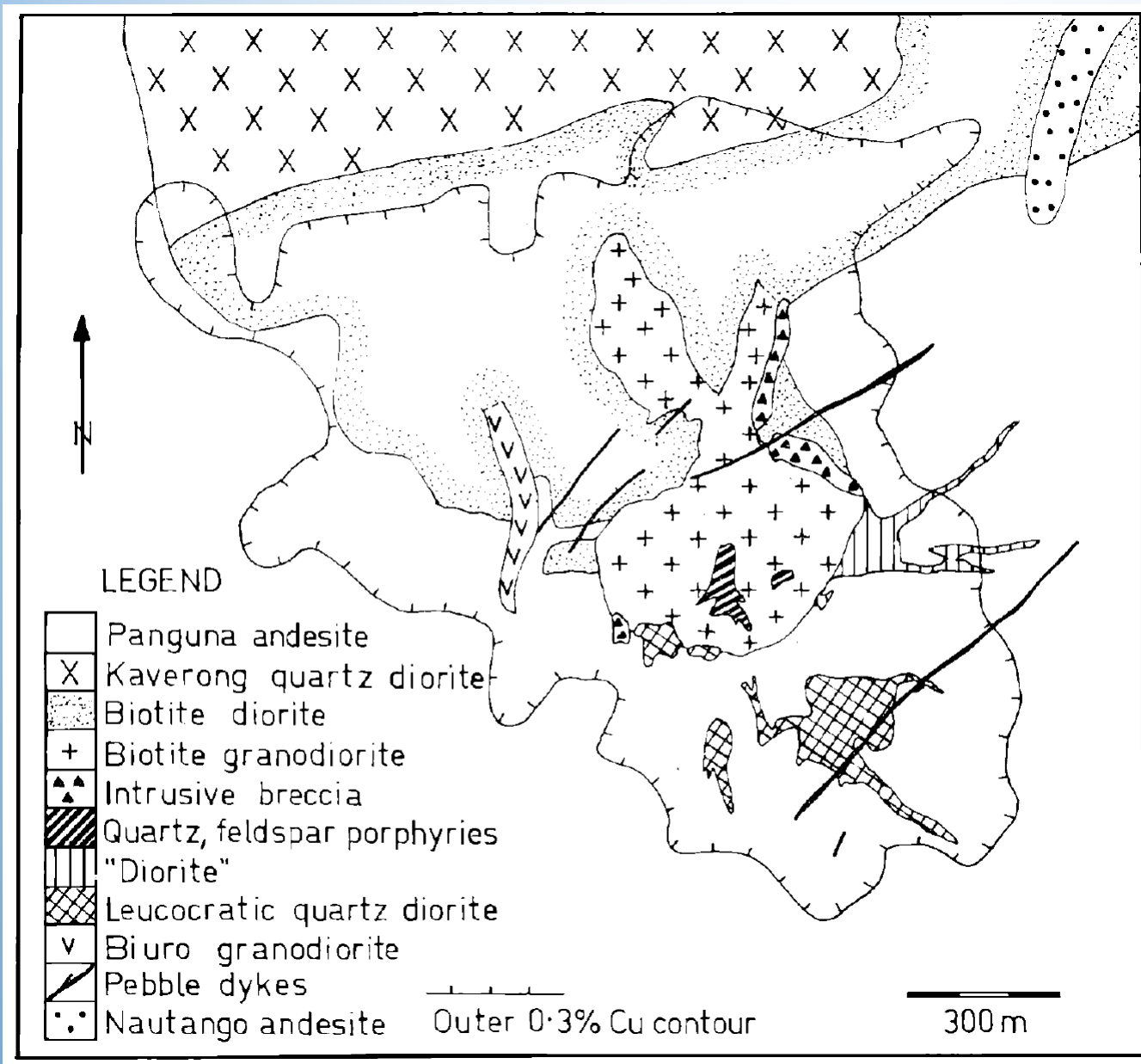
Panguna mine, 1974



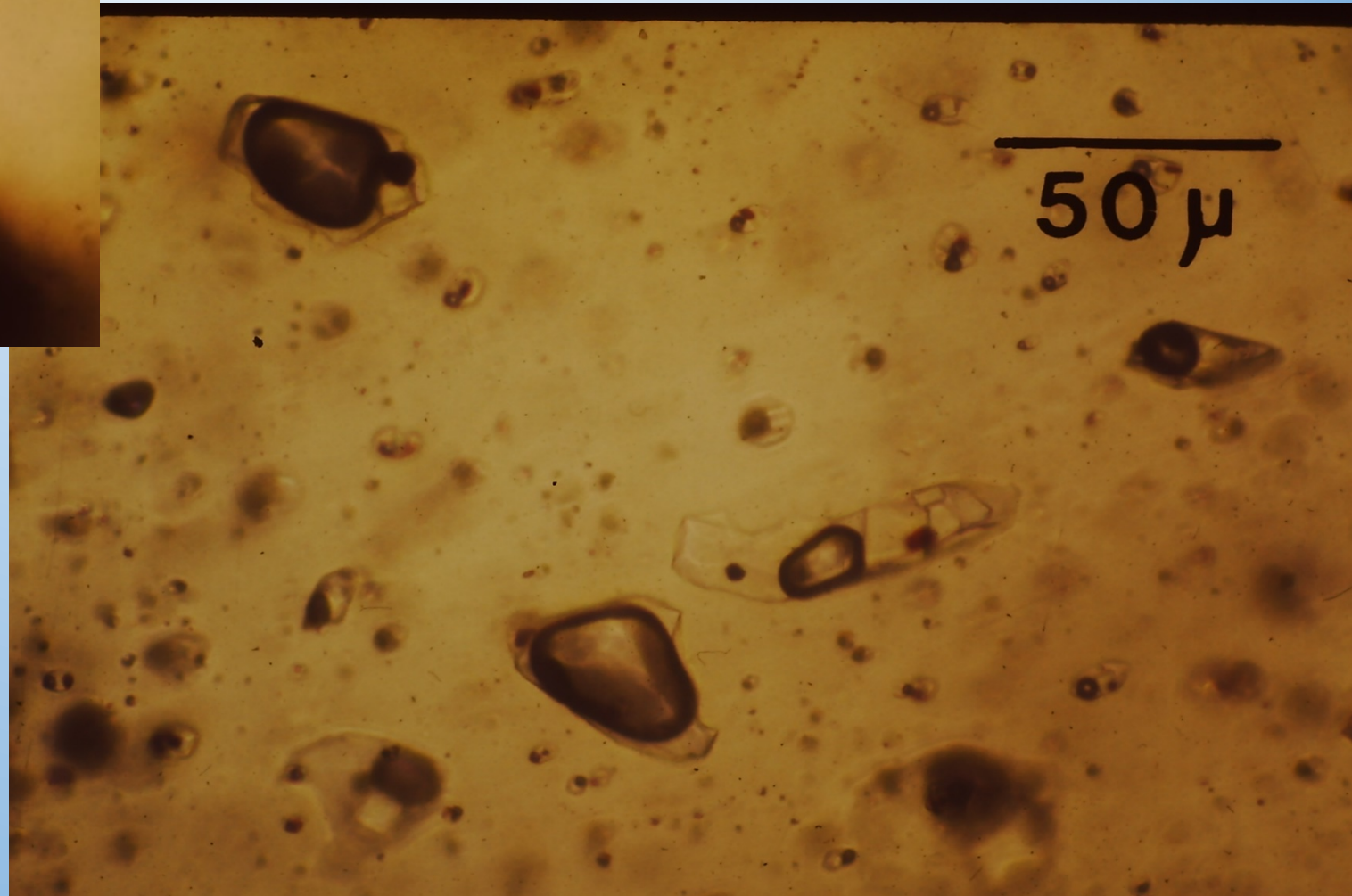
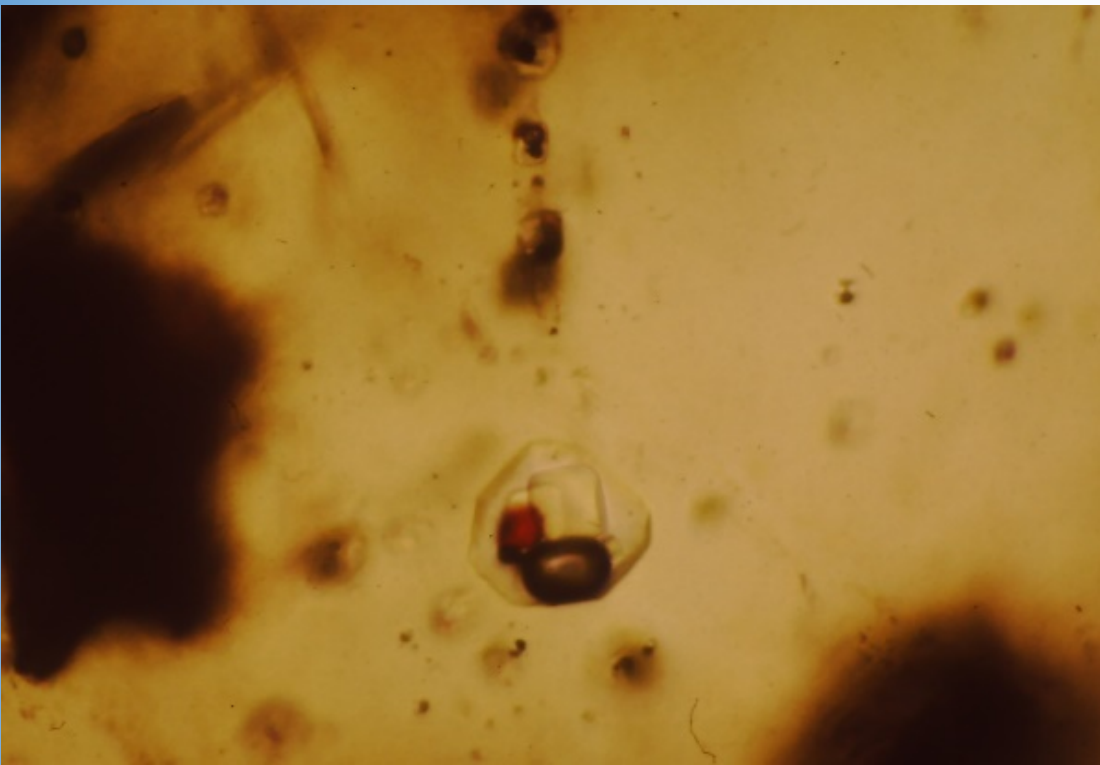
Bingham Canyon Mine



