FLUID INCLUSION EVIDENCE FOR P-V-T-X
EVOLUTION OF HYDROTHERMAL SOLUTIONS IN
LATE-ALPINE GOLD-QUARTZ VEINS AT BRUSSON,
VAL D'AYAS, NORTHWEST ITALIAN ALPS

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ABSTRACT. The auriferous veins at Brusson formed in active normal faults and dilatent joints during uplift and cooling of the Western Alps approx 32 Ma ago, some 4 to 8 Ma after the peak of local greenschist-facies metamorphism. The veins traverse a variety of countryrocks, and gold is found in all but the segments of veins enclosed by serpentinite or metacarbonate wallrocks.

Fluid inclusion petrography, microthermometry, laser Raman spectroscopy, and crush-leach analyses show that the main-stage vein minerals, quartz + dolomite ± magnesite + muscovite + rutile + pyrite + chalcopyrite + gold, precipitated from a homogeneous fluid composed of (in mol percent) 90.9 H2O, 5.9 CO2, 1.47 Cl, 1.47 Na, 0.15 N2, 0.06 K, 0.02 S, 0.02 Ca, 0.003 Mg, 0.002 CH4. Thermodynamic calculations and fluid inclusion data indicate that these minerals precipitated between 300°C, 1300 bars and 240°C, 650 bars, in response to fluid-wallrock reactions and to P-T decreases imposed by regional uplift.

The latest generation of fluid inclusions, coeval with minor final-stage calcite + tetrathedrite + galena + gold, is made up of low-XCO2 and high-XCO2 assemblages that satisfy requirements of immiscibility in the system H2O–CO2–N2–CH4–NaCl. Immiscibility was attained via retrograde boiling of the main-stage fluid at 230°C and 600 bars. The compositional evolution of the fluid caused by boiling was slow enough to allow fluid-wallrock reactions to continue controlling the spatial distribution of gold, and flow in the veins ceased before the residual liquid had significantly changed its composition. This case study thus demonstrates that ore-grade gold does not necessarily result from boiling in mesothermal quartz veins.

INTRODUCTION

The mesothermal gold-quartz-carbonate-sulfide veins found in metamorphic terranes constitute an important class of epigenetic, hydrothermal ore deposits (Knopf, 1929: Henley, Norris, and Paterson, 1976; Boyle, 1979; Kerrich and Fyfe, 1981; Groves and Phillips, 1987: Colvine and others, 1988). Phase rule analysis shows that the common vein mineral assemblages, such as quartz + ankerite + muscovite + pyrite + rutile, are characterized by high thermodynamic variance. Therefore, as little information regarding the compositions of the ore transporting solutions can be deduced alone from the mineral assem-

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blages, fluid inclusion studies are an indispensable prerequisite for understanding the chemical processes of ore formation in these deposits.

Studies of fluid inclusions in mesothermal gold veins (Krupka, Ohmoto, and Wickman, 1977; Roedder, 1984a; Smith, Cloke, and Kesler, 1984; Ho, 1987; Robert and Kelly, 1987; Touray, 1987; Goldfarb and others, 1988) have revealed compositional similarities between the ore-bearing solutions, despite the wide range in ages and host lithologies of the investigated deposits. Invariably the inclusions are found to be weakly saline (<3 equivalent mol percent NaCl), CO₂-bearing (3–30 mol percent) aqueous solutions, but in general their detailed chemistry remains poorly defined. Furthermore, whereas mixing and unmixing of fluids are known to be principal causes of ore deposition within certain hydrothermal environments, compelling evidence for the importance of such processes in mesothermal lode-gold deposits is still sparse. Therefore, this fluid inclusion study of a specific field example aims to (1) characterize the P–V–T–X evolution of the vein-forming hydrothermal fluids and (2) identify the relationship between wallrock-independent fluid evolution and the deposition of vein minerals, in particular gold.

The investigated deposits are located at Brusson in central Val d'Ayas, in the Northwest Italian Alps (fig. 1). Their mineralogy and collisional orogenic setting are typical of mesothermal gold-quartz veins worldwide, but they are situated within minor extensional faults and joints rather than within ductile shear zones. The interpretation of fluid inclusion assemblages is therefore greatly simplified, as much of the vein quartz is undeformed.

In this paper the results of petrographic, microthermometric, Raman spectroscopic, and bulk leachate analyses are integrated with available experimental data to provide quantitative estimates of fluid inclusion composition in terms of 10 chemical components. The compositional, microthermometric, and phase-equilibrium data permit inclusion densities to be estimated, which in turn place constraints on the possible P-T conditions of mineralization.

As in most fluid inclusion work, the significance of this study for the understanding of vein formation depends on the validity of two well-known assumptions, namely, that the volume and the composition of the examined fluid inclusions have remained constant since the moment of inclusion entrapment. The observational and experimental bases for these assumptions is discussed elsewhere (Roedder and Skinner, 1968; Pecher, 1981; Roedder, 1984b; Sterner and Bodnar, 1984), but specific justification for applying the assumptions to the Brusson inclusions will be given below.

**GEOLOGY OF THE BRUSSON VEINS**

The auriferous quartz veins at Brusson belong to the Monte Rosa Gold District, a province of scattered hydrothermal mineralization that
Fig. 1. Geological map of the Brusson gold-quartz veins, Val d'Ayas. Many of the veins cross cut several lithologic units.
stretches through a 130 km length of the western Alpine arc (Huttenlocher, 1934: Curti, 1988). Situated in the south of the ore province, the Brusson locality consists of a swarm of more than 100 veins (fig. 1) that has produced approx 1000 kg of gold at grades of between 3 and 30 g/ton, mostly from the now abandoned Fenilia, Bechaz, and Orbeillaz mines (Reinhold, 1916: Huttenlocher, 1934; Stella, 1943; Richard, 1981).

The steeply-dipping, sheet-like veins discordantly traverse two major tectonic nappes folded and metamorphosed under greenschist-facies conditions during the Meso-Alpine phase of the Alpine Orogeny (Dal Piaz, Hunziker, and Martinotti, 1972: Frey and others, 1976: Dal Piaz and Ernst, 1978: Gosso and others, 1979). The lowermost nappe, known as the Arcesa-Brusson Unit (an equivalent of the Penninic Monte Rosa Nappe), includes pre-Alpine granitic augen-gneisses and a variety of mostly pelitic metasediments. The overlying Piemonte Ophiolite Nappe consists of metabasites, metacarbonates, and metaserpentinites of Mesozoic age. Some of the longest quartz veins, such as the Fenilia (fig. 1), transect this entire range of countryrocks. The Austroalpine Sesia-Lanzo Nappe is the highest tectonic unit in the area, but it is not known to host auriferous quartz veins. At Brusson the nappe pile is folded into an elongate dome, which on its northern limb is truncated and downthrown by the Aosta-Ranzola fault (fig. 1)—a major post-mineralization structure (Diamond, ms). Most of the gold veins are found within the erosional window that exposes the core of the dome.

A K-Ar radiometric age of 32 Ma obtained on vein muscovites (Diamond and Wiedenbeck, 1986) assigns vein formation to an extensional tectonic phase of rapid uplift and cooling of the Western Alps, some 4 to 8 Ma after the local peak of Meso-Alpine metamorphism (Dal Piaz, Hunziker, and Martinotti, 1972; Hunziker, 1974). The deposits are unaffected by any post-emplacement regional deformation or metamorphism.

The Brusson veins range from a few millimeters to 4 m in thickness, and up to hundreds of meters in vertical and horizontal extent. The largest (Fenilia, Orbeillaz, Gaebianche; fig. 1) were formed by multiple injections of hydrothermal fluid along normal faults, both during and following minor displacement. Thus early generations of extensively deformed quartz are overgrown and crosscut by successive generations of less deformed crystals. Also common are swarms of regularly spaced, joint-hosted veins (Bechaz, Mae; fig. 1) that contain relatively undeformed minerals. Open vugs lined with faceted quartz crystals up to 30 cm in length occur in both fault- and joint-hosted veins, indicating that minerals deposited in part within wide, fluid-filled channels.

Two paragenetic stages of vein mineralization are recognized according to petrographic criteria (Diamond, ms): (1) a main stage, dominated by quartz, with subordinate ferroan dolomite (or magnesite in veins enclosed by metaserpentinites) and minor muscovite, pyrite,
chalcopyrite, rutile, and gold; (2) a final stage, which locally replaces the main-stage assemblage, consisting of widespread but mostly small quantities of galena, tetrahedrite, gold, and calcite.

Each vein is rimmed by narrow zones of wallrock alteration. The veinward zones include the same minerals as the adjacent main-stage vein paragenesis, plus a few relic metamorphic minerals that have survived metasomatism: albite and ilmenite in metasites, metagranites and metasediments, graphite in some metasediments, and microcline and tourmaline in some metagranites. Metamorphic epidote, biotite, amphibole, titanite, and garnet in the wallrocks are completely replaced by the hydrothermal assemblage at the boundaries of the veinward alteration zones. No alteration is recognized in association with the final-stage vein assemblage.

Mine records (Reinhold, 1916) and petrography carried out for this study reveal that the spatial distribution of gold correlates with wallrock composition: gold occurs as inclusions within pyrite or as free blebs in all but the sections of veins enclosed by metacarbonate or metaserpentinite wallrocks (Fenilia, fig. 1). From the outset, this observation emphasizes the importance of fluid-wallrock interaction in governing gold solubility at Brusson. The negative correlation between gold and specific wallrocks is also a critical observation in evaluating the significance of boiling for ore formation, as discussed below. The process of fluid-wallrock interaction itself is addressed in detail elsewhere (Diamond, 1986, and in preparation).

**Fluid Inclusion Petrography**

*Sampling.*—This investigation deals principally with fluid inclusions found in the later generations of vein quartz, in which the effects of brittle deformation have been weak. Although many late quartz crystals are cut by sets of subparallel, annealed fractures, optical extinction of the crystal domains between fracture planes is sharp and uniform. Therefore, it is assumed that apart from cases of direct cross-cutting, the various episodes of fracturing have not altered the properties of pre-existing fluid inclusions. In contrast, fluid inclusions in the early generations of quartz are unreliable, as deformation may have altered their original density and composition.

Reconnaissance analyses show that ferroan dolomite contains inclusions identical to those in coexisting quartz, thus the data obtained from quartz-hosted inclusions are considered valid for the entire main-stage vein paragenesis. Inferences regarding the final-stage fluid are supported by reconnaissance analyses of inclusions in vein calcite.

The detailed fluid inclusion analyses reported here are restricted to samples from the Fenilia, Bechaz, and Orbeilaz mines (locations and wallrock lithologies are shown on fig. 1). However, the results are consistent with cursory analyses (Diamond, ms) of samples from the Bochey, Cheverin, Crête di Naie, Gaëbianche, and Mae localities (fig. 1).
Fluid inclusion compositional types.—At room temperature, all the examined inclusions contain a carbonic (CO$_2$-rich) liquid and an immiscible aqueous liquid. Many inclusions also contain a CO$_2$-rich vapor bubble. The fraction of fluid inclusion volume occupied by the carbonic phase follows a bimodal distribution, defining two bulk compositional types: “low-XCO$_2$,” consisting of 15 to 25 volume percent carbonic liquid (fig. 2), and “high-XCO$_2$,” consisting of 85 to 95 volume percent carbonic liquid (fig. 3). Low-XCO$_2$ inclusions are vastly more abundant than the high-XCO$_2$ type. Three-dimensional microscopy of uncut quartz crystals shows that spatially distinct assemblages of fluid inclusions generally comprise either exclusively low-XCO$_2$ inclusions or exclusively high-XCO$_2$ inclusions (figs. 4 and 5). Within assemblages of each compositional type the range in phase volume fractions is less than 10 volume percent.

Based on the fundamental assumptions that fluid inclusions in quartz behave as isoplethic, isochoric systems, and given that the carbonic and aqueous liquids within individual inclusions are miscible under high P-T conditions (Takenouchi and Kennedy, 1965: Gehrig,

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Fig. 2. Low-XCO$_2$ inclusion in quartz from the Speranza vein, Fenilia Mine (sample LD925). In addition to three fluid phases at +25°C, this inclusion contains accidental solid inclusions of muscovite and rutile. Photographed in plane-polarized, transmitted light. Scale bar represents 50 μm.
1980), the uniformity of phase volume ratios is strong evidence that two physically separate, compositionally distinct, homogeneous fluids were originally trapped in the respective inclusion assemblages: a fluid of low-XCO$_2$ bulk composition on the one hand and a high-XCO$_2$ fluid on the other.

Inclusions with unusual phase volume fractions do occur within otherwise uniform assemblages, but most cases appear to be the product of necking-down (Roedder, 1962), following exsolution of separate carbonic and aqueous phases under low P-T conditions. Such inclusions are ignored in this study. Very rarely, entire assemblages occur in which phase ratios vary widely between the low-XCO$_2$ and high-XCO$_2$ compositional types (fig. 6) or show a more bi-modal distribution of compositions (fig. 7). Assuming again isoplethic and isochoric conditions, the possibility exists that these “variable-XCO$_2$” assemblages genuinely represent an originally inhomogeneous hydrothermal fluid. The likelihood of this interpretation will be discussed below.

Three main-stage vein minerals are found occasionally within the low-XCO$_2$ fluid inclusions. Muscovite, dolomite, and rutile were recognized by their characteristic optical properties and crystal habits (fig. 2),
Fig. 4. Low-XCO₂ fluid inclusions in quartz crystal LD888B from the Fenilia vein. Early pseudosecondary inclusions are cross cut by an assemblage of late pseudosecondary inclusions. Note that within each assemblage the volumetric ratios of carbonic:aqueous liquids are constant. The similarity in compositions and densities (indicated by the microthermometric data) suggests the two generations are temporally contiguous. Inclusions are traced at +30°C from a microscope projection of a polished thin section.
Fig. 5. Assemblages of pseudosecondary low-XCO₂ and high-XCO₂ fluid inclusions in quartz crystal LD926 from the Bechaz Mine. The assemblages contrast in bulk composition and density, as indicated by the microthermometric data and by the volumetric ratios of aqueous:carbonic liquids. The respective uniformity of phase ratios shows that each assemblage formed from a locally homogenous vein fluid: a low-XCO₂ fluid above, and a high-XCO₂ fluid below. Inclusions are traced at +30°C from microscope projections of a polished thick section.
Fig. 6. Late-pseudosecondary assemblage of fluid inclusions in quartz crystal LD888 from the Fenlia Mine, showing variable volumetric ratios of carbonicaqueous liquids. The volume occupied by the carbonic phase ranges from approx 15 to 85 percent of individual inclusions (figs. 4 and 5). Such "variable-XCO₂" assemblages are extremely rare in the Brusson veins. Traced at +30°C from a microscope projection of a polished thick section.

and the identification of muscovite was confirmed by qualitative laser Raman spectroscopy and semi-quantitative SEM-EDS analysis. Application of criteria given by Roedder (1984b, p. 53-58) suggests that these solids are accidental inclusions rather than daughter minerals.

The low-XCO₂ fluid inclusions exhibit mostly irregular morphologies (fig. 4), but negative crystal forms are also common on healed fractures. High-XCO₂ inclusions are generally larger and more frequently in negative crystal shape (figs. 3 and 5). Inclusion dimensions range from submicroscopic to 300 x 300 x 700 µm, but no pattern in size distribution is obvious. Microthermometric analyses do not appear to vary as a function of inclusion size, and therefore it is presumed that during inclusion formation, the local composition and density of the vein fluid were not differentially influenced by any physicochemical effects dependent on surface area.
Fig. 7. Late-pseudosecondary assemblage of inclusions in quartz crystal LD928 from the Orbeillaz Mine. The volumetric ratios of carbonic-aqueous liquids in individual inclusions show an approximately bimodal distribution; inclusions of typically high-XCO₂ composition are intimately associated with low-XCO₂ inclusions. Relatively few inclusions show intermediate compositions and densities (see microthermometric data; compare fig. 6). Assemblages of this type are extremely rare. Traced at +30°C from a microscope projection of a polished thick section.
Generations of fluid inclusion assemblages.—Large quartz crystals occasionally contain planes of mica, dolomite, and quartz inclusions, which outline the euhedral ghosts of former crystal growth surfaces (fig. 8A). Sequences of such growth surfaces provide a temporal or “stratigraphic” framework (fig. 8B), to which the spatial distribution of fluid inclusion assemblages may be referred (fig. 8C). Thus, five broad generations of inclusions are distinguished (using the nomenclature and diagnostic criteria of Roedder, 1984b):

1. Clusters of early, primary, low-XCO₂ inclusions without a planar or other clear geometric distribution. They are abundant near the base of large quartz crystals and are compositionally indistinguishable from later primary inclusions.

2. Late primary low-XCO₂ inclusions in planar arrays along former growth surfaces of the host crystal and within primary solid inclusions and their interstices.

3. Pseudosecondary, low-XCO₂ inclusions in planar arrays along discordant, annealed fractures (fig. 4). Petrographic relationships shown in figure 9 prove these inclusions are indeed pseudosecondary and not secondary.

4. Planar arrays of low-XCO₂ inclusions along annealed fractures that intersect quartz crystal boundaries (fig. 4). Identical inclusions occur in final-stage calcite, although their relative age with respect to calcite is not discernible from petrographic criteria. These inclusions are designated late pseudosecondary, as their compositional similarity to earlier generations (fig. 4) suggests they are related through a continuous temporal sequence.

5. Planar arrays of high-XCO₂ inclusions on annealed fractures that intersect quartz crystal boundaries (fig. 5). These assemblages have not been found in final-stage calcite (perhaps because of autodecreeptation and leakage along cleavage planes), but three observations collectively indicate that they are broadly contemporaneous with the late pseudosecondary, low-XCO₂ generation: (1) both high-XCO₂ and late pseudosecondary, low-XCO₂ assemblages post-date the early pseudosecondary generation; (2) some high-XCO₂ assemblages are cross-cut by younger arrays of late-pseudosecondary, low-XCO₂ inclusions (fig. 10; the reverse cross-cutting relationship has not been observed); (3) the late pseudosecondary, low-XCO₂ inclusions are interpreted to be temporally contiguous with the early pseudosecondary generation. Based on these observations, the high-XCO₂ inclusions are also classified as late pseudosecondary.

The rare variable-XCO₂ assemblages (figs. 6 and 7) are assigned to the late-pseudosecondary generation as well, since they lie on healed fractures that intersect quartz crystal boundaries, and their compositions are transitional to the low-XCO₂ and high-XCO₂ assemblages.

Table 1 shows generalized temporal relationships between the fluid inclusion generations and the vein mineral parageneses. Although fluid inclusions and gold have not been found in physical contact, their
Fig. 8(A) Euhedral quartz crystal LD927 from the Bechaz mine, sectioned parallel to the crystallographic “c” axis (photographed in cross-polarized, transmitted light); (B) distribution of solid inclusions (quartz, dolomite, muscovite) that outline crystal growth surfaces; (C) distribution of fluid inclusions with respect to the growth surfaces traced from (B); fluid inclusion generations are identified by their spatial relationship to growth surfaces and healed fractures.
relative ages are deduced from the following observations. In the main-stage paragenesis: (1) gold is included in pyrite and in deformed quartz that pre-dates the studied fluid inclusions; (2) gold also occurs within quartz crystals on growth zones that are synchronous with the primary and early pseudosecondary inclusion generations (fig. 11). In the final-stage paragenesis: (3) gold blebs occupy the same fracture trace as late-pseudosecondary fluid inclusions in a sample from the Fenilia
Fig. 10. Intersecting arrays of late pseudosecondary, low-XCO\textsubscript{2} and high-XCO\textsubscript{2} fluid inclusions in sample LD907-X from the Bechaz Mine. The low-XCO\textsubscript{2} array is continuous, whereas the high-XCO\textsubscript{2} array is cross cut at the intersection point, demonstrating that at least some of the high-XCO\textsubscript{2} fluid inclusions pre-date late pseudosecondary, low-XCO\textsubscript{2} assemblages. Uncut, euhedral crystal photographed in plane-polarized, transmitted light. Scale bar represents 100 μm.

vein: (4) in the Fenilia and other veins, although notably not at Bechaz, free gold overgrows euhedral quartz crystals in open vugs; (5) Colomba (1907) reports gold within (presumably final-stage) calcite of the Fenilia vein. Thus in at least some veins, as shown on table 1, gold is coeval with all the studied fluid inclusion generations.

MICROTHERMOMETRY

Analytical method.—Microthermometry was carried out at ETH, Zurich, on approx 40 doubly-polished sections (30μm thick) and small uncut crystals of quartz. An early model, gas-cooled Chaixmeca heating/freezing stage was used for analysis (Poty, Leroy, and Jachimowicz, 1976), as modified by Mercolli (1979). The stage was calibrated using
Table 1

Generalized temporal correlation between fluid inclusions and vein minerals.

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Magnesite is an additional main-stage phase in veins hosted by metaserpentinites. Gold outlasts the main-stage paragenesis in the Fenilia, Orbeilaz, and other mines but not at Bechaz. Gold is absent in veins hosted by metacarbonate and metaserpentinite wallrocks.

standard chemical compounds and synthetic fluid inclusions, and the resulting temperature corrections applied to microthermometric measurements range progressively from $+1^\circ\text{C}$ at $-60^\circ\text{C}$ to $-3^\circ\text{C}$ at $+250^\circ\text{C}$. Owing to the steepness of temperature gradients across the heating stage, measurements were made only on inclusions centered on the stage by hand. Taking account of reproducibility and read-out precision, the recorded temperatures of phase transitions below $+30^\circ\text{C}$ have an estimated uncertainty of $\pm 0.2^\circ\text{C}$, whereas measurements around $250^\circ\text{C}$ are accurate to $\pm 1.5^\circ\text{C}$.

A standard analytical procedure was followed: each sample was preheated to $+50^\circ\text{C}$ and then rapidly cooled to $-155^\circ\text{C}$, during which
Fig. 11(A) Cross section of an euhedral quartz crystal from the Fenilia vein, showing main-stage gold outlining a former crystal growth zone (Au-1) and final-stage gold overlying the outer quartz surface (Au-2). Sketch made from sample B1293, Natural History Museum of Bern. (B) Overgrowths of gold on main-stage pyrite from the Fenilia vein. Sketch made from sample 325, Natural History Museum of Bern.

vapor, CO₂-clathrate (gas-hydrate), ice, salt-hydrates, and solid CO₂ formed in place of the carbonic and aqueous liquids. Upon progressive heating from −155°C, up to six equilibrium phase transitions were observed in each inclusion. Heating was stopped upon complete homogenization of the fluid at about +250°C. Most measurements were made at a heating rate of approx +0.3°C/min, as in calibration. Clathrate dissociation was determined with extreme care by temperature cycling (Roedder, 1963) at lower heating rates (0.1-0.2°C/min). The temperature recorded for each transition corresponds to the final disappearance of the respective phase.

Results of microthermometry.—Solid CO₂ melts within individual inclusions over a temperature interval of approx 0.1°C. The measurements of final melting (Tm_mar; fig 12A) form two well-defined peaks at −56.8 and −57.5°C, corresponding respectively to low-XCO₂ and high-XCO₂ inclusion types. Data from the rare variable-XCO₂ inclusions are intermediate (fig. 7). The slight depression of the melting points relative to the triple point of pure CO₂ (−56.6°C) indicates low concentrations of additional volatile species in the low-XCO₂ inclusions and slightly higher concentrations in the high-XCO₂ type. These species have been identified by Raman spectroscopy as nitrogen and methane. Note that, within each of the two main compositional types of fluid inclusions, the melting behavior varies little with respect to locality (fig. 12B-D) or generation (fig. 12E-H).

The presence of CO₂-clathrate obscures the initial melting of salt-hydrates and ice. Consequently, the temperatures recorded as the apparent eutectic of the salt-H₂O subsystem (Te; fig. 13) refer to the lowest temperatures at which the liquidus assemblage, ice + CO₂-clathrate + vapor + carbonic liquid + aqueous liquid, could be recognized. The microthermometric results given on figure 13 therefore provide only a maximum value for the true eutectic temperature. The
Fig. 12. Frequency-temperature histograms of fluid inclusion microthermometric data. (A) complete data set; (B-D) data grouped according to vein locations; (E–H) data grouped according to relative age, all vein localities combined.
histogram peak between $-11^\circ$ and $-16^\circ$ C suggests that NaCl and/or KCl are the dominant salts in the aqueous phase (NaCl eutectic at $-20.8^\circ$ C, NaCl + KCl eutectic at $-22.9^\circ$ C; Linke, 1965) and rules out appreciable presence of CaCl$_2$ and MgCl$_2$.

Ice melts in the presence of CO$_2$-clathrate + vapor + carbonic liquid + aqueous liquid. Microthermometric measurements of $T_{m,\text{ICE}}$ in low-XCO$_2$ inclusions peak at $-5.4^\circ$ C (fig. 14A), but owing to observational uncertainty caused by the presence of clathrate, not all the plotted data actually reflect the upper stability limit of ice. As the difficulty in observation varies between inclusions, the peak is presumably displaced a few tenths of a degree below the true mean and slightly flattened. There are no significant differences between inclusions grouped according to vein locality (fig. 14B-D) or generation (fig. 14E-H). Only five high-XCO$_2$ inclusions yielded $T_{m,\text{ICE}}$ determinations, and these data cluster at $-4.5^\circ$ C.

The dissociation temperatures of CO$_2$-clathrate ($T_{m,\text{CLA}}$; fig. 15A) define two distinct peaks: the mean value of low-XCO$_2$ inclusions is $+8.4^\circ$ C, whereas the mean of high-XCO$_2$ inclusions is $+9.5^\circ$ C. Clathrate dissociation in most inclusions occurs in equilibrium with
ICE MELTING TEMPERATURE (Tm\text{ICE})

Fig. 14. Frequency-temperature histograms of fluid inclusion microthermometric data. (A) complete data set; (B–D) data grouped according to vein location; (E–H) data grouped according to relative age, all vein localities combined.

vapor, carbonic liquid, and aqueous liquid. In several of the denser high-XCO\textsubscript{2} inclusions, however, the vapor phase condenses prior to clathrate breakdown, leaving only the carbonic- and aqueous liquids present at the phase transition. The microthermometric characteristics of the two inclusion types are again virtually constant, regardless of locality (fig. 15B–D) or generation (fig. 15E–H). As in the Tm\text{CAR} and Tm\text{ICE} determinations, the Tm\text{CLA} measurements of variable-XCO\textsubscript{2}...
CLATHRATE DISSOCIATION TEMPERATURE \( (T_{m_{CLA}}) \)

(A) ALL DATA
N = 186
HIGH - XCO₂
N = 21
\( \bar{x} = 9.5 \) °C
\( \sigma = 0.26 \)
LOW - XCO₂
N = 165
\( \bar{x} = 8.4 \) °C
\( \sigma = 0.3 \)

(B) FENILIA VEIN

(C) BECHAZ VEIN

(D) ORBEILLAZ VEIN

(E) PRIMARY

(F) LATE PRIMARY

(G) EARLY PSEUDOSECONDARY

(H) LATE PSEUDOSECONDARY

Fig. 15. Frequency-temperature histograms of fluid inclusion microthermometric data. (A) complete data set; (B–D) data grouped according to vein location; (E–H) data grouped according to relative age, all vein localities combined.
inclusions (fig. 7) are transitional to the low-XCO₂ and high-XCO₂ data.

The carbonic phase of low-XCO₂ inclusions homogenizes in equilibrium with aqueous liquid via all three possible transitions: (1) bubble point: vapor → carbonic liquid; (2) critical point: carbonic liquid + vapor → supercritical carbonic fluid; (3) dew point: carbonic liquid → vapor. Homogenization temperatures range between +25.2° and +29.5°C (ThCAR; fig. 16A). As critical temperatures coincide with the rare dew points and with the highest bubble points, and as the associated TmCAR, Te, TmICE, and TmCLA data indicate only slight compositional variation within the low-XCO₂ inclusions, the average of the 11 critical point determinations (+29.1°C) is presumed valid for the entire low-XCO₂ type. In high-XCO₂ inclusions, the carbonic phase always homogenizes via a bubble point between +5.0 and +20.5°C (ThCAR; fig. 16A). Note that clathrate is present in the inclusions with ThCAR below +9°C. High-XCO₂ inclusions belonging to the same assemblage homogenize within 3° of each other (fig. 5), but variable-XCO₂ assemblages span 25° (fig. 7).

Total homogenization of low-XCO₂ inclusions occurs via shrinkage of the carbonic phase in a bubble-point transition: aqueous liquid + supercritical carbonic fluid → low-XCO₂ “liquid”. Conversely, the carbonic phase of high-XCO₂ inclusions expands to homogenize on a dew point: aqueous liquid + supercritical carbonic fluid → high-XCO₂ “vapor”. The terms “liquid” and “vapor” are set in quotation marks to denote the relative bulk densities of the homogenized fluid inclusions. All high-XCO₂ inclusions decrepitate before completely homogenizing, at temperatures below +200°C. Large low-XCO₂ inclusions also occasionally decrepitate, and in general, low-XCO₂ and high-XCO₂ inclusions of similar sizes and shapes decrepitate at approximately the same temperature, provided they lie at the same depth within a sample. Nothing resembling critical behavior was observed upon total homogenization of the low-XCO₂ inclusions.

The temperatures of total homogenization (ThTOT) of low-XCO₂ inclusions range from +226° to +272°C (fig. 17A) and show no well defined mode. As in all the other phase transitions, no significant differences in ThTOT are found between vein localities (fig. 17B-D). However, a clear trend emerges according to inclusion generation: progressively younger inclusions homogenize at progressively lower temperatures (fig. 17E-G). In keeping with this trend, low-XCO₂ inclusions in final-stage calcite homogenize at approx +220°C.

Inasmuch as the temperatures of phase transitions reflect inclusion composition and density, the systematic variation and narrow ranges of the microthermometric data are consistent with the initial assumption that the fluid inclusions have not leaked or changed volume. Moreover, the measurements of TmCAR, Te, TmICE, TmCLA, and ThCAR indicate...
CARBONIC PHASE HOMOGENIZATION TEMPERATURE ($\text{Th}_{\text{CAR}}$)

Fig. 16. Frequency-temperature histograms of fluid inclusion microthermometric data. (A) Complete data set; (B–D) data grouped according to vein location; (E–H) data grouped according to relative age, all vein localities combined.

that there is little compositional variation within each of the low-$\text{XCO}_2$ and high-$\text{XCO}_2$ inclusion types, irrespective of vein location, wallrock lithology, or fluid generation. Superimposed on this compositional uniformity, the $\text{Th}_{\text{TOT}}$ trend in low-$\text{XCO}_2$ inclusions throughout the Brusson vein swarm reveals a gradual evolution of fluid density toward
Fig. 17. Frequency-temperature histograms of microthermometric data of low-XCO₂ fluid inclusions. (A) complete data set; (B–D) data grouped according to vein location; (E–H) data grouped according to relative age, all vein localities combined.

higher values with time. Observe on the frequency histograms (figs. 12–17) that the few measurements of late-pseudosecondary and primary fluid inclusions that coexist with gold are typical of the low-XCO₂ data set.

RAMAN MICROPROBE ANALYSIS

Eleven fluid inclusions from the three main vein localities were quantitatively analyzed by Raman spectroscopy at the Centre de
Recherches sur la Géologie de l'Uranium (CREGU) in Nancy, France. Each of these inclusions is statistically representative of its respective compositional type and generation, as demonstrated by the histograms of microthermometric data (figs. 12–17).

Analyses were made on a monochannel, Jobin-Yvon M.O.L.E. laser microprobe (Delhaye and Dhamelincourt, 1975) using the instrumental conditions described by Ramboz, Schnapper, and Dubessy (1985) to attain a spectral resolution of 3 cm⁻¹. The homogenized carbonic phase of each inclusion was scanned at +31°C for the characteristic Raman peaks of CO₂, CO, N₂, CH₄, and H₂S (Herzberg, 1967). CO₂, N₂, and CH₄ were detected, and their peak areas were integrated by planimeter and corrected for differential detector sensitivity using the following laboratory-specific instrument factors: 0.8786 for CO₂, 0.6286 for CH₄, and 0.7286 for N₂. Mole fractions were calculated from the Placzek formulae (Placzek 1934; Rosasco, Roedder, and Simmons, 1975; Dhamelincourt and others, 1979) using the following 1 bar effective relative cross sections of Raman scattering for 514.5 nm exciting radiation: \( \sigma_{\text{CO}_2} = 1.21 \), \( \sigma_{\text{CH}_4} = 9.0 \), \( \sigma_{\text{N}_2} = 1.0 \) (Schröter and Klöckner, 1979). The combined uncertainties in spectral reproducibility and planimeter measurement lead to a maximum relative uncertainty in calculated mol fractions of around 10 percent.

Compositions calculated from the Raman spectra are shown in table 2. No significant H₂S peaks were found, and, therefore, based on the signal:noise ratio of measured N₂ spectra, the mol fraction of any H₂S in the carbonic phase is inferred to be less than 0.002. Consistent with microthermometric trends, the Raman analyses show that the carbonic phases of the fluid inclusions are mixtures dominated by CO₂, with small amounts of N₂, and very small amounts of CH₄. The high-XCO₂ type is enriched in N₂ relative to the low-XCO₂ inclusions, and this accounts for the systematic differences in \( T_{m_{\text{CAR}}} \) data (fig. 12). Although the analyzed inclusions are representative of a variety of generations, compositional types, and vein localities, their range in composition is very narrow.

The accuracy of the analyses cannot be assessed directly because the cross sections of Raman scattering used in the calculations are not necessarily valid for the relatively high internal pressures of the fluid inclusions (Dubessