

The magmatic-hydrothermal transition: Volatile separation in silicic rocks at Bajo de la Alumbrera porphyry Cu-Au deposit, NW Argentina

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INTRODUCTION

Ore-bearing hydrothermal alteration in porphyry-related deposits largely form from exsolved magmatic fluids derived from crystallising, upper crustal silicic magmas (e.g., Hedenquist & Lowenstern 1994). If the original water content is sufficiently high, crystallisation causes an aqueous phase to separate from the melt, a process referred to as 'second' or 'resurgent boiling' (Burnham 1979, 1981; Burnham & Ohmoto, 1980). Despite this process being well constrained by numerical models (e.g., Shinohara & Hedenquist 1997), physical evidence for the physical separation and accumulation of an aqueous volatile phase has been limited. We present petrographic observations combined with silicate-melt and fluid inclusion studies of quartz from porphyritic intrusions at Bajo de la Alumbrera Cu-Au deposit, NW Argentina, that complete the continuum of petrological features preserving evidence of volatile exsolution linking magmatic and hydrothermal systems.

DEPOSIT GEOLOGY

Bajo de la Alumbrera is a Au-rich porphyry Cu deposit where Cu-Fe sulfide-bearing pervasive and fracture-controlled potassic (biotite-K-feldspar-quartz±magnetite) alteration assemblages overprint several phases of intrusive rocks. At least five high-K calc-alkaline to shoshonitic plagioclase-biotite(hornblende)-phyric dacite porphyries occur. Medium- to coarse-grained (up to 5 mm) plagioclase phenocrysts (<30%) are common, with lesser hornblende (2-3 mm, <2%), biotite (<5 mm, <5%) and quartz (<5 mm, <15%) crystals; the groundmass is quartzo-feldspathic. A minor amount of K-feldspar also occurs in the late intrusions. Accessory minerals include apatite, zircon, magnetite and titanite. Most disseminated Cu-Fe sulfide and Au mineralization occurs in the potassic alteration zone (J.M. Proffett *writ. comm.* 2001; Ulrich & Heinrich 2001). Fluid inclusion studies and stable isotope geochemistry reveal that a high temperature (between 350°C and 550°C, up to 750°C) and saline (>30 wt.% NaCl equivalent) fluid of magmatic origin (inferred from the calculated $\delta^{18}\text{O}$ and δD isotopic compositions) produced this alteration (Ulrich *et al.* 2001).

QUARTZ IN DACITE PORPHYRIES

Quartz in the porphyritic dacite intrusions at Bajo de la Alumbrera occurs, not only as a hydrothermal mineral, but also as a major phase in primary igneous textures (e.g., quartz eyes and comb-quartz layered textures). There are two petrographically distinct types of quartz eyes (Harris *et al.* 2003). Type 1 consists of typical quartz phenocrysts (Fig. 1A); they are large (up to 8 mm in diameter), rounded and irregular anhedral crystals. Individual crystals are dispersed throughout the groundmass, and may have distinct crystal edges, and contain small inclusions of feldspar and magnetite. Some quartz phenocrysts are embayed and apparently resorbed, giving them an ameboid appearance (Fig. 1B). Type 2 quartz eyes are elliptical, small (<2 mm), and consist of sugary aggregates of anhedral quartz crystals (Fig. 1C). They are distinctly different from quartz phenocrysts. Crystals of feldspar and magnetite are intergrown with the quartz. Some type 2 quartz eyes have empty voids in the core.

Although mostly randomly distributed throughout the groundmass, type 2 quartz eyes may exhibit an apparent linear arrangement. These quartz eyes appear to represent quartz (and other mineral phases) formed from an exsolved magmatic aqueous fluid at the earliest stages of its separation from a silicic magma (Harris *et al.* 2003). In essence, type 2 quartz eyes are a type of miarolitic cavity (e.g., Candela & Blevin, 1996).

Comb-quartz layered, or unidirectional solidification textures, have been found along the margins of several porphyries at Bajo de la Alumbrera. More commonly reported in granite-related Sn \pm W and Mo systems (e.g., Lowenstern & Sinclair 1996), these textures consist of alternating bands (0.5 to 2.0 cm thick) of coarse-grained prismatic quartz, and radial intergrowths of biotite and sugary quartz-feldspar. Apical terminations of the quartz crystals are directed towards the related intrusions. Distinct primary fluid inclusion trails define growth band in individual quartz crystals (Fig. 1D). Some quartz layers have a wavy texture, with very fine-grained quartz intergrowths imparting a diffuse contact with the aphanitic groundmass of the related porphyritic intrusion.

Magmatic inclusion populations

The silicate-melt and fluid inclusion populations present in both types of quartz eyes and the comb-quartz layered textures are similar. Two populations of silicate-melt inclusions are recognised (Table 1). Volatile-rich silicate inclusions are most common, and have an irregular negative crystal form (Fig. 2A). Room temperature observations reveal small angular, crystalline silicate aggregates throughout: they vary mostly between 5 and 35 μm in diameter. A brine phase also occurs – this brine portion of the silicate-melt inclusion becomes visible following prolonged heating (Fig 2C; see micro-thermometry experiments below). A vapour bubble (20-40 vol.% vapour) is normally present. These composite inclusions contain several opaque phases (possibly chalcopyrite and magnetite). The second and less abundant silicate-melt inclusion population lacks the salt phase (Table 1; Fig. 2D) so prominent in the volatile-rich group IA inclusions (Table 1); these inclusions have a negative crystal or spherical shape and contain a shrinkage bubble (between 20 and 60 vol.%). Their size varies mostly between 15 and 45 μm , rarely up to 60 μm . Opaque daughter crystals (chalcopyrite?) are rare.

In the type 1 quartz eyes, silicate-melt inclusions coexist with vapour and polyphase brine inclusions (Fig. 2B) containing numerous daughter minerals such as halite, anhydrite, chalcopyrite and magnetite (hematite; Table 1). Little to no liquid is visible. Vapour inclusions (Table 1) are larger but less abundant when associated with the polyphase brine inclusions. Some quartz phenocrysts, especially in the earliest porphyry phases, are characterized by vapour inclusions only. Silicate-melt inclusions in the type 2 quartz eyes coexist with brine inclusions that have a higher proportion of liquid. Moreover, they are crowded with halite-anhydrite \pm magnetite(hematite)-sylvite-chalcopyrite and numerous unidentified phases. Similar inclusion assemblages exist in comb-quartz layered textures (Fig 2E, F). Coexisting vapour inclusions are rare in either case. The polyphase brine inclusions in the quartz eyes and comb-quartz layers are petrographically similar to those found in the earliest potassic alteration at Bajo de la Alumbrera (Ulrich *et al.* 2001; Harris 2002).

Silicate-melt and fluid inclusion micro-thermometry

Homogenization experiments on silicate-melt and fluid inclusions were performed at 1-atm external pressure using a LINKAM TS1500 heating stage. When individual quartz crystals are heated to 800°C for several hours and then quenched, the crystalline silicate aggregates in the melt inclusions fuse and do not reform on cooling; however, well-formed salt crystals and a vapour bubble appear when the inclusions are cooled below 250°C.

Typically, these salts appear in small (<1 to 8 μm) spherical globules crowded with salt crystals and a vapour bubble (< 2 μm) – this makes them morphologically similar to adjacent polyphase brine inclusions.

Micro-thermometric experiments reveal that for the silicate-melt inclusions in quartz eyes (type 1 and 2), the first dissolution of the salt phases occurs by 165°C, and is typically completed by 450°C, whereas vapour bubble disappearance in the brine component is as high as 550°C (Harris *et al.* 2003). The minimum trapping temperature of the silicate-melt inclusions ranges from 750°C to 780°C, based on extended heating experiments on the volatile-poor melt inclusions (Harris *et al.* 2003). Adjacent polyphase brine inclusions also homogenise at high temperatures (615°C to 695°C; by vapour disappearance). Assuming a simple NaCl-H₂O system, the calculated salinities of the inclusions average 45 wt.% NaCl equivalent.

Polyphase brine inclusions trapped in the comb-quartz layered textures exhibit homogenisation by halite dissolution; i.e., vapour disappearance occurs between 315°C and 365°C, whereas the large halite crystal typically disappears by 405°C. On the basis of these phase changes, combined with experimental data, the salinity is between 45 and 47 wt.% NaCl equivalent (as determined by Cline & Bodnar 1994). Reconstruction of the pressure-temperature trapping conditions (following the procedure outlined by Cline & Bodnar 1994) confirms that these inclusion fluids were probably trapped at pressures >0.8 kbar. By contrast, the majority of fluid inclusions in most vein and alteration stages at Bajo de la Alumbrera record fluid pressures of 0.3 kbar (Ulrich *et al.* 2001) – this fluid pressure is commonly reported for fluid inclusions in many porphyry ore deposits.

DISCUSSION AND CONCLUSIONS

The clearest evidence that some silicic magmas exsolve large volumes of magmatic aqueous fluids comes from geologic features, such as the occurrence of voluminous greisens, and the preservation of miarolitic cavities and comb-quartz layered textures in the carapace of some granites (e.g., Candela & Blevin 1995; Lowenstern & Sinclair 1996). In porphyry-related ore deposits, features such as interconnected miarolitic cavities may have been previously overlooked because of intense texturally destructive hydrothermal alteration. Their recognition at Bajo de la Alumbrera, combined with aqueous fluid phase equilibria from inclusion micro-thermometry, provide important constraints for the magmatic-hydrothermal transition.

Physical models (Shinohara & Kazahaya 1995; Shinohara & Hedenquist 1997) for the exsolution of volatiles from a convecting magma body show that at low degrees of crystallisation, individual vapour bubbles formed in the magma will buoyantly rise and coalesce at the top of the magma body. The accumulation of volatiles causes the internal pressure of the system to rise, leading to sudden and rapid failure of the carapace and adjacent wallrock – this occurs once the vapour pressure is greater than the confining pressure and tensile strength of the host rocks. Magmatic fluids escape via the extensive fracture network, and through water-rock interaction, cause hydrothermal alteration. Precipitation of alteration minerals seals the system, and the process is repeated. As the volume of crystals increases in the magma and the viscosity of the residual melt rises, aqueous fluid that has not previously escaped becomes trapped (e.g., Harris *et al.* 2003). At Bajo de la Alumbrera, textures representative of each critical stage are preserved.

Silicate-melt and polyphase brine inclusions from the quartz phenocrysts in the mineralised porphyries preserve the earliest stages of volatile exsolution (e.g., Lowenstern *et al.* 1990). Previous studies have taken such inclusion populations to indicate that silicic melt coexisted with hypersaline fluids (Roedder and Coombs, 1967); however, salt immiscibility is

better preserved by composite silicate-melt inclusions (e.g., Kamenetsky & Naumov 2002). In these inclusions, a non-silicate volatile-rich hypersaline phase is immiscible with the magma from which it exsolved (e.g., Reyf & Bazheyev 1977; Frezzotti 1992; Kamenetsky & Naumov 2002). Reconstruction of the volcanic architecture above Bajo de la Alumbrera suggests that this source magma body probably occurred below 3 km (≥ 0.7 kbar lithostatic pressure; Harris 2002). Boiling of an originally supercritical fluid (<10 wt.% NaCl equivalent) exsolved at 1 kbar pressure and 680°C will result in a liquid with a salinity of 45 wt.% NaCl equivalent (Cline & Bodnar 1994 and references therein). Alternatively, as found elsewhere (Cline & Bodnar, 1994), the observed inclusion populations may indicate that aqueous fluids with salinities up to 45 wt. % exsolved directly from the crystallizing melt. If this latter scenario is correct, abundant vapour-rich fluid inclusions should coexist with the saline inclusions (see discussion by Cline and Bodnar, 1994), which is not the case here.

Comb-quartz layered textures are thought to preserve pockets of overpressured magmatic fluid separated from magma during secondary or resurgent boiling processes (Lowenstern & Sinclair 1996). Evidence of this overpressure is preserved in the fluid inclusions from the comb-quartz layered textures at Bajo de la Alumbrera; the inclusions exhibit liquid-vapour homogenisation between 315°C and 365°C , and halite dissolution by 405°C . Where observed (e.g., Cline and Bodnar, 1994), such homogenisation behaviour has been related to the entrapment of a halite-saturated fluid at high temperature and pressure. Over-pressuring causes fracturing of the carapace. Quartz-rich biotite-K-feldspar alteration assemblages probably formed as the pocket was drained of its fluid (Lowenstern & Sinclair 1996). Moreover, melt may also enter the fractures, forming thin dyke-like bodies, referred to as vein-dykes – these features are common in many porphyry ore deposits (e.g., Heathersay & Walshe 1995). In either case, sealing the fracture network above the magma causes the system to re-pressurise. Repeated volatile exsolution and/or degassing, volatile accumulation, over-pressuring and fracturing explains the complex alteration and mineralization patterns that exist in all porphyry ore deposits.

Features similar to those reported here are being increasingly recognised in other deposits (e.g., E26N porphyry Cu-Au, Australia; Lickfold *et al.* 2003). Quartz in the porphyries at Bajo de la Alumbrera records the earliest stages of exsolution, bubble formation (vesiculation), and volatile accumulation, culminating in hydrothermal alteration caused by magmatic aqueous fluids. Aqueous fluid phase equilibria observed during microthermometric studies reveal an apparent increase in pressure of the exsolved fluid prior to rupturing of the magma's carapace and the adjacent wallrock. When the volatile pressure exceeds the confining pressure (i.e., > 0.7 kbar), the carapace cracks and hydrothermal alteration and associated ores develop. Data obtained from silicate-melt and fluid inclusions, like that presented here, are providing important insights into the processes that form intrusion-related ore deposits.

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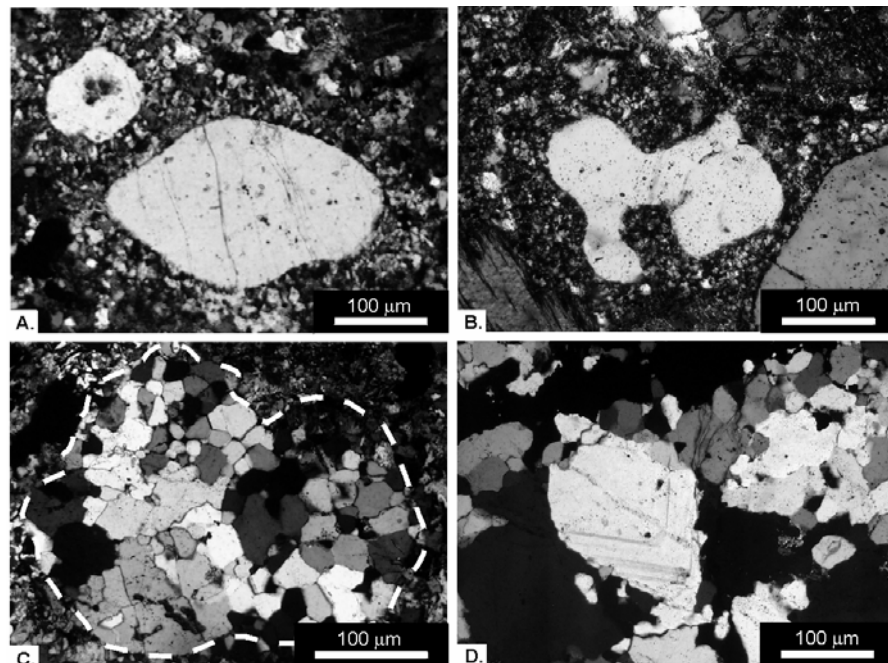


Figure 1. Quartz in dacite porphyries from Bajo de la Alumbrera. A. Type 1 quartz eyes or phenocrysts. B. Some quartz phenocrysts have an ameboid appearance because of embayments. C. Type 2 quartz eyes appearing as polycrystalline quartz aggregates. D. Prismatic quartz crystal, with distinct primary fluid inclusion trails, in comb-quartz layered texture.

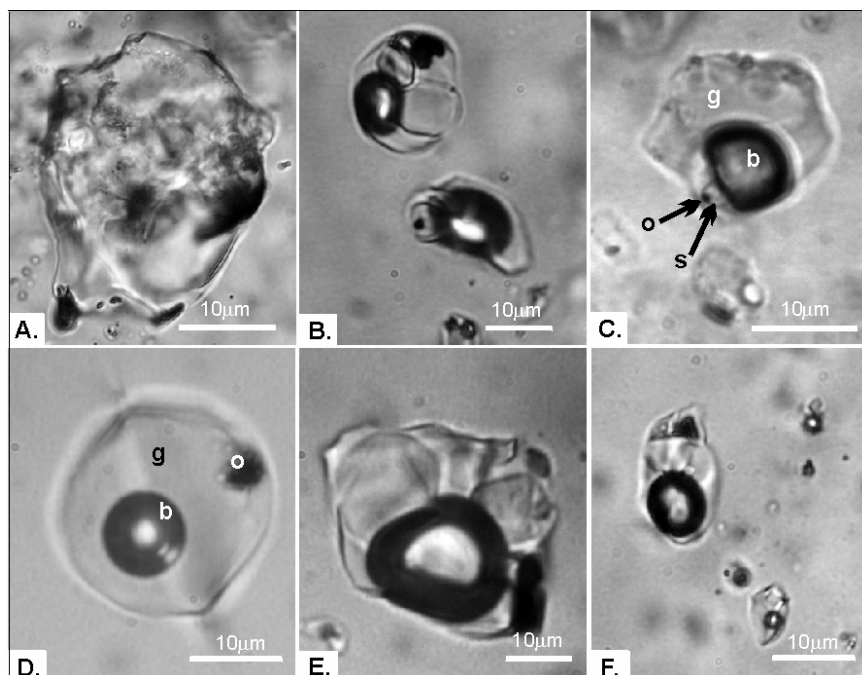
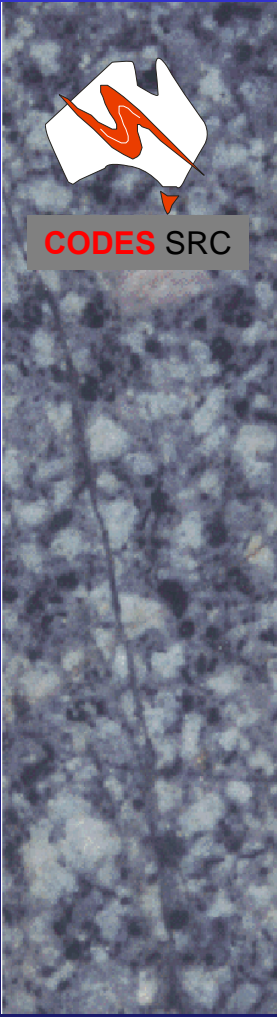


Figure 2. Magmatic inclusion populations in igneous quartz at Bajo de la Alumbreira. A. Silicate-melt inclusion in type 1 quartz eyes. B. Polyphase brine and vapour-rich fluid inclusions that coexist with silicate-melt inclusions in type 1 quartz eyes. C. Heated and quenched volatile-rich silicate-melt inclusion (Group IA; Table 1) with distinct volatile-rich globule containing a large vapour bubble (b), cubic salt (s), and an opaque (o) daughter crystal, surrounded by homogenised silicate glass (g). D. An example of a heated and quenched volatile-poor, silicate-melt inclusion from a late stage dacite porphyry (Group IB). Note the prominent vapour bubble (b) and opaque (o) phase encapsulated by homogenised silicate glass. E. Polyphase brine fluid inclusion (Group II) in comb-quartz layered texture. Note that the inclusion is crowded with salts. F. A primary inclusion trail in comb-quartz layered texture. In these inclusions, a distinct triangular chalcopyrite crystal is clearly visible.

Table 1. Summary of magmatic inclusions in quartz from dacite porphyries at Bajo de la Alumbreira

Inclusion Group	Description	Distribution	
IA	<i>Volatile-rich silicate-melt inclusion</i>	Silicate crystals-vapour-salt(s) ± cpy.-mt.	Found as primary inclusions in quartz eyes. Coexists with group II and III inclusions. They also appear as primary inclusions in comb-quartz layered quartz textures. In this case, they coexist with group II inclusions.
IB	<i>Silicate-melt inclusion</i>	Silicate crystals (rare glass)-vapour ± opaque (?cpy.)	Rare in primary inclusion trails in quartz eyes. Isolated inclusions.
II	<i>Polyphase brine fluid inclusion</i>	Salt(halite-sylvite)-anhydrite-vapour-liquid ± cpy.-mt. (hem.)	Occurring in quartz eyes and comb-quartz layered textures. More commonly seen in primary and secondary inclusion trails in potassic alteration assemblages. Coexists with group III inclusions.
III	<i>Vapour-rich fluid inclusion</i>	Vapour-opaque (?cpy.) ± liquid	Abundant in primary inclusion trails in some quartz eyes; however, these inclusions are less abundant than group II inclusions.

Abbreviations: cpy. = chalcopyrite; mt. = magnetite; hem. = hematite.



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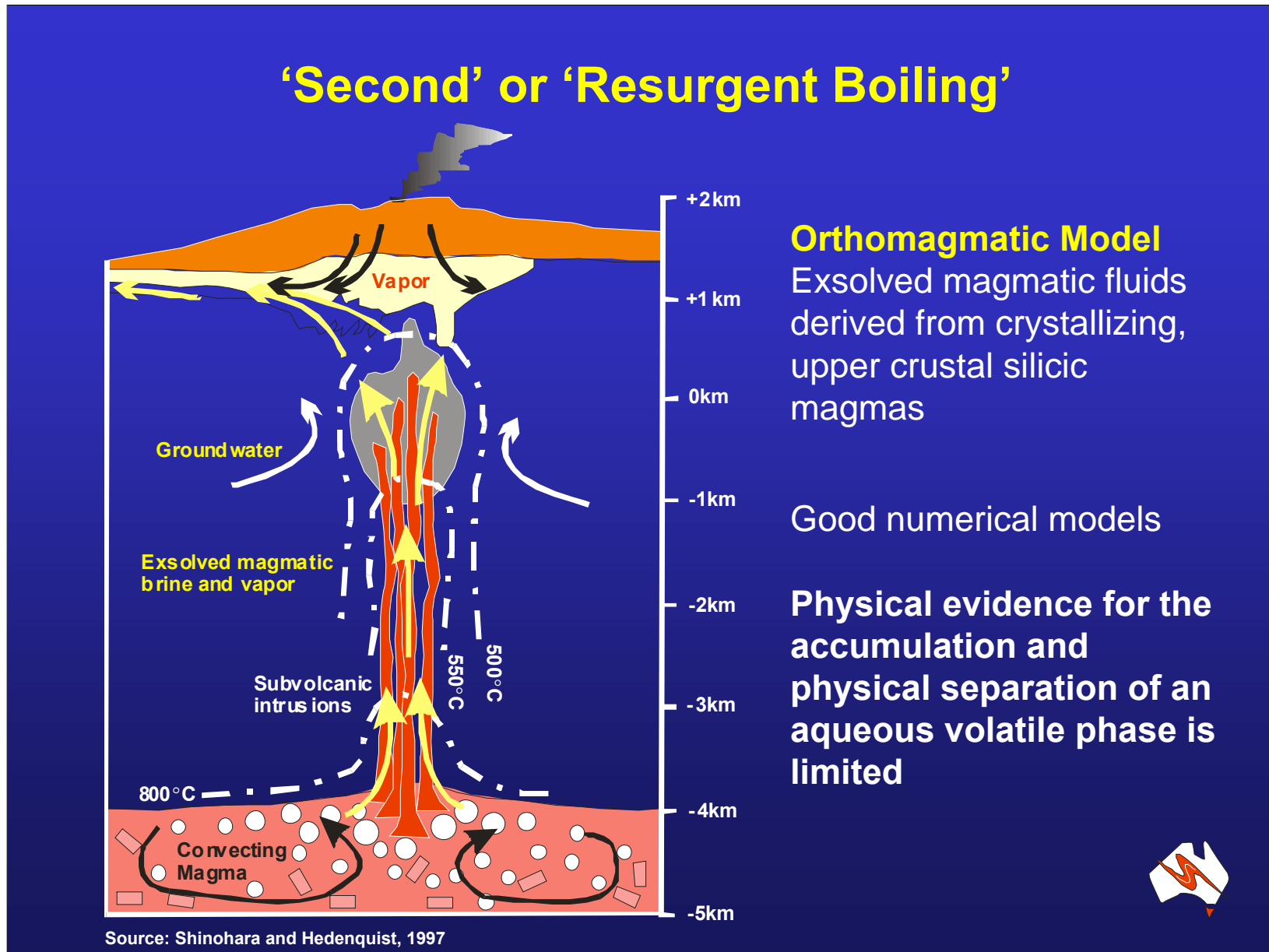
Bajo de la Alumbreira
NW Argentina

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Magmatic-Hydrothermal Transition

This subject has been studied from the:

1. Magmatic perspective
2. Hydrothermal perspective



Bajo de la Alumbreira



Malakhitovy, Kamchatka

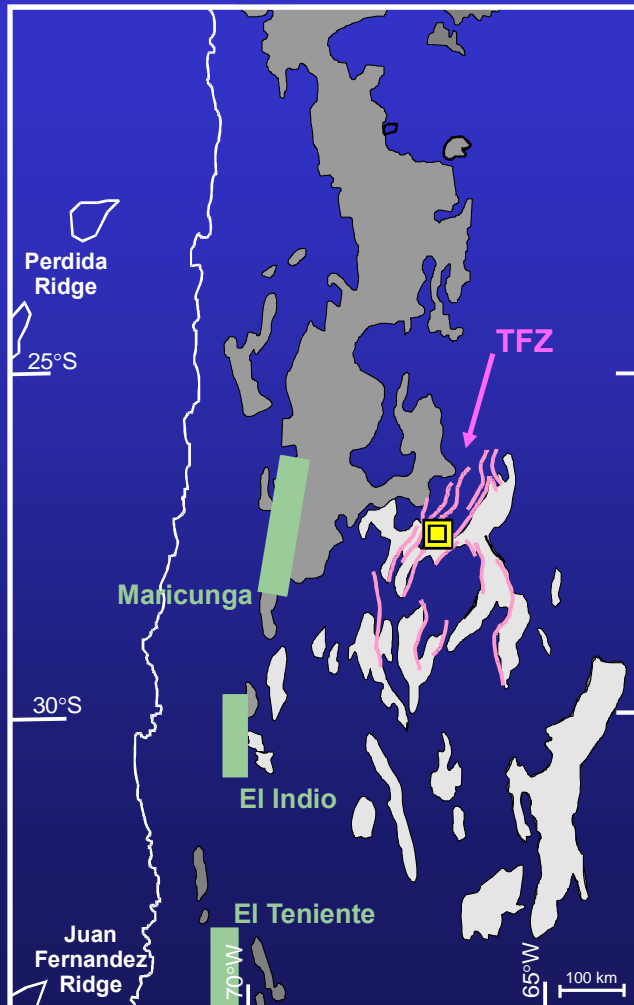
- Petrographic observations
- Inclusion studies

Completing the continuum...



Farallón Negro District

Regional Geologic Setting



Farallón Negro Volcanic Complex occurs well inboard (~200 km) of the main Late Miocene arc



Farallón Negro District

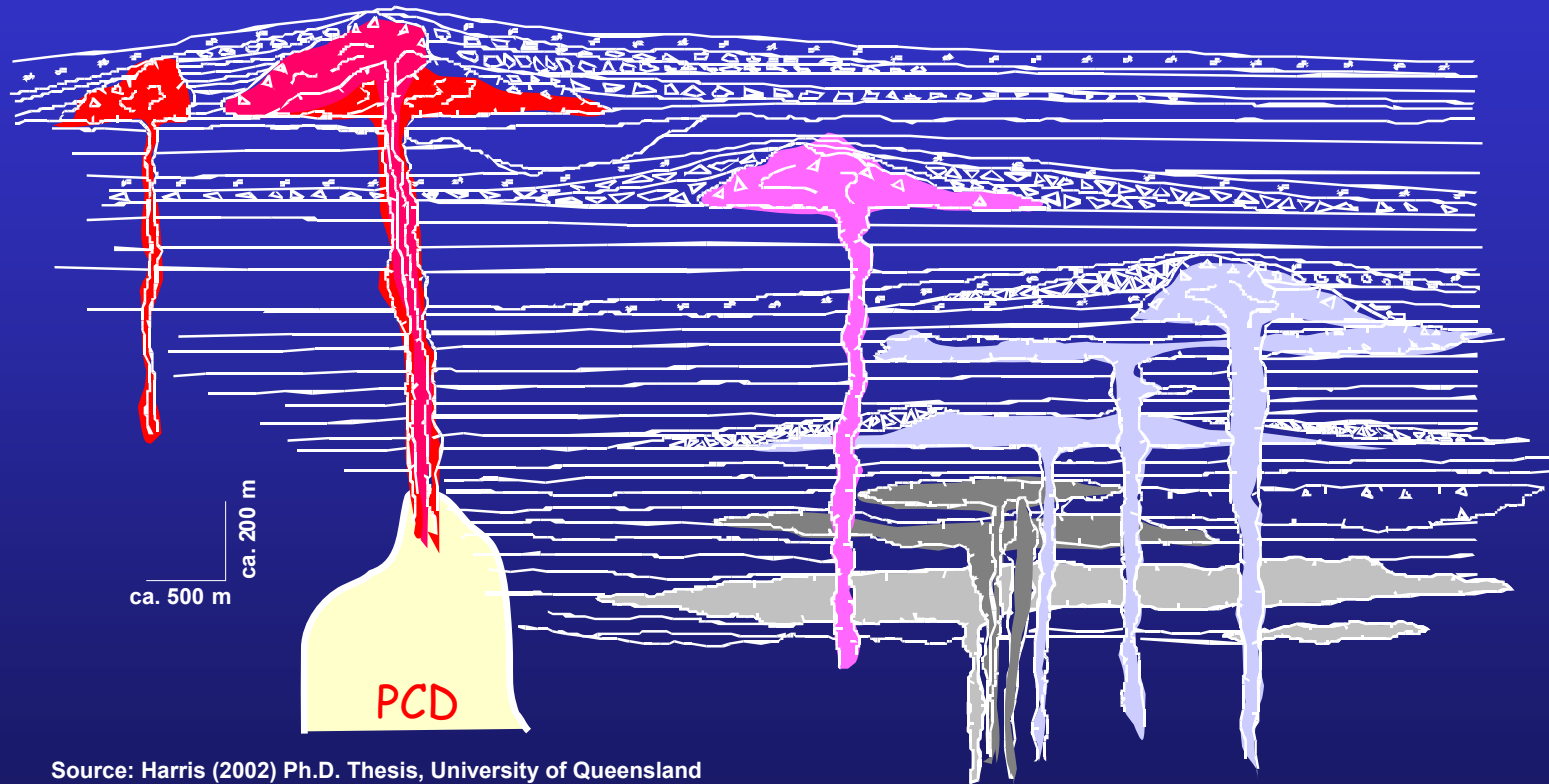
Regional Geology



Mineralized porphyries and their extrusive equivalents are preserved



Farallón Negro District



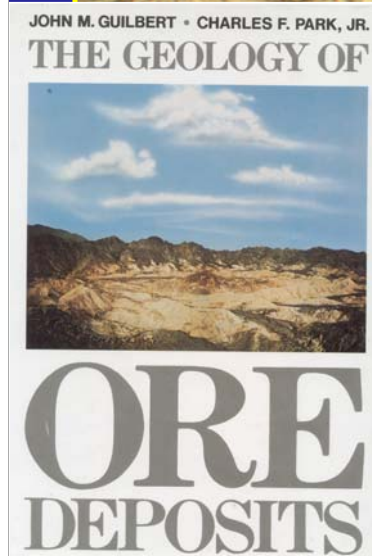
Source: Harris (2002) Ph.D. Thesis, University of Queensland

Consequently, we have good constraints on the depth of porphyry emplacement...



Bajo de la Alumbrera

Hydrothermal Alteration



Source: Noel C. White

Near perfect zonal arrangement of hydrothermal alteration

Involvement of magmatic fluids

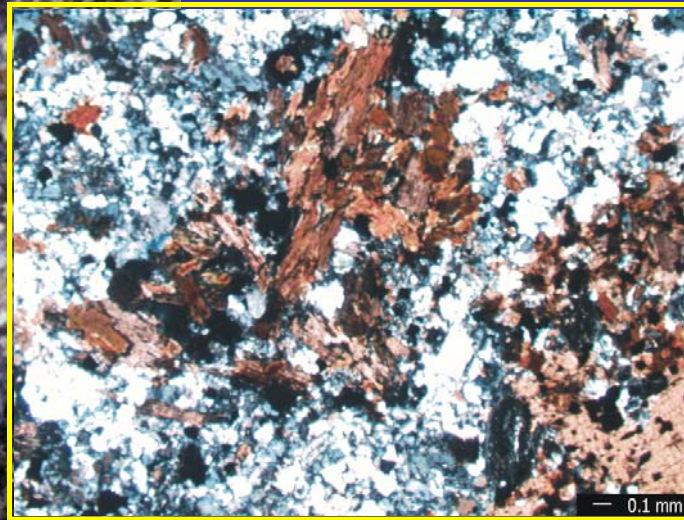


Bajo de la Alumbreira

Hydrothermal Perspective

Potassic alteration assemblages

- Bt – K-flds – qtz – mt
- Cu-Fe sulfides & Au



Fluid inclusions & stable isotopes:

- high temperature (350°C and 550°C, up to 750°C)
- saline (>30 wt.% NaCl equiv.)
- magmatic origin

Cu-Au bearing hydrothermal alteration associated with several porphyry phases



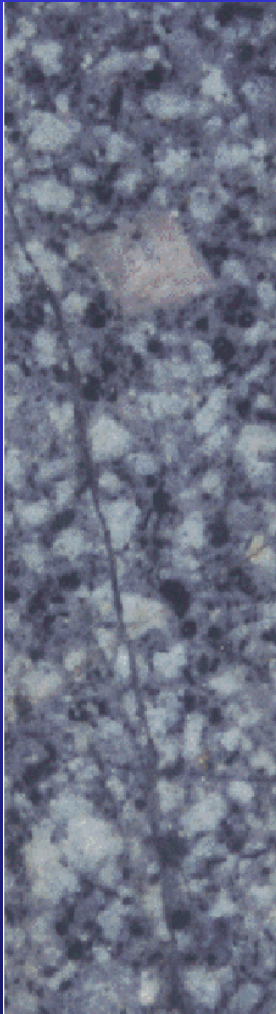
Bajo de la Alumbrera

Intrusion Geology

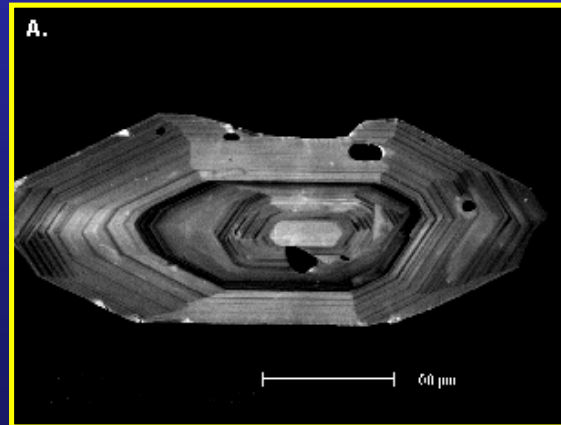
Petrography and Geochemistry

High-K Calc-alkalic Dacite

- Basaltic andesite to Rhyodacite
- Multiple phases of ore-related intrusion:
 - evidence of incomplete mixing and/or mingling
 - youngest intrusions are more mafic



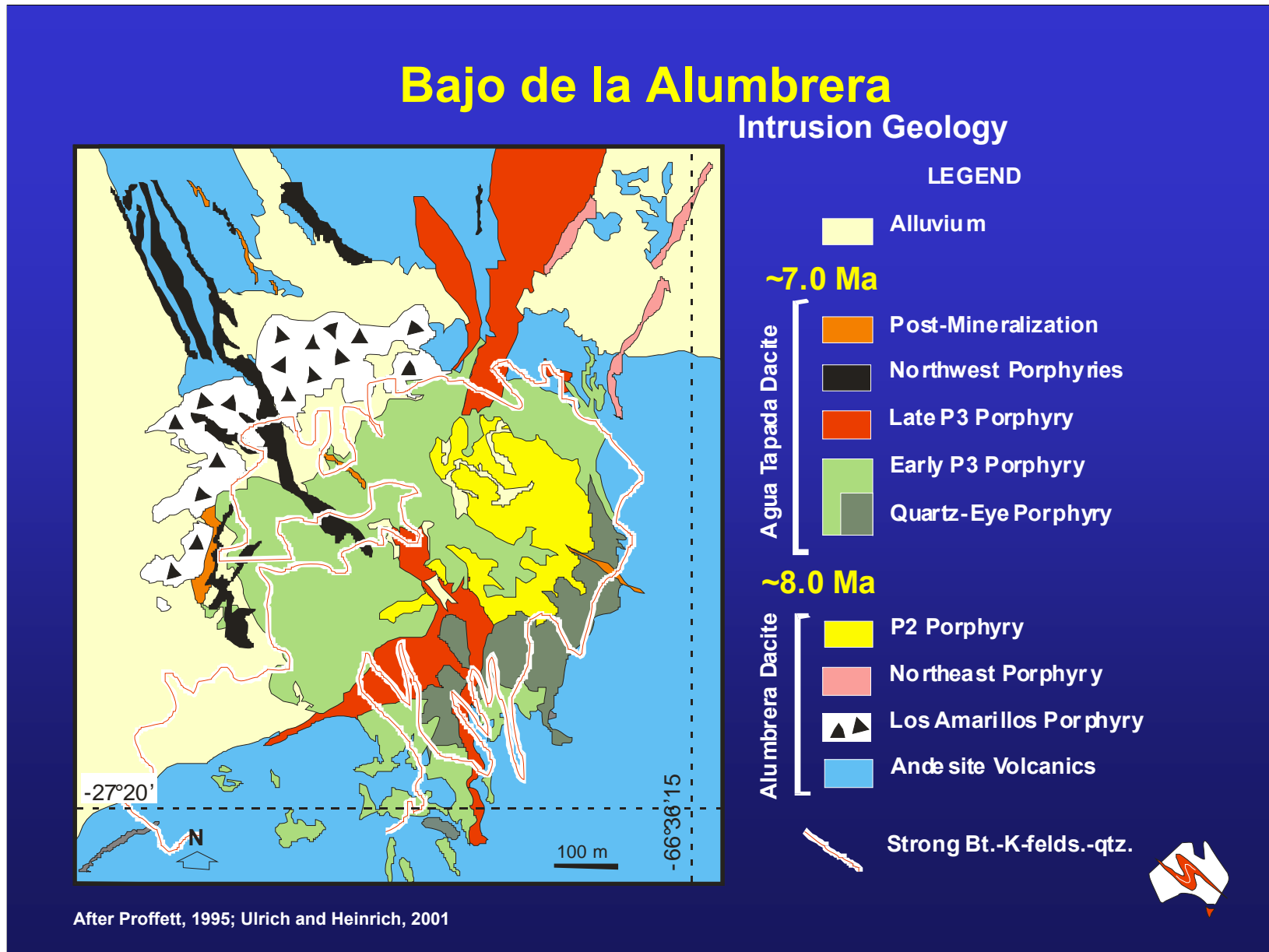
Late P3 Porphyry



The timing of things is important...

Source: Harris et al. (2003) in press Mineralium Deposita





Bajo de la Alumbrera

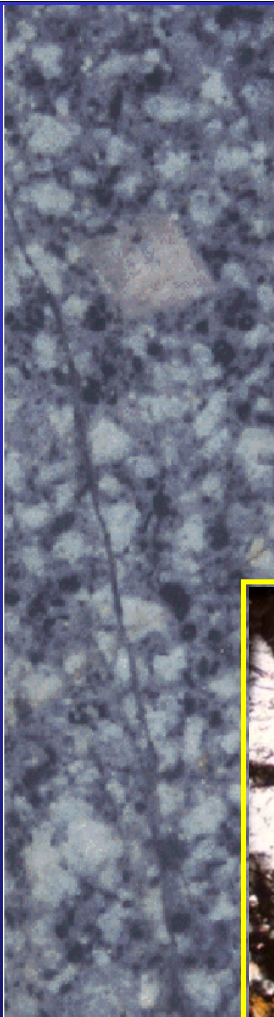
Intrusion Geology

Early and Late P3 Porphyry

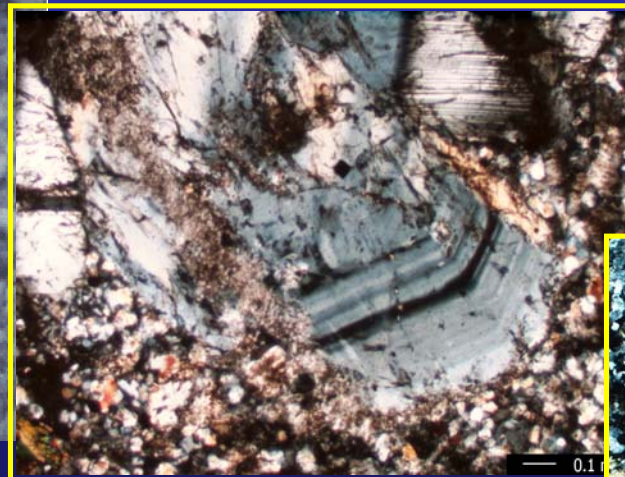
- Several phases (Proffett, 1997)

Biotite-hornblende bearing plagioclase-phyric dacite

- Amphibole-biotite clots



Late P3 Porphyry



Water content >3 wt.%,
consistent with phenocrystic
populations

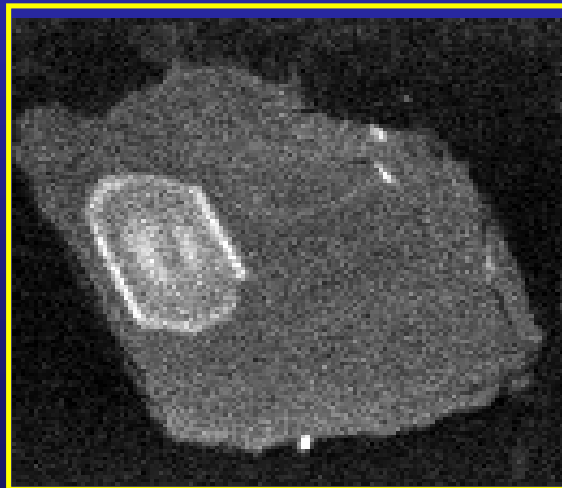
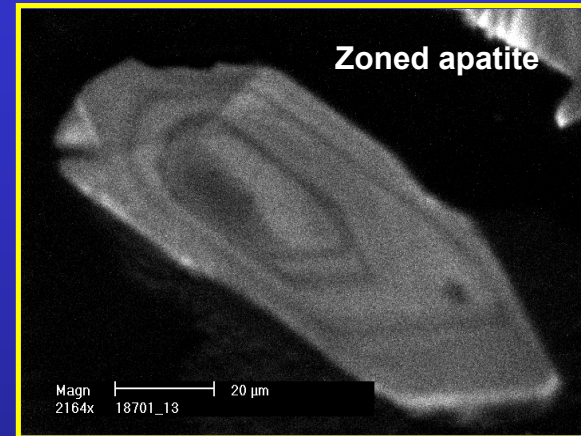


Bajo de la Alumbrera

Magmatic Perspective

Microprobe studies have found:

- Enriched S (+ Cl) in Cu-Au Dacites (i.e., up to 0.6 wt% SO₃ and 3.7 wt% Cl);
- Enriched F in post-mineral porphyries



This trend is similar to modern volcanoes

Volatile exsolution and degassing is ordered:

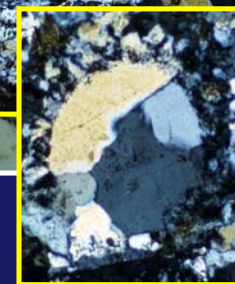
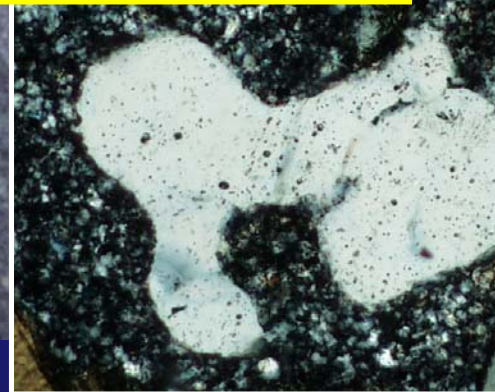
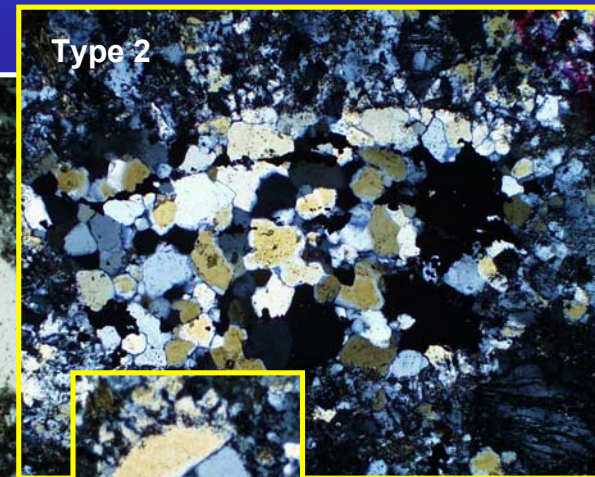
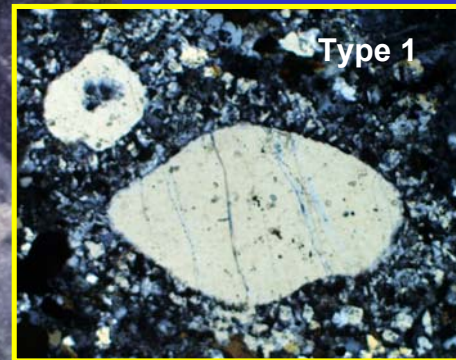
S + Cl-rich V-L ⇒ F-rich V-L



Petrographic Observations

Quartz in dacite porphyries

1. Hydrothermal
2. Primary igneous textures



Each represent a critical stage...



Petrographic Observations

Quartz in the porphyries at Bajo de la Alumbreira records:

1. the earliest stages of exsolution – quartz phenocrysts
2. bubble formation (vesiculation) – miarolitic cavities
3. volatile accumulation – comb quartz layer textures (UST)
4. culminating in hydrothermal alteration

WHERE do these textures occur?

WHAT characterises these textures?

WHAT do the inclusion population tell us?

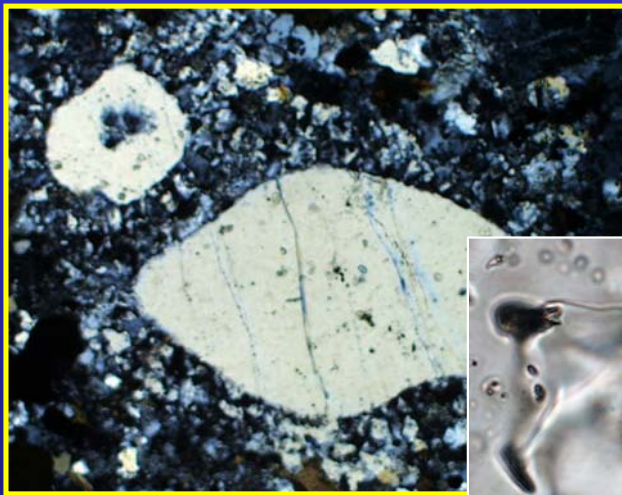
HOW these textures are interpreted to form?



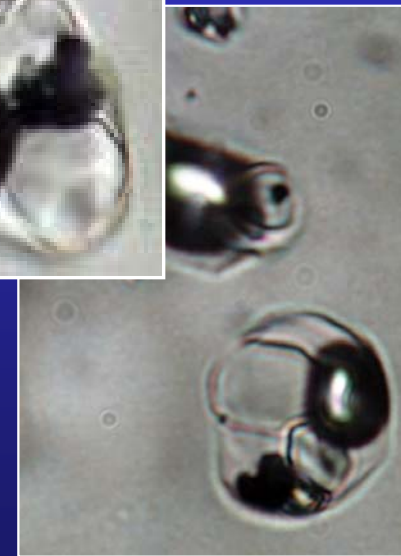
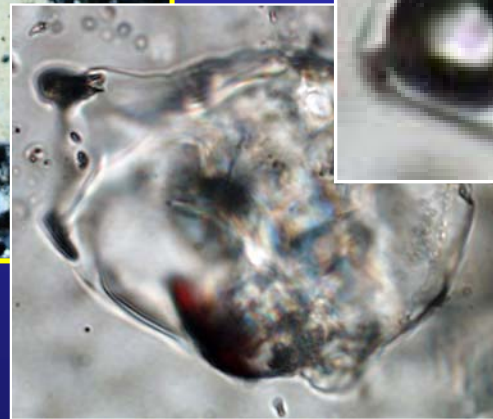
Petrographic Observations

1. Earliest stages of exsolution – quartz phenocrysts

Type 1 Quartz Eyes



Th ~ 615 °C - 695 °C,
X ~ 45 wt.% NaCl equiv.



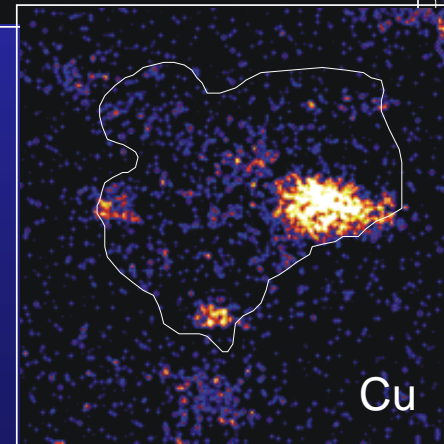
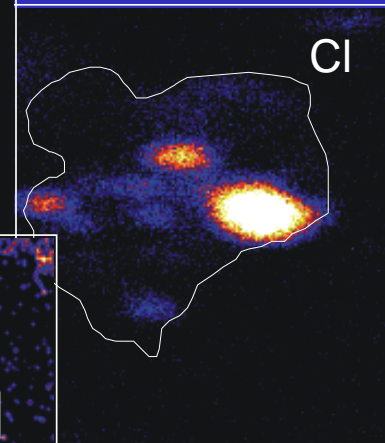
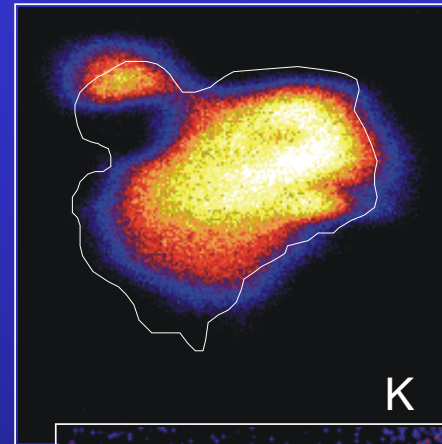
Silicate-melt ~ 750°C - 780°C

Silicate-melt + fluid inclusion ⇒ Salt Immiscibility

Hypersaline fluid exsolved?



Petrographic Observations



Cu and Cl are partitioned to the exsolved fluid rather than the K-rich melt



Petrographic Observations

2. Bubble formation (vesiculation) – miarolitic cavities

Type 2 Quartz Eyes



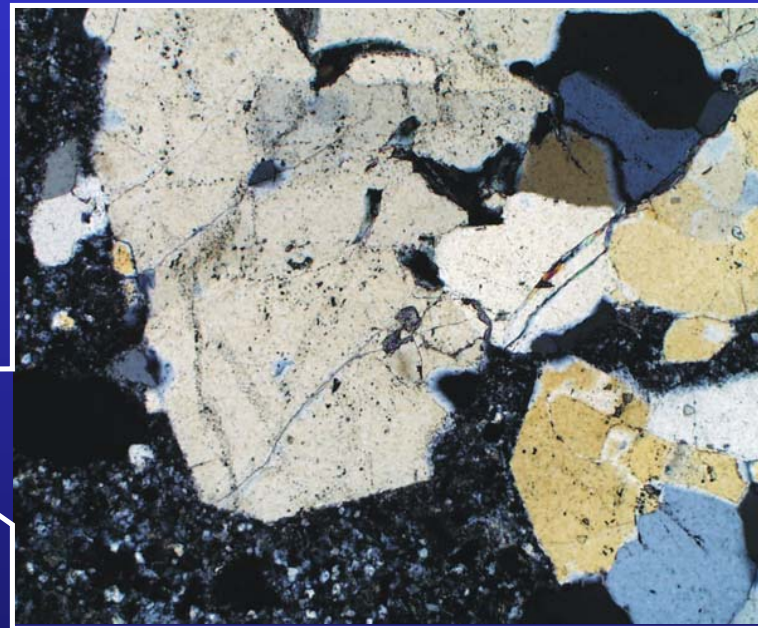
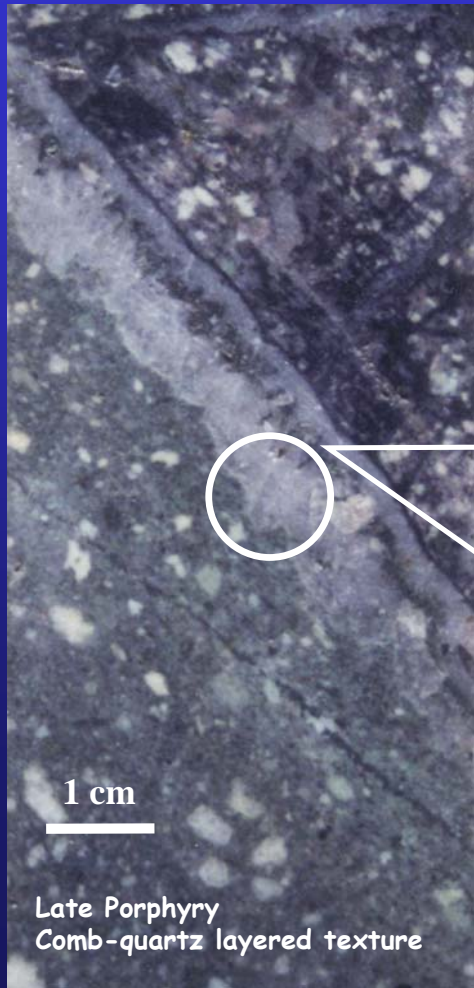
Silicate-melt + fluid inclusions



Petrographic Observations

3. Volatile accumulation – comb quartz layer textures

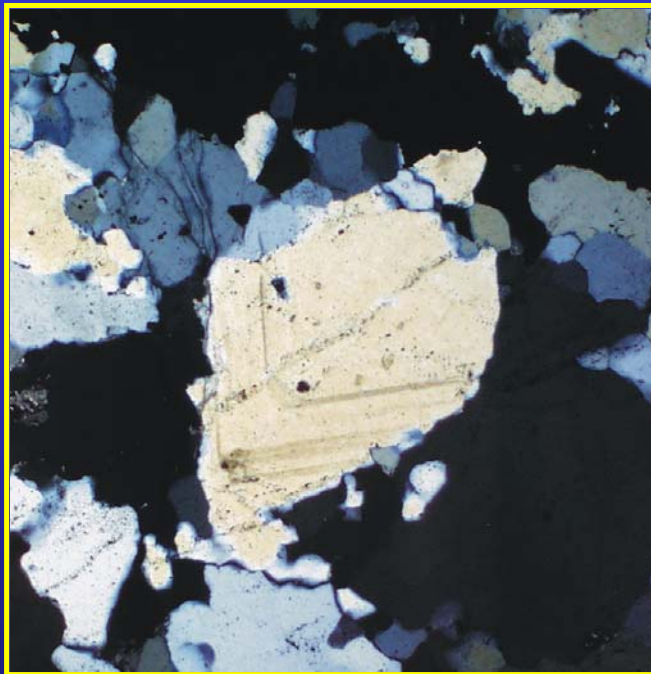
Unidirectional Solidification Textures (UST's)



Textural evidence volumes of magmatic fluid exsolved



Petrographic Observations

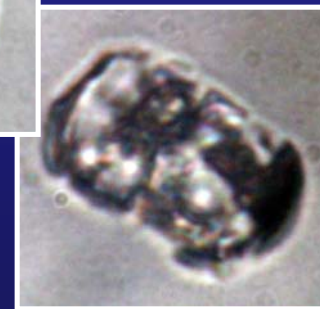


Homogenisation by halite dissolution...

Th (V→L): 315 °C - 365°C

Tm (halite): <405 °C

X: 45- 47 wt.% NaCl equiv.



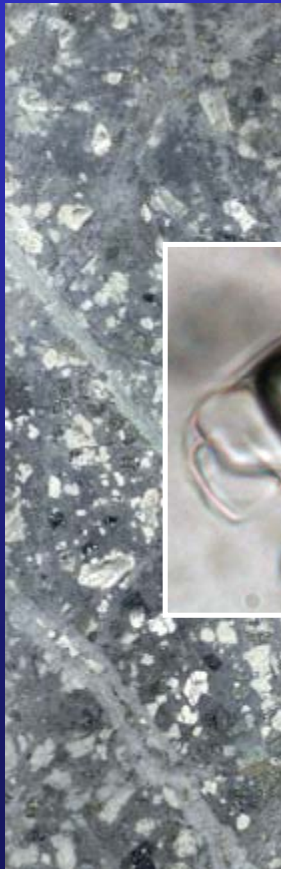
Entrapment of a single-phase fluid at pressures above the two-phase boundary – high pressure fluid



Petrographic Observations

4. Hydrothermal alteration

Transition Magmatic-Hydrothermal Veins



Th (V → L): 815°C
X: 62 wt.% NaCl equiv.
P: 0.7 kbar



Early Qtz-K-flds vein
P2 Porphyry



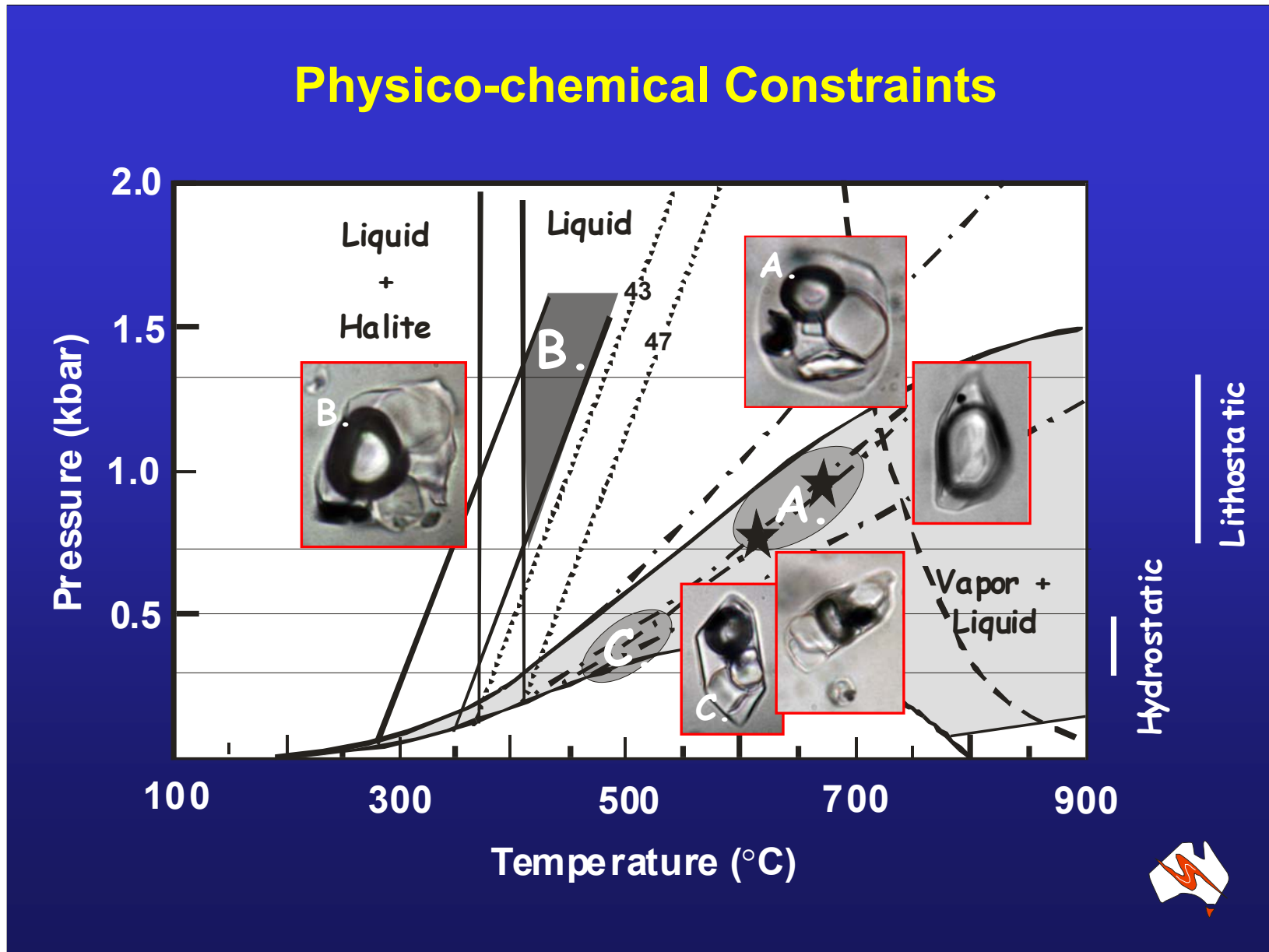
Th: >350°C
X: >32 wt.%
NaCl equiv.
P: 0.3 kbar

Hydrothermal Veins



Qtz-cpy vein bt. alt.
Andesite





Discussion

Clearest evidence that some silicic magmas exsolve large volumes of magmatic aqueous fluids comes from geologic features best preserved in granites

In porphyry-related ore deposits, these features may have been previously overlooked because of intense texturally destructive hydrothermal alteration

Primary igneous textures + microthermometry data constrain the magmatic-hydrothermal transition

We are working towards a physical model

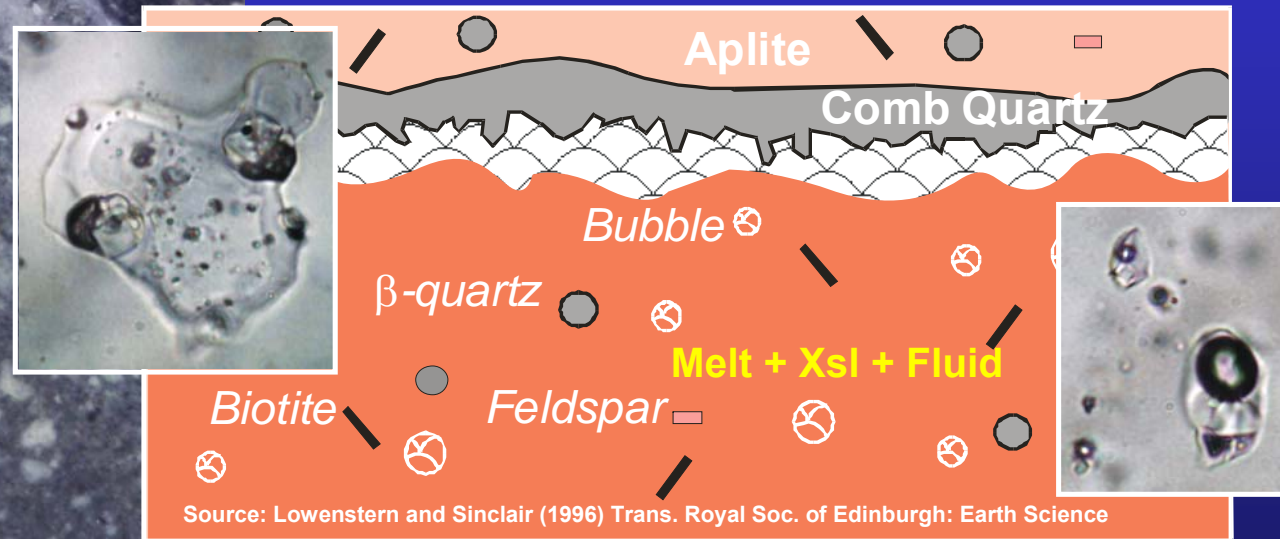


Discussion

A revised physical model

1. Bubble separation and coalescence

At low degrees of crystallization:

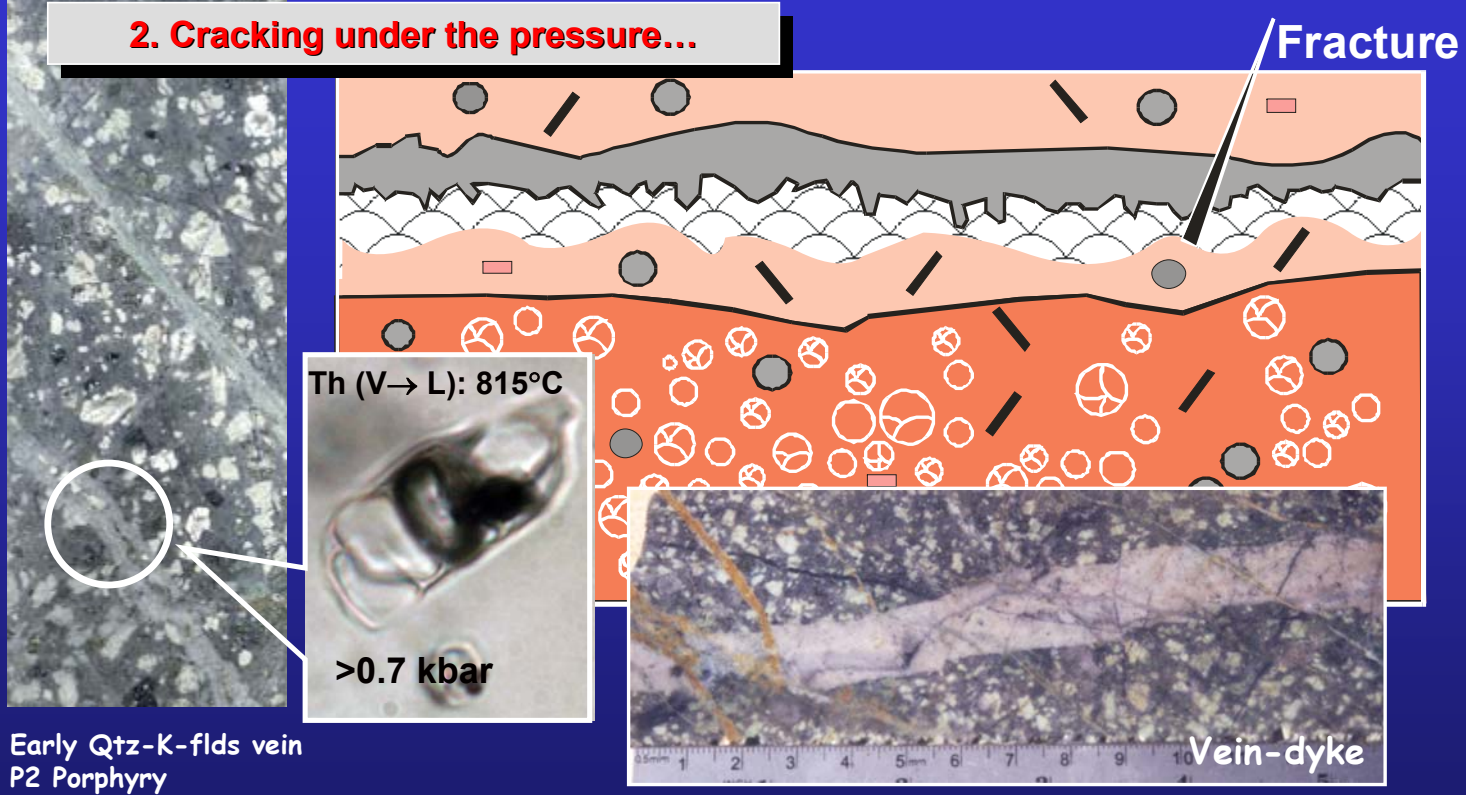


Comb-quartz layered textures – preserved pockets of overpressured magmatic fluid



Discussion

2. Cracking under the pressure...

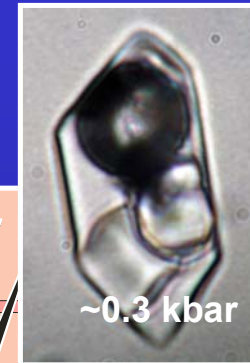
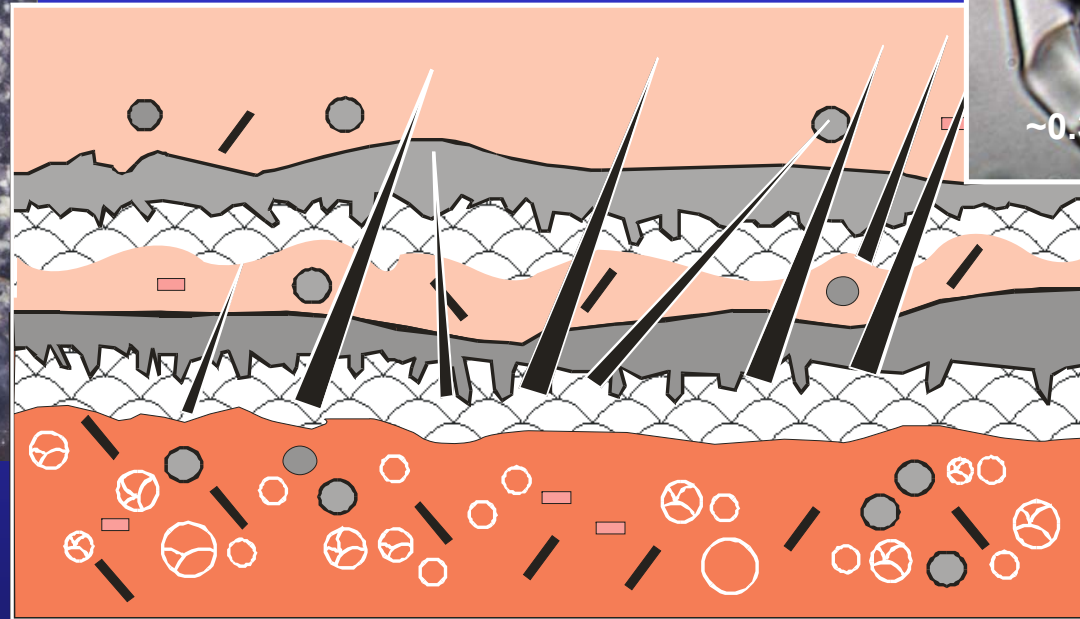
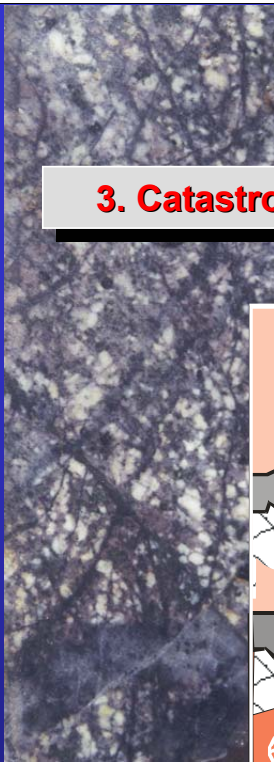


**Accumulation of volatiles ↑'s internal pressure ⇒
rapid and sudden failure of the carapace and
adjacent wall-rock**



Discussion

3. Catastrophic failure and rupturing



Magmatic fluids escape via the extensive fracture network, and through water-rock interaction, causes hydrothermal alteration.

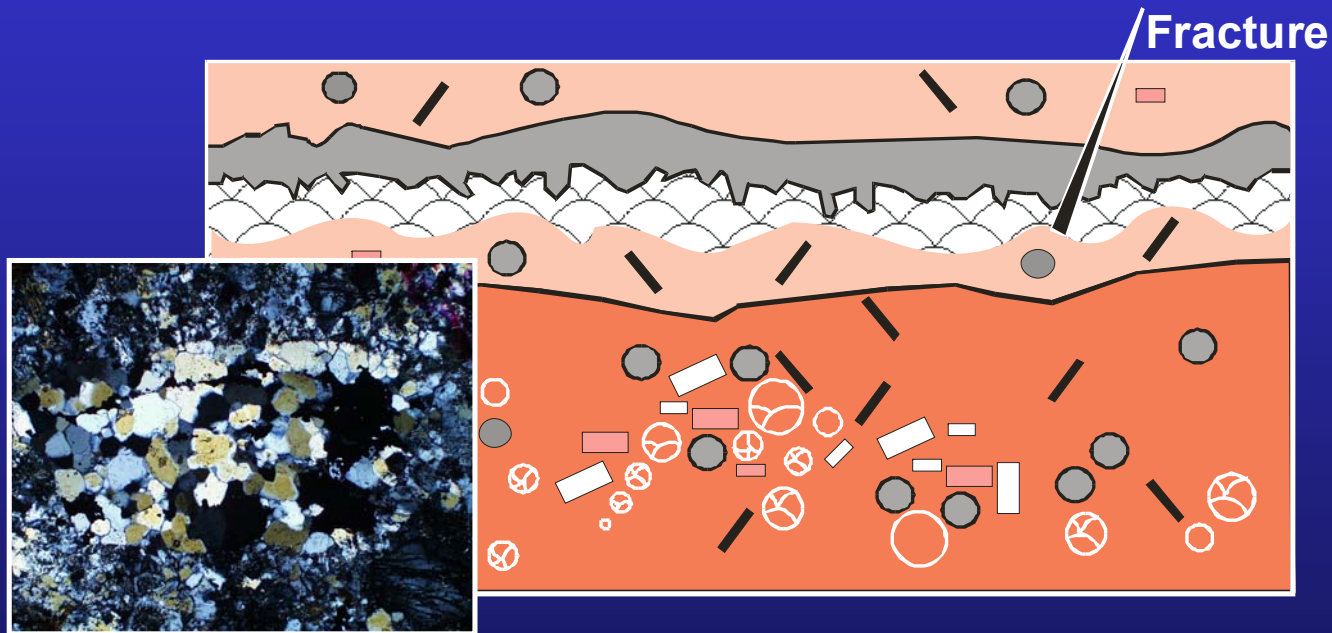
System seals, and the process is repeated.



Discussion

4. System shuts down

At high degrees of crystallization:



At Bajo de la Alumbrera, textures representative of each critical stage are preserved.



Summary

Quartz in the porphyries at Bajo de la Alumbreira records:

- the earliest stages of exsolution,
- bubble formation (vesiculation),
- and volatile accumulation,
- culminating in hydrothermal alteration caused by magmatic fluids.

Aqueous fluid phase equilibria \Rightarrow \uparrow pressure of the exsolved fluid prior to rupturing of the magmas carapace and adjacent wallrock