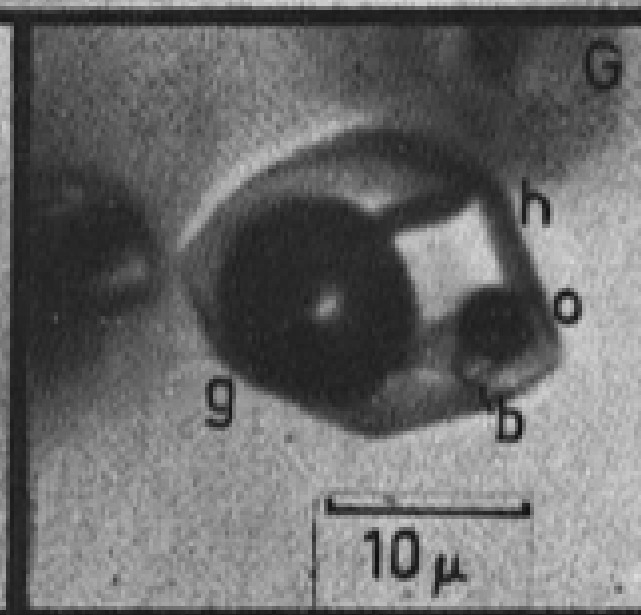
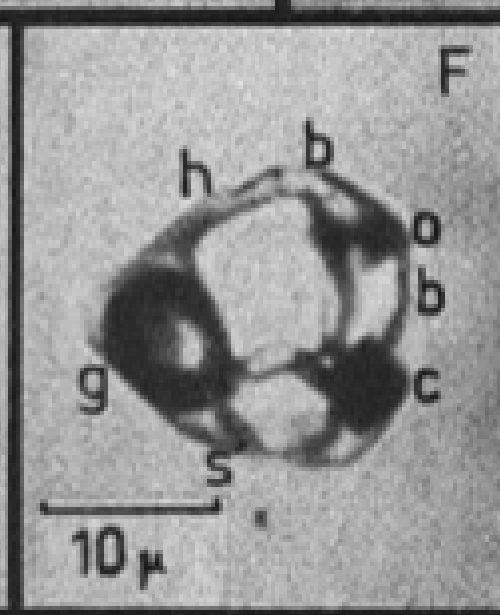
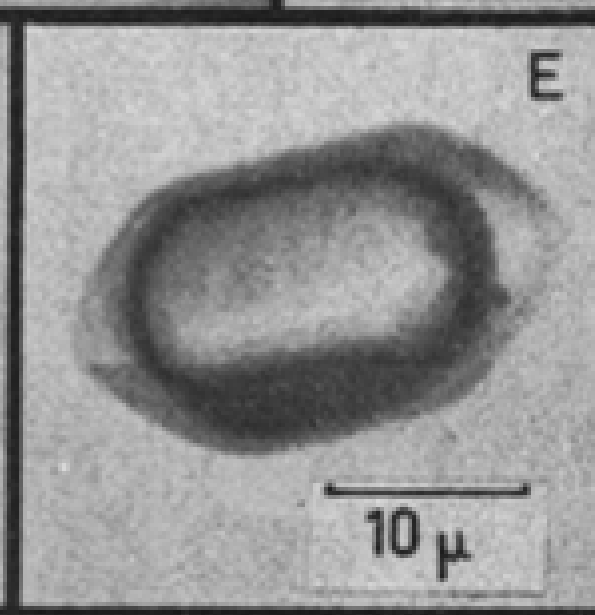
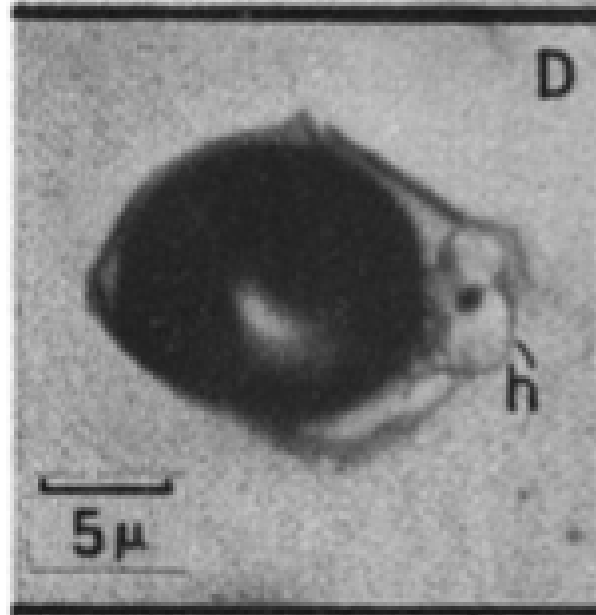
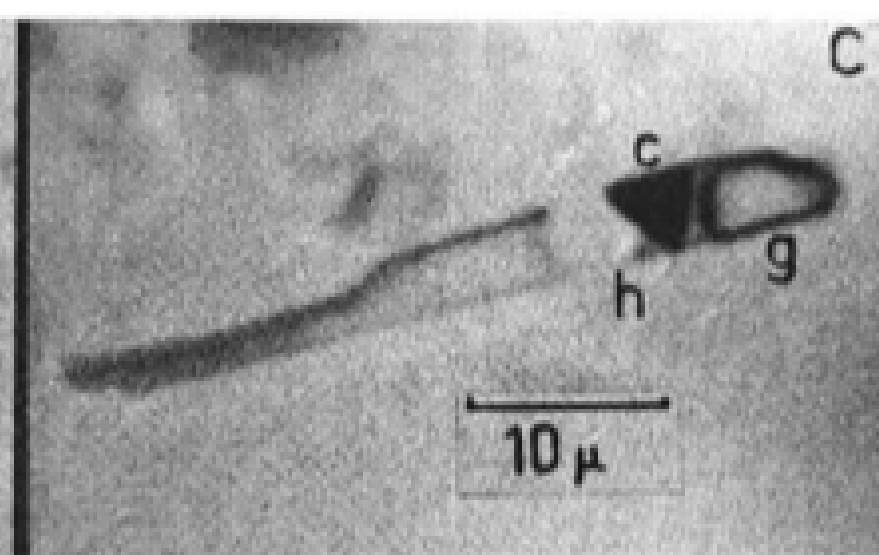
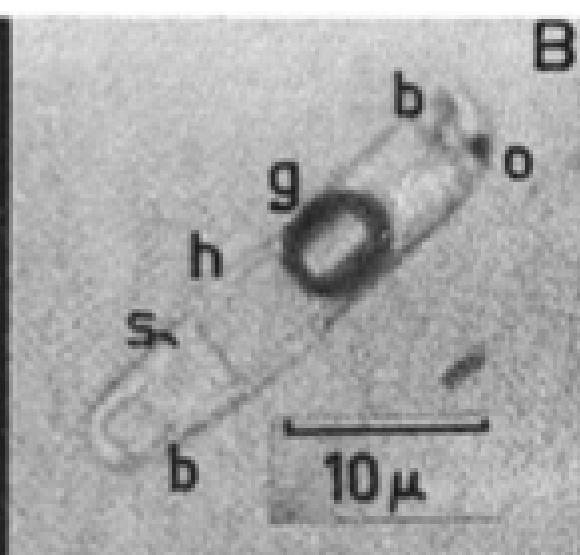
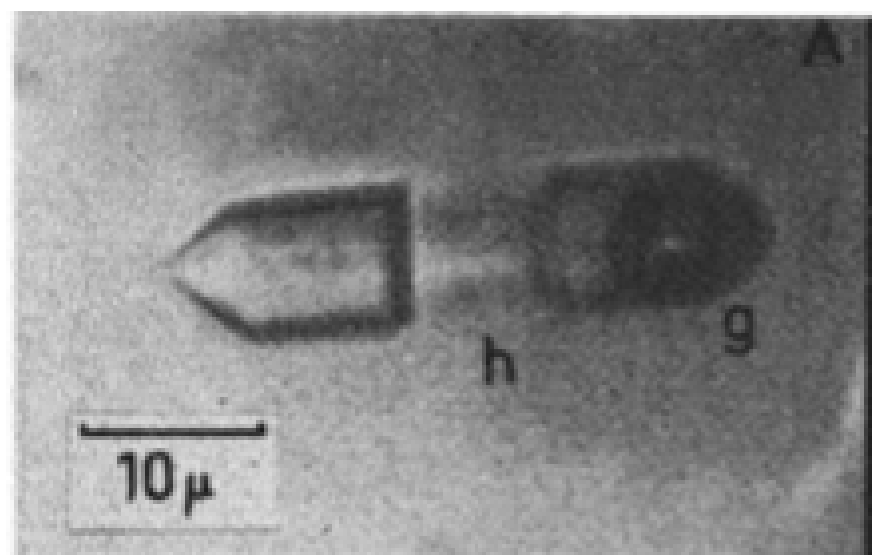
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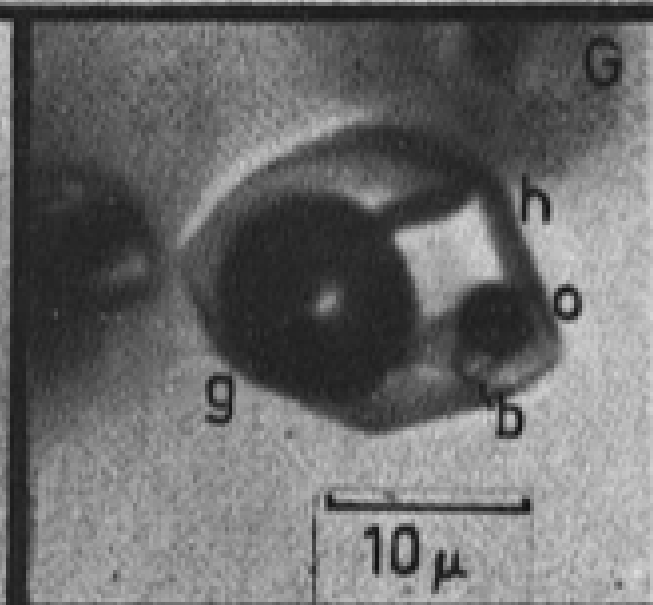
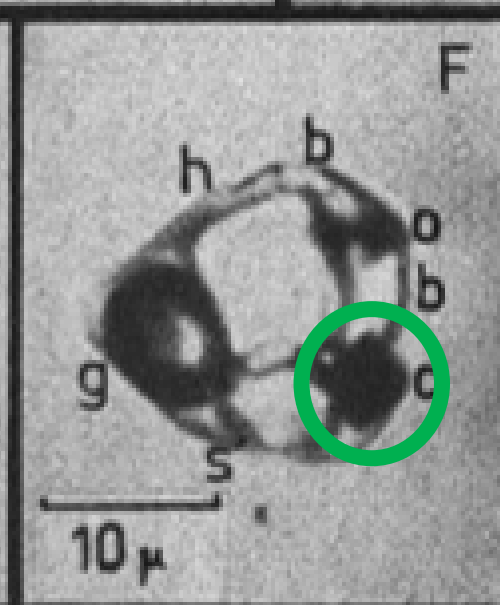
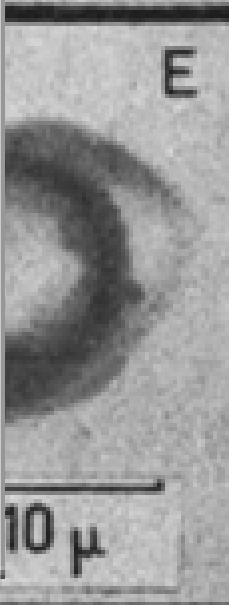
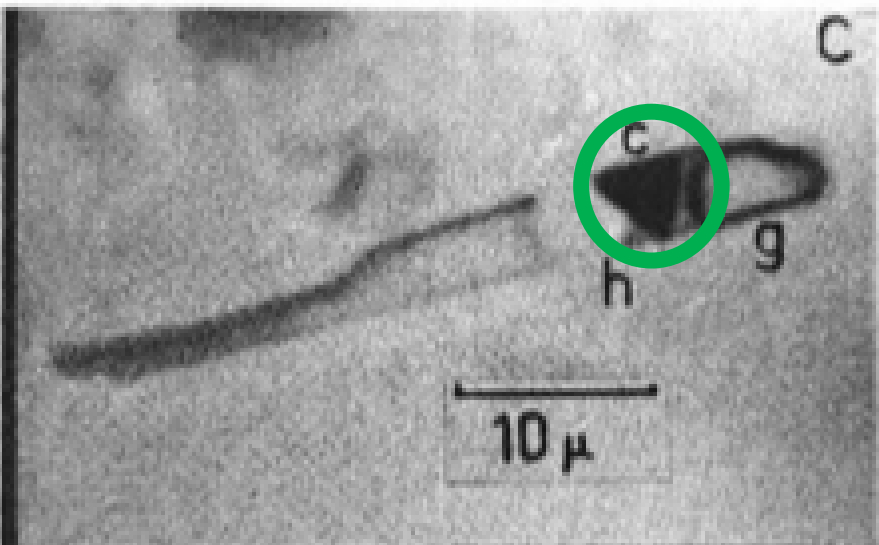
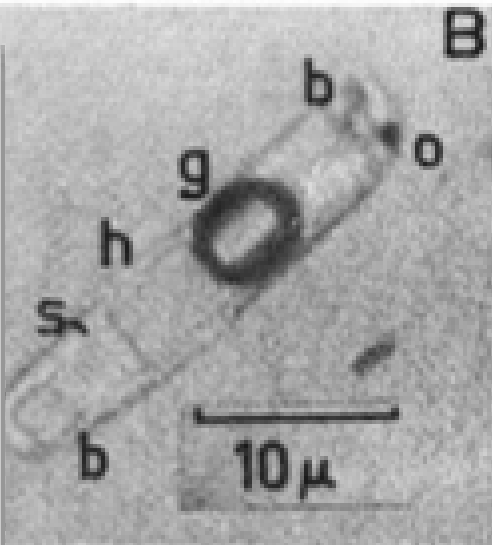
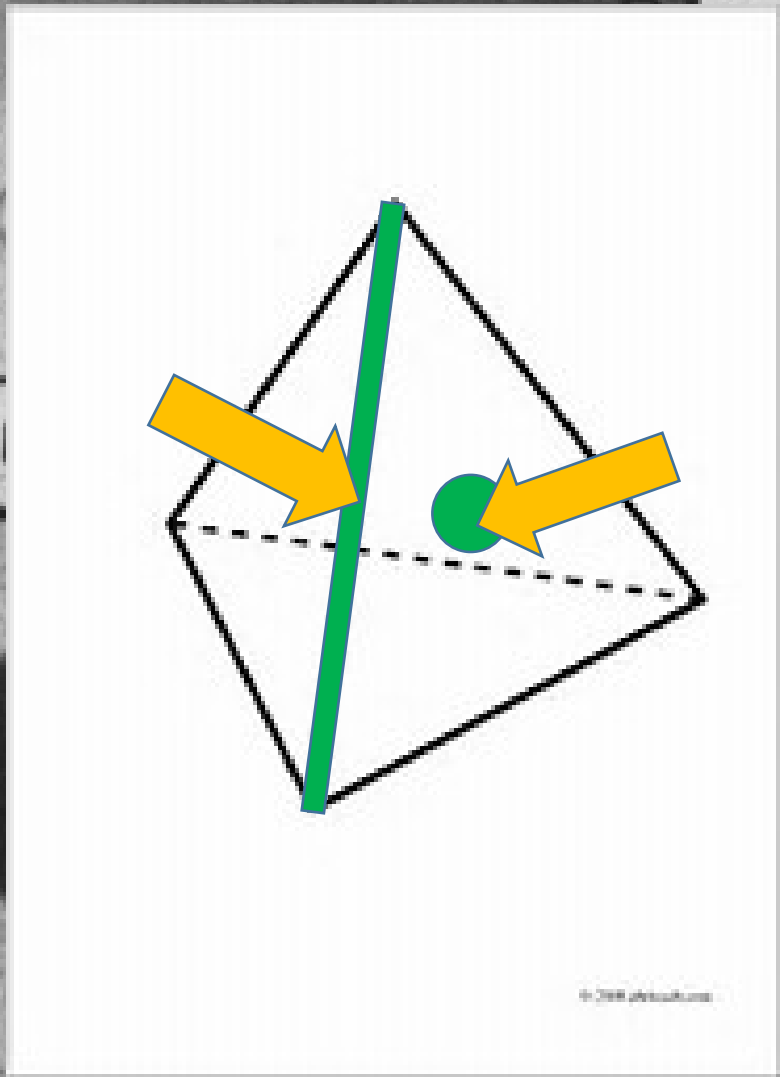


Panguna: Open pit geology, 1974



**Panguna: fluid inclusions
in quartz-chalcopyrite
veins**





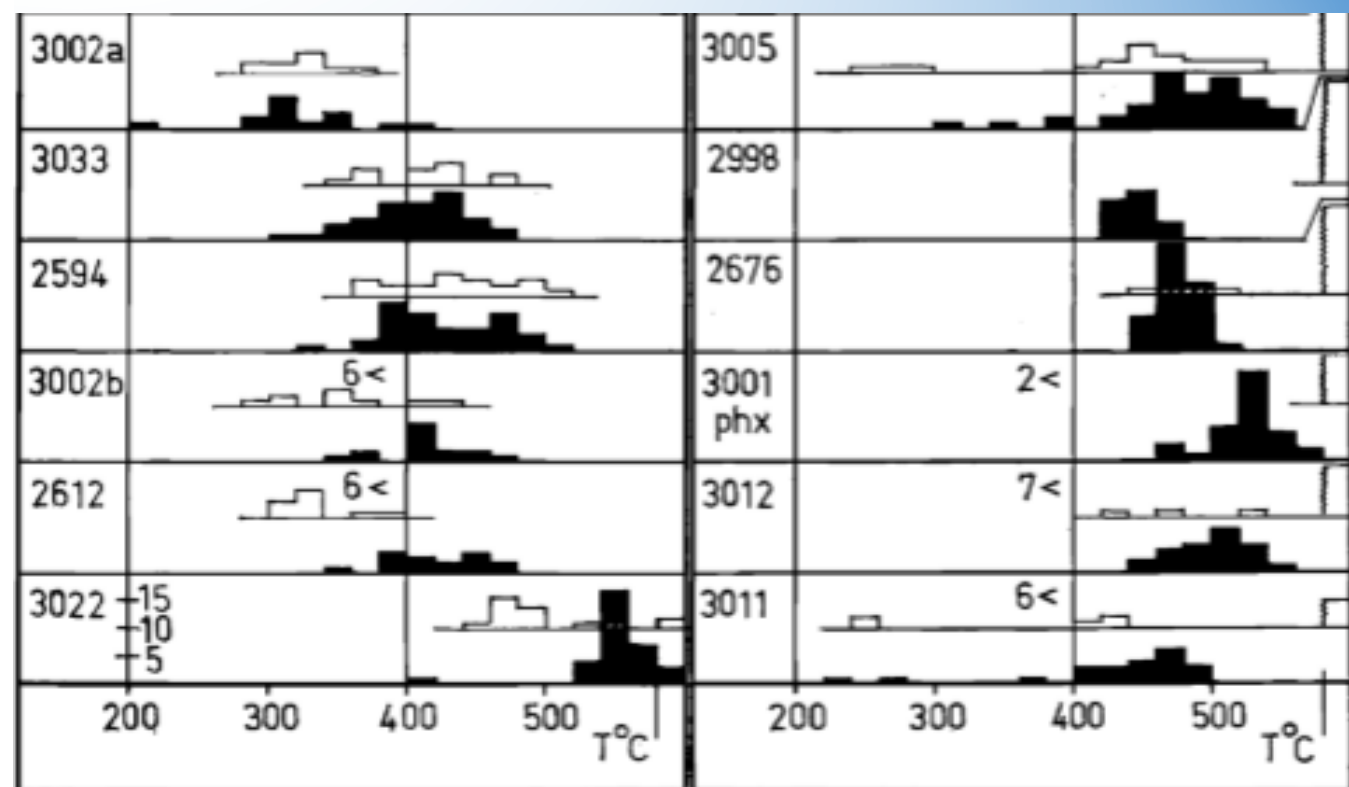
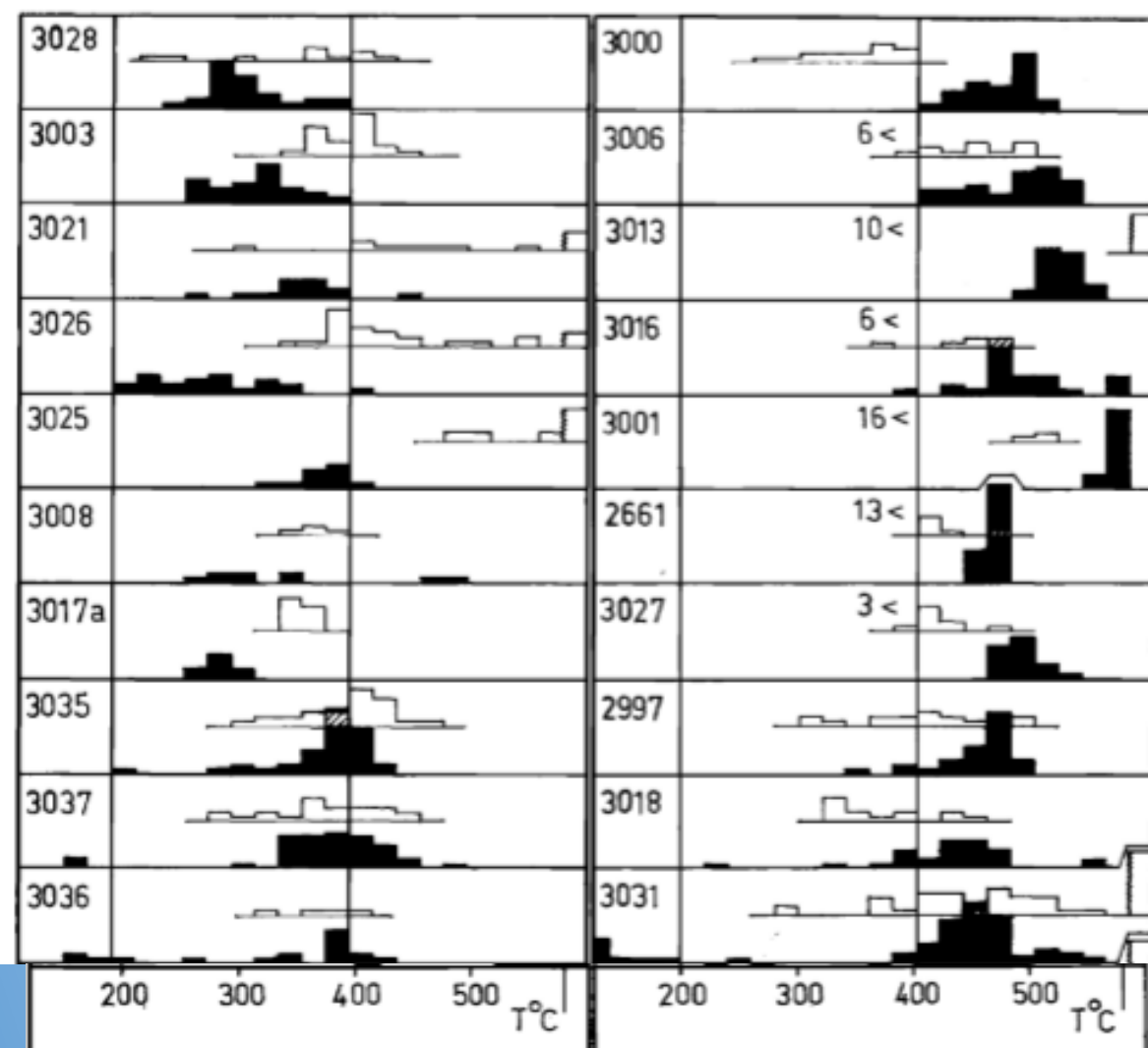
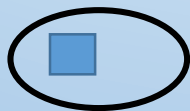
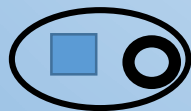


FIG. 5. Data for type III inclusions in quartz-Cu, Fe sulfide veins and phenocrysts (phx). The black histograms give T_{NaCl} and the white T_b . Hatching indicates the overlap of columns. Spatially separate groups of inclusions from a single sample are differentiated by letters, e.g., 3002a, 3002b. "13<" indicates that 13 T_b measurements were not precisely recorded but were recorded as being less than T_{NaCl} in their respective inclusions. The temperature scale breaks at 580°C; columns beyond this correspond to higher temperature results which could not

HOMOGENIZATION ORDER

Temperature increasing 



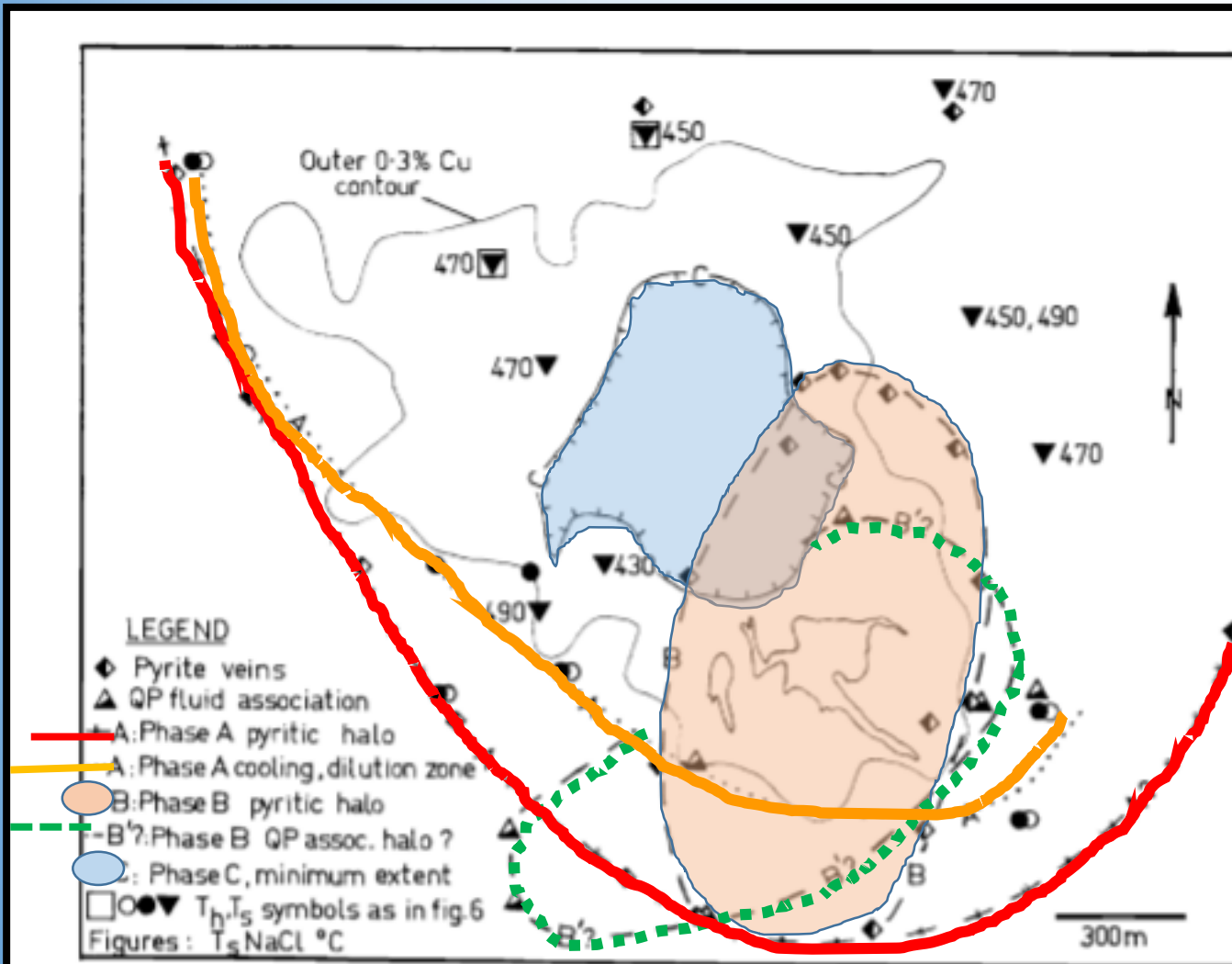


FIG. 12. A map of phase A mineralization. Phase B and C mineralization has been removed (cf. Fig. 6 in which the same symbols were used). T_s NaCl modes are given in figures in the 420° to 500°C range. The locations of pyrite veins from the pyritic halos of phases A and B of the QP fluid association (see section Quartz-Pyrite Veins) and of the Leucocratic Quartz Diorite (see Fig. 1) are shown.

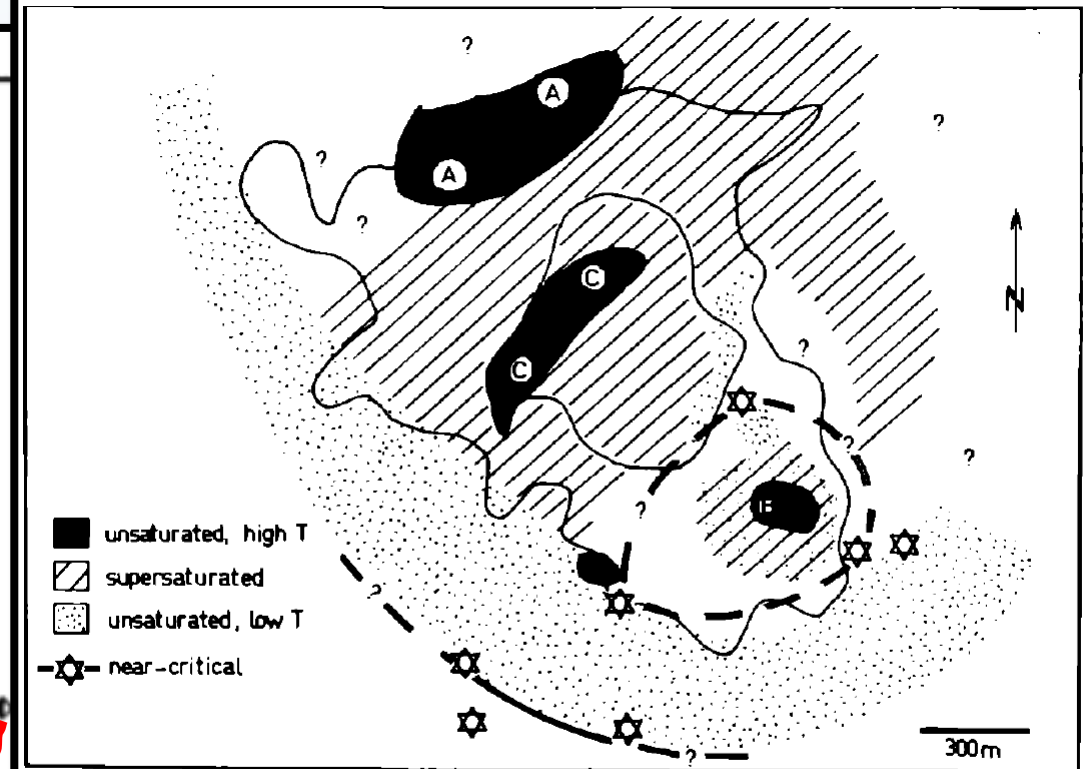
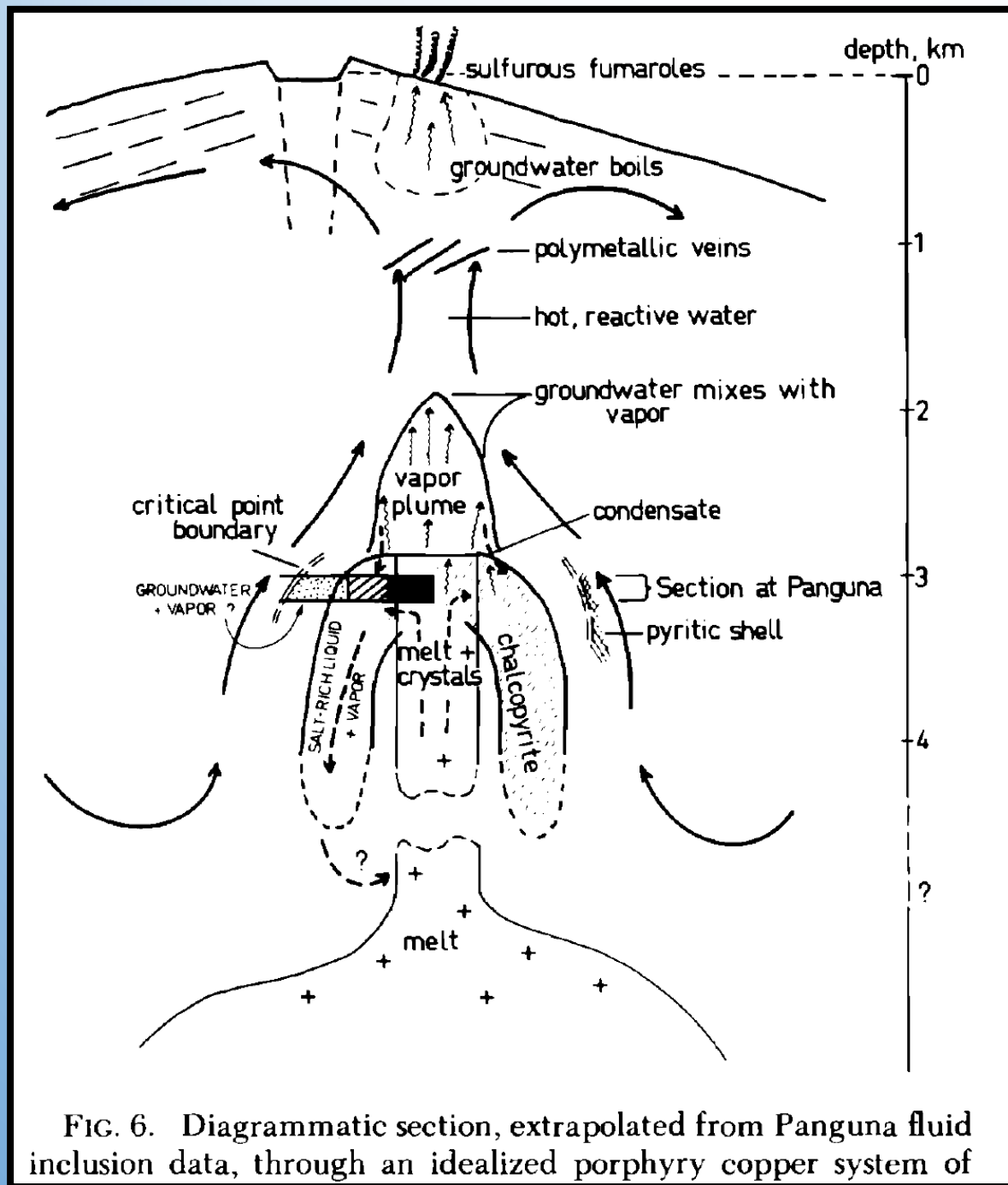


FIG. 3. Distribution of the various types of phase behavior in salt-water liquids. Letters refer to phases A, B, and C of copper

Unsaturated: T_h (vapor) > T_s (halite)

Supersaturated: T_h (vapor) < T_s (halite)

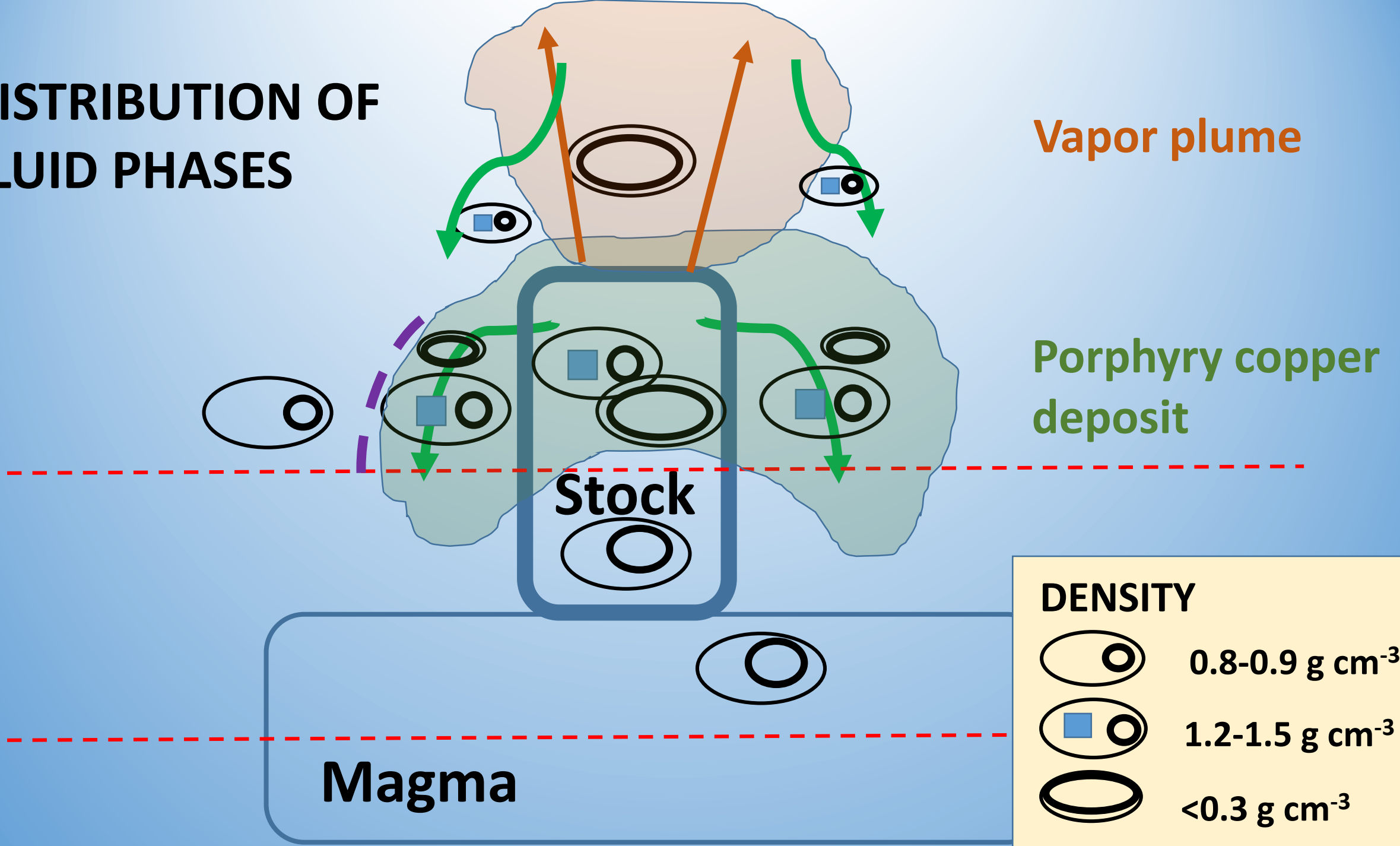
Vapor-rich inclusions throughout



INTERPRETED VERTICAL SECTION OF PANGUNA PORPHYRY COPPER SYSTEM

FIG. 6. Diagrammatic section, extrapolated from Panguna fluid inclusion data, through an idealized porphyry copper system of

DISTRIBUTION OF FLUID PHASES



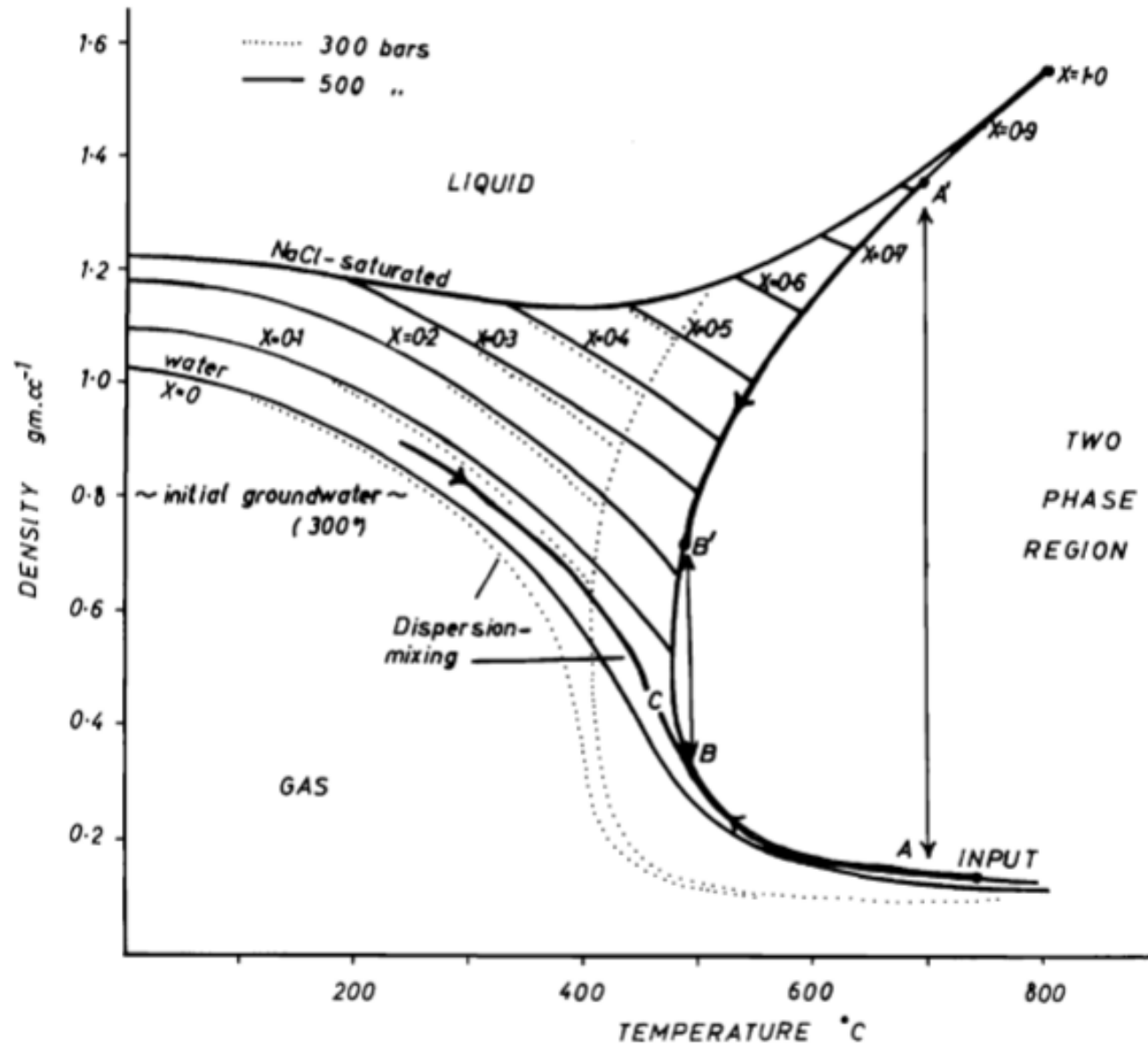
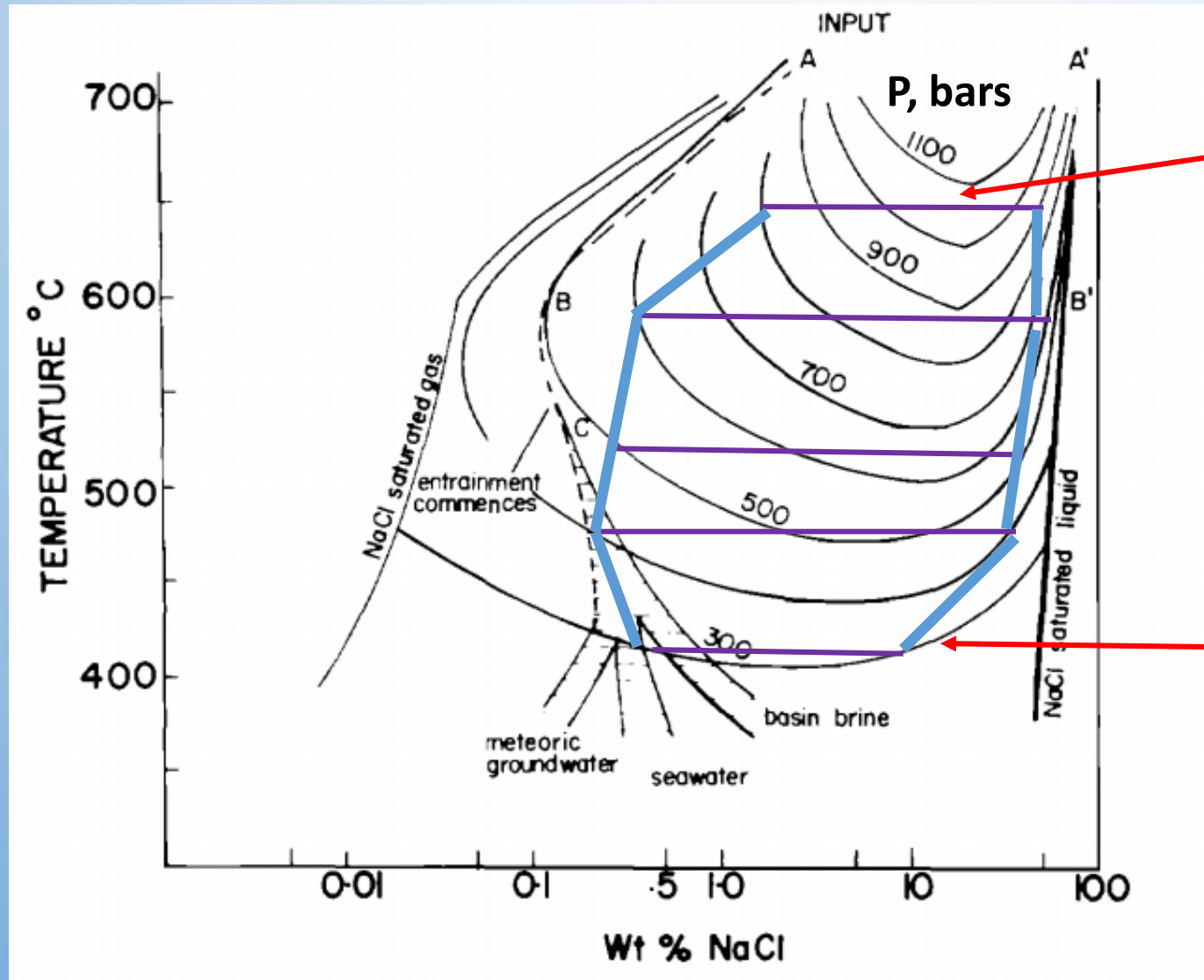


FIG. 4. Density-temperature relations in the system NaCl-H₂O at 500 bars and 300 bars fluid pressure. Data from Ellis and Golding (1963) and Urasova (1975). Explanation of A through C as for Figures 3 and 5. X = mole fraction of NaCl.

Evolution of a vapor plume

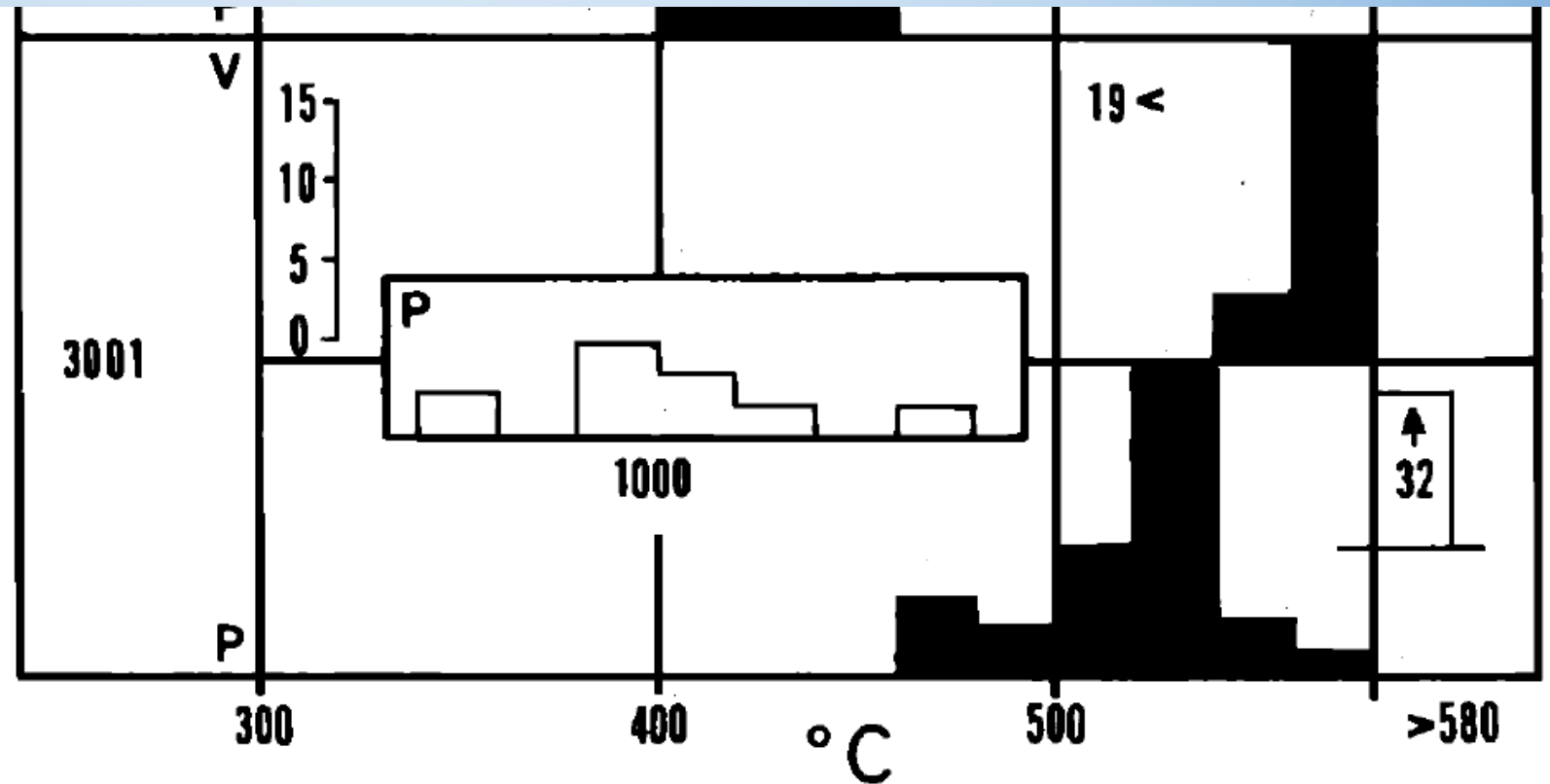
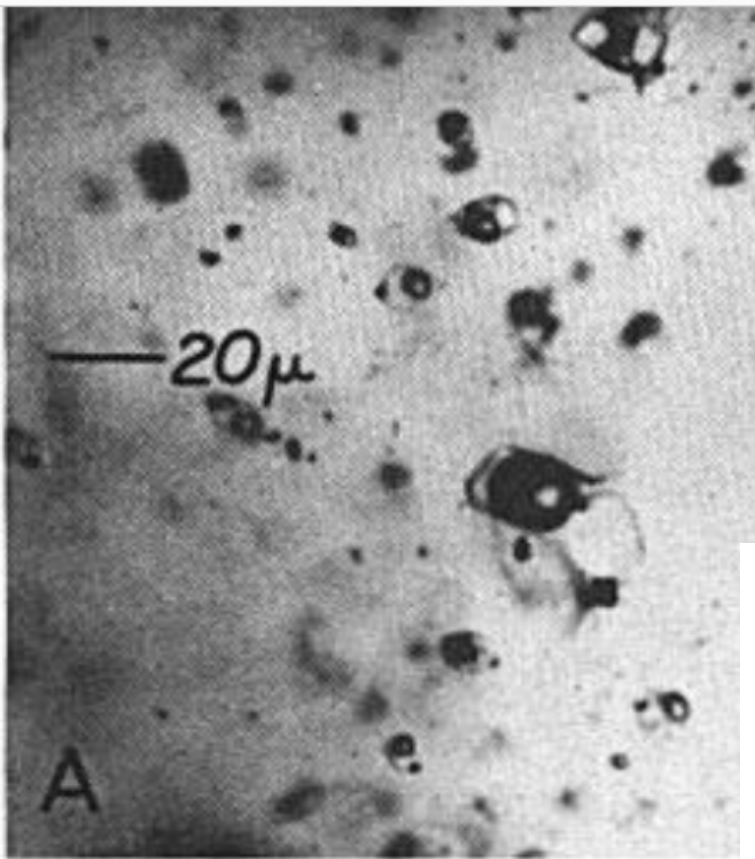


Magma: lithostatic pressure

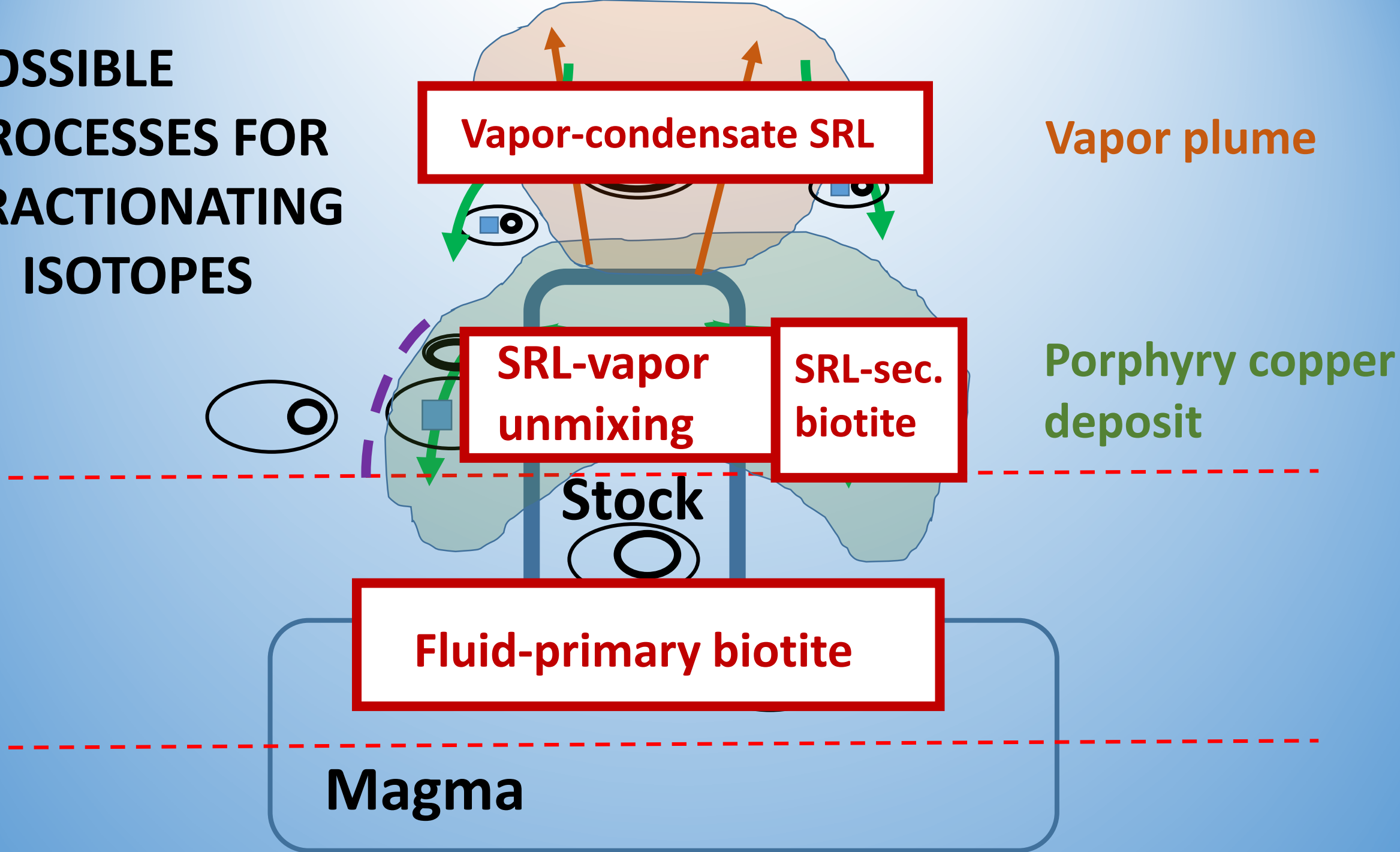
Surrounding volcanic rock: hydrostatic pressure

After Henley & McNabb, 1978

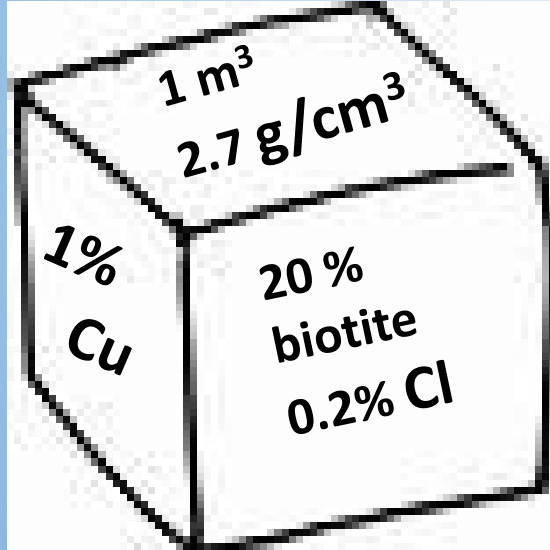
Inclusions in a quartz phenocryst



**POSSIBLE
PROCESSES FOR
FRACTIONATING
Cl ISOTOPES**



DO WE NEED TO CONSIDER BIOTITE?



$$\text{Rock} = 2.7 \times 10^6 \text{ g}$$

$$\text{Biotite} = 5.4 \times 10^5 \text{ g}$$

$$\text{Cl in biotite} = 1.1 \times 10^3 \text{ g}$$

$$\text{Cu} = 2.7 \times 10^4 \text{ g}$$

Cu deposited by fluid, 50% NaCl, that loses 1000 ppm Cu

$$\text{Weight fluid} = 2.7 \times 10^7 \text{ g}$$

$$\text{Weight NaCl} = 1.35 \times 10^7 \text{ g}$$

$$\text{Weight Cl} = 8.2 \times 10^6 \text{ g}$$

Cu deposited by fluid, 3% NaCl, that loses 10000 ppm Cu

$$\text{Weight fluid} = 2.7 \times 10^6 \text{ g}$$

$$\text{Weight NaCl} = 8.1 \times 10^4 \text{ g}$$

$$\text{Weight Cl} = 4.9 \times 10^4 \text{ g}$$

Bingham Canyon, deep sampling, Nahnybida et al. 2009

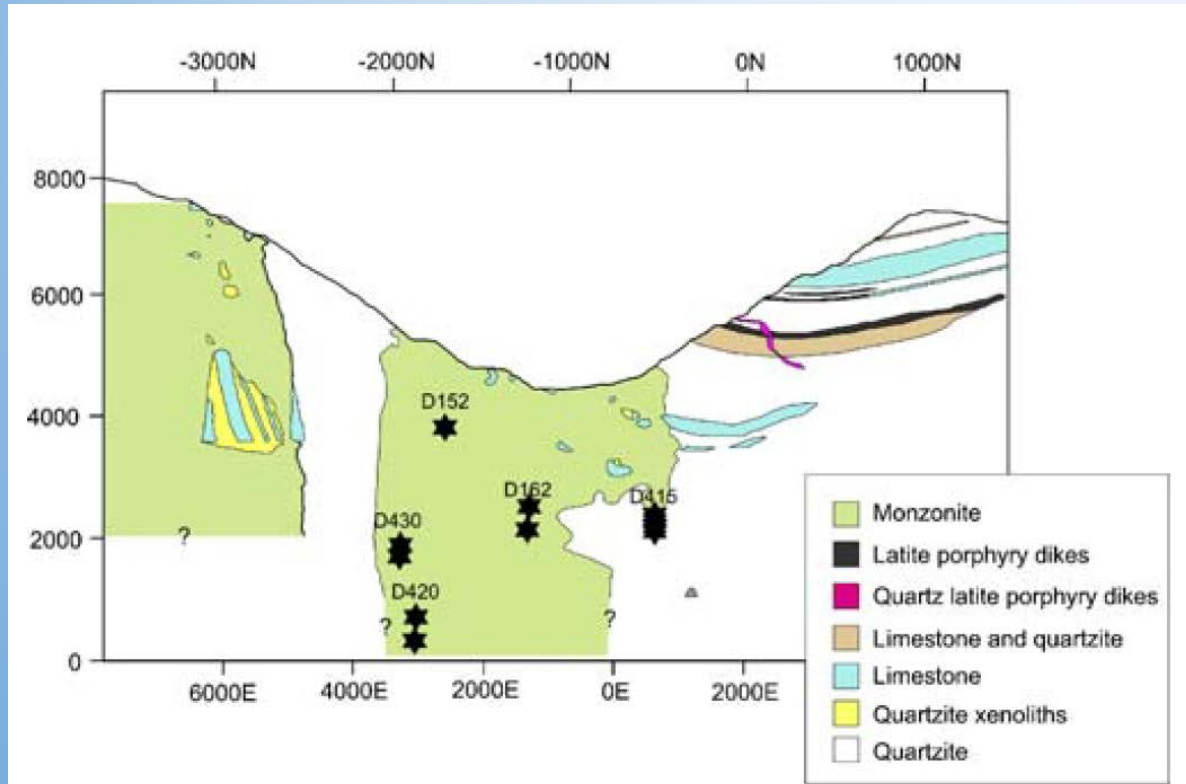
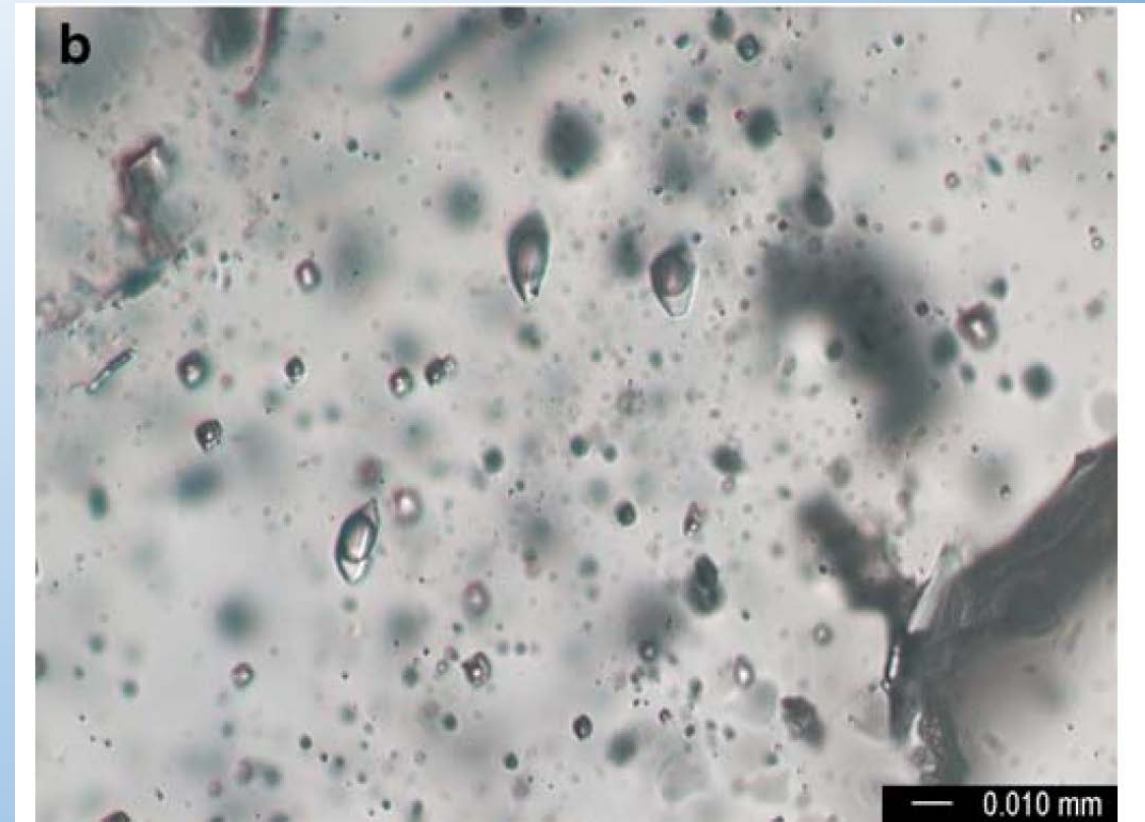


Fig. 2 Sketch cross-section through the Bingham deposit with sample locations. Note that mine north is not true N. The samples from drill



Bingham: Salt rich inclusions in deposit core -- level of Open Pit

$T_h > 400^\circ \text{C}$, in some cases 600-700 $^\circ \text{C}$.

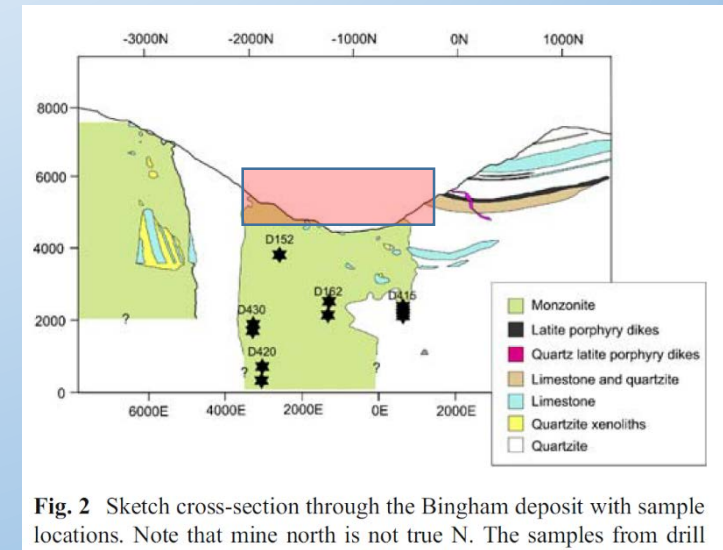
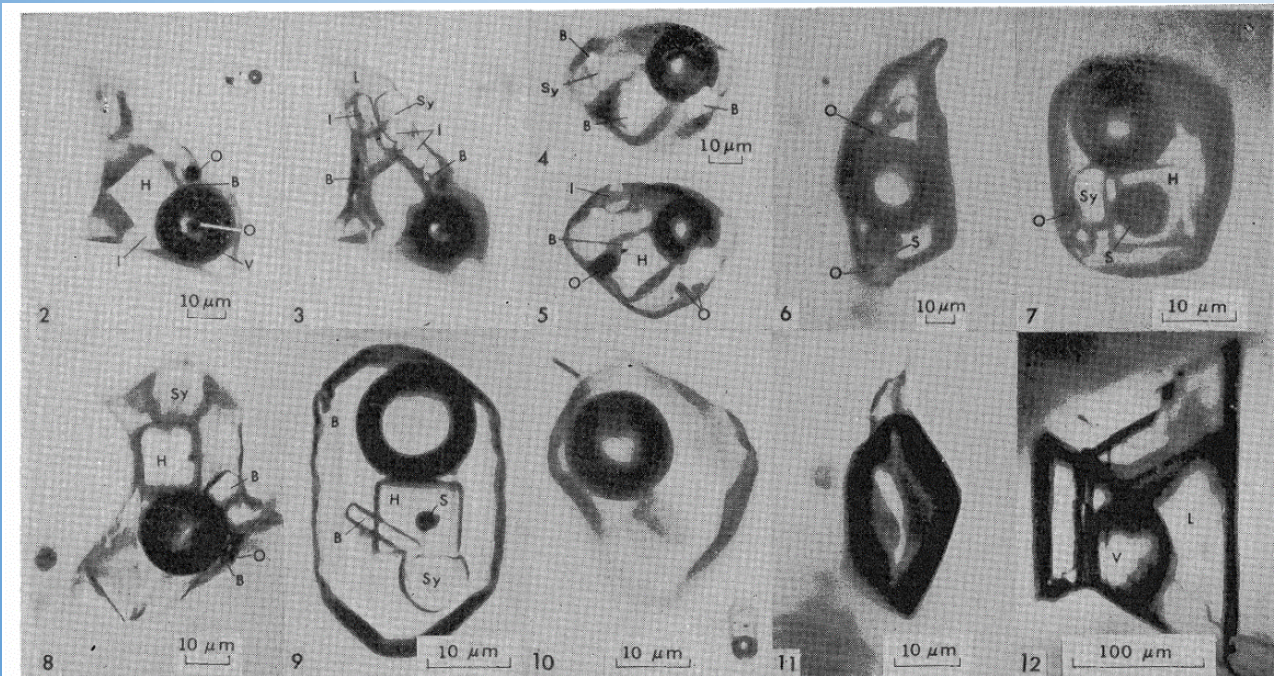


Fig. 2 Sketch cross-section through the Bingham deposit with sample locations. Note that mine north is not true N. The samples from drill

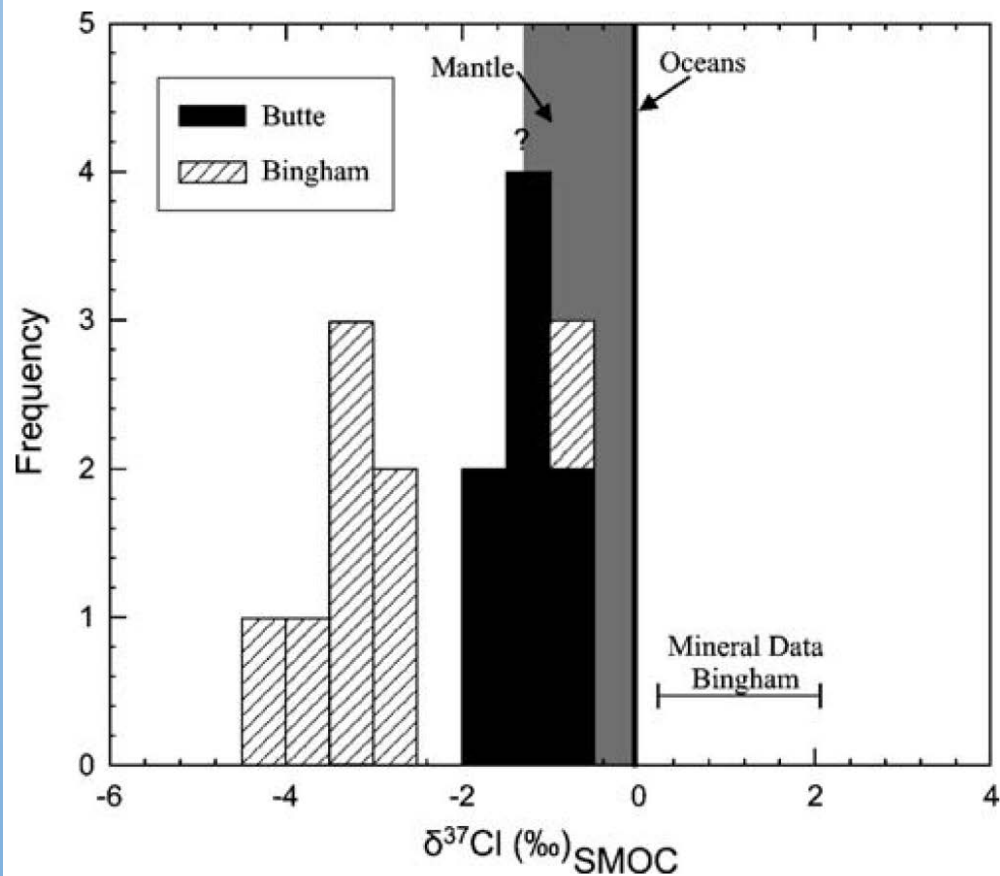


Fig. 5 $\delta^{37}\text{Cl}$ values for Butte and Bingham Canyon porphyry Cu deposits. $\delta^{37}\text{Cl}$ values are similar in pre-Main stage and Main stage

Nahnybida et al., 2009

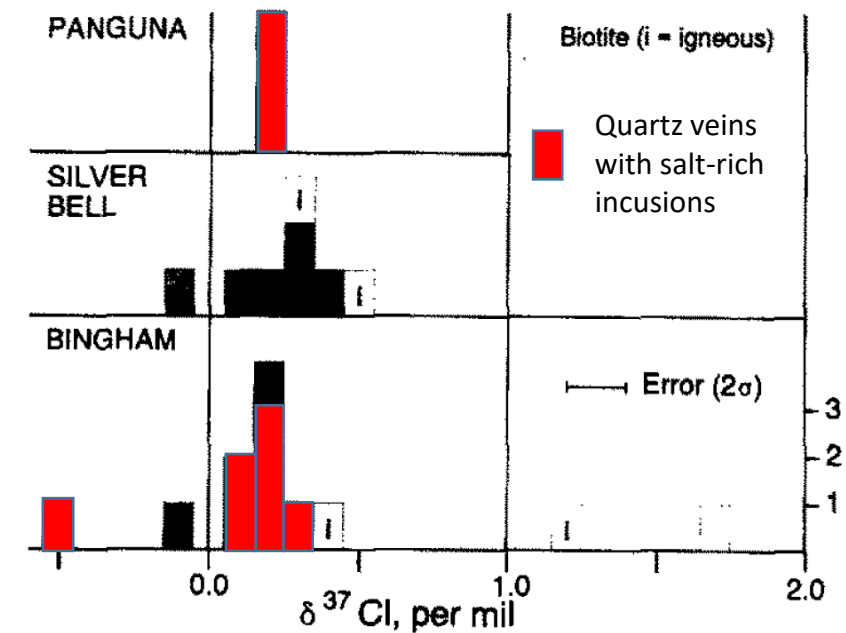


FIG. 7. Frequency histogram of $\delta^{37}\text{Cl}$ data from porphyry copper deposits. Early veins are quartz-Cu, Fe sulfide veins at Bingham and Panguna, and quartz-molybdenite veins associated with K-feldspar at Silver Bell. Late veins are pyrite at Bingham, and quartz-pyrite associated with sericite at Silver Bell. Igneous biotite is marked "i".

Eastoe and Guilbert, 1992

Could large sample size be causing the difference in $\delta^{37}\text{Cl}$?

Nahnybida et al. 0.5 to 2 g

Eastoe & Guilbert 50 g

Response:

Even a 0.5 g sample is large relative to fluid inclusion size

Fluid inclusion, 30 μm cube: $\sim 3 \times 10^{-8} \text{ g}$

**Sample sizes: $0.5 \times 10^0 \text{ g}$ to $5 \times 10^1 \text{ g}$ 2 orders of magnitude,
compared to 7-9 orders of magnitude**

Could mixing of different fluid types cause the difference in $\delta^{37}\text{Cl}$?

E & G samples were dominated by salt-rich inclusions

If fluid volume in quartz is

50% salt-rich liquid, 50% NaCl, $\delta^{37}\text{Cl} = 0\text{‰}$

50% dilute liquid, 5% NaCl, $\delta^{37}\text{Cl} = -2\text{‰}$

Mixture $\delta^{37}\text{Cl} = -0.18 \text{‰}$

barely measurable, doesn't explain differences of 2 to 4 ‰.

Could loss of HCl on crushing cause the difference?

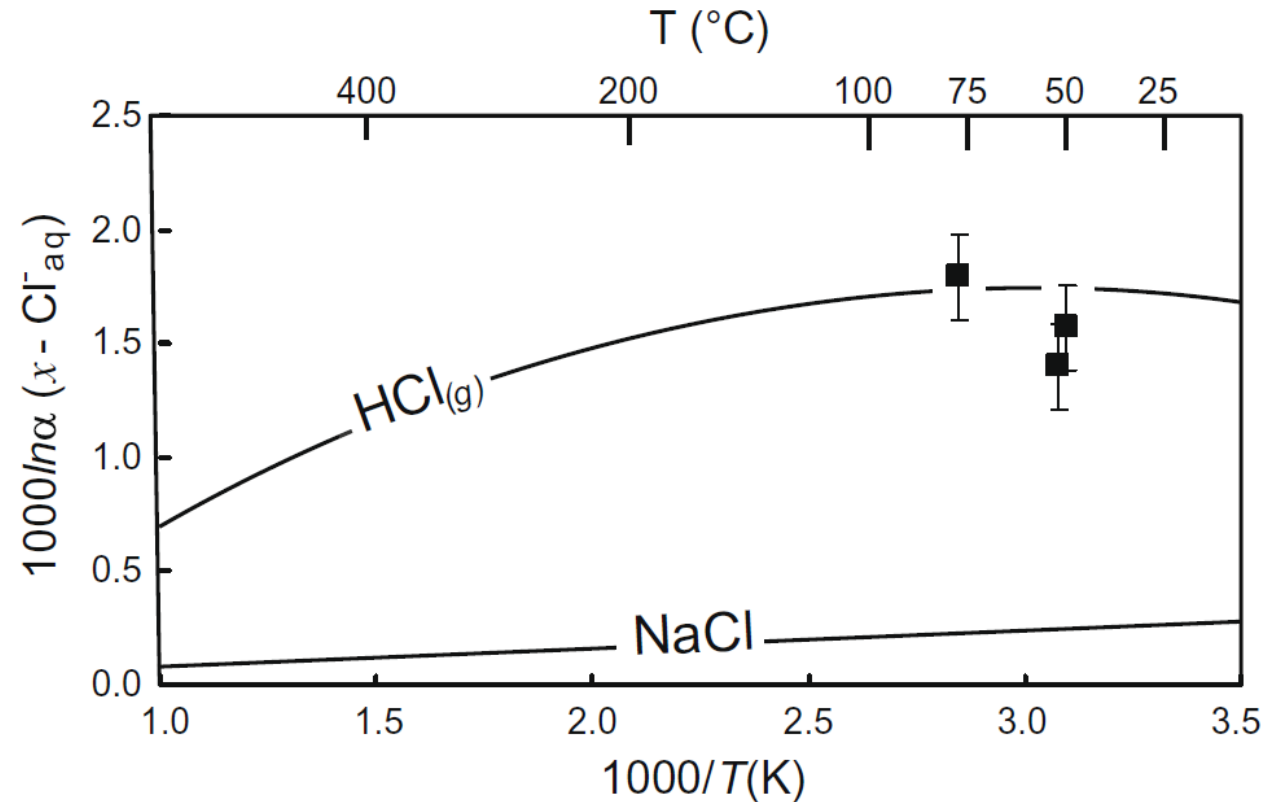


Fig. 4. Equilibrium isotopic fractionation between $\text{HCl}_{(\text{g})}$ and aqueous Cl^- dissolved in hydrochloric acid obtained using apparatus illustrated in Fig. 1. Theoretical curve from Schauble et al. (2003). Errors bars show analytical error of a single measurement based on long-term running errors of seawater solutions (see Sharp et al., 2007, supplemental information for details).

Could loss of HCl on crushing cause the difference?

- Leaching experiments on Panguna quartz, dominated by salt-rich inclusions as salinity source
 - Method collects volatiles and non-volatiles
 - Measured: Na, K, Ca, Mg, Cl, SO₄
 - Characteristic charge imbalance ~ 11%, anions > cations
 - Possible causes: H, Cu, Zn, others?
- Assume missing charge is due to HCl; H⁺ makes up 11% of charges
 - Assume $\Delta^{37}\text{Cl}$ (HCl – non-volatile Cl) = 1.5‰
 - Isotope balance δ (trapped fluid) *1 = $\delta(\text{HCl}) * 0.11 + \delta(\text{non-vol. Cl}) * 0.89$

$$\delta \text{ (trapped fluid) } *1 = 1.7 * 0.11 + 0.2 * 0.89 = 0.37\text{‰}$$

which is nearly undetectable.

**POSSIBLE
PROCESSES FOR
FRACTIONATING
Cl ISOTOPES**

**Vapor $\delta^{37}\text{Cl} < -4\text{‰}$?
Condensate $\delta^{37}\text{Cl} < 0\text{‰}$?**

**Vapor plume Cl is
NaCl or NaFeCl_x ,
not HCl?**

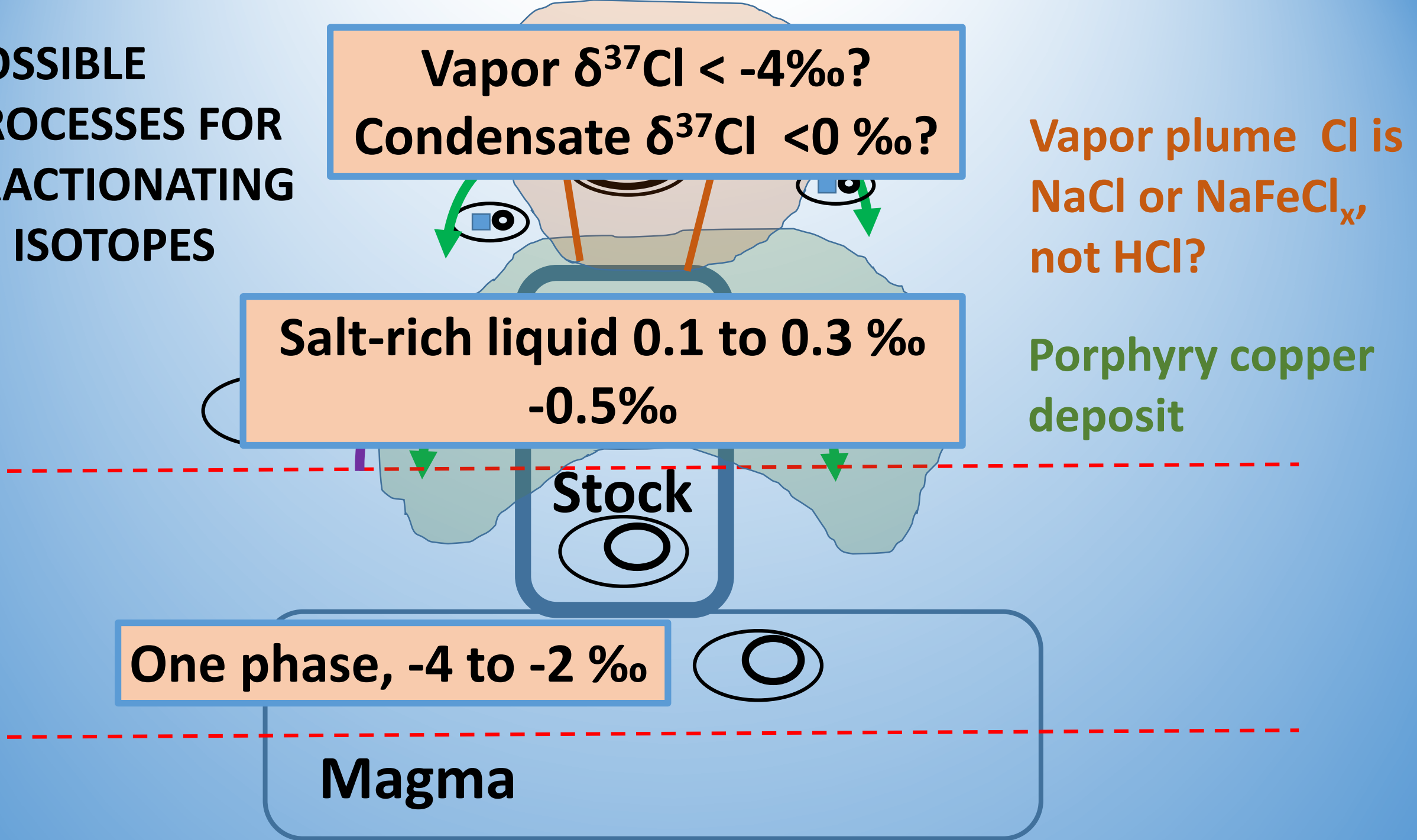
**Salt-rich liquid 0.1 to 0.3 ‰
-0.5‰**

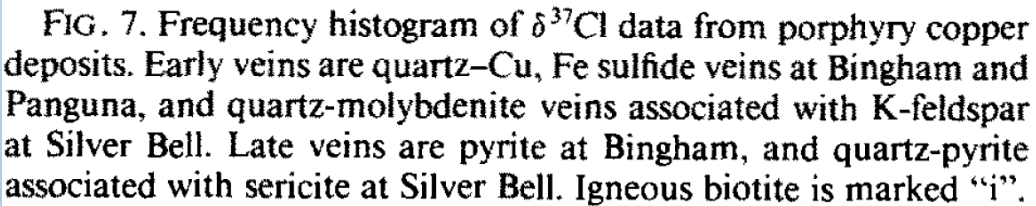

**Porphyry copper
deposit**

Stock

One phase, -4 to -2 ‰

Magma





WHERE COULD WE UNDERTAKE FURTHER RESEARCH?

- Must be a high-temperature porphyry copper deposit
- Panguna is no longer accessible – politics
- Bingham pit had major landslide
- Dexing : not high temperature? Cu and Mo deposited < 400 °C
- Other SW Pacific deposits are high temperature.

WHAT PARTS OF THE SYSTEM?

- Assume the studies to date are correct
- We need more veins from the orebody – is there more evidence for negative $\delta^{37}\text{Cl}$?
- Overlying hydrothermal system – not present at Bingham.
- Lateral parts of system – present in Oquirrh Mountains.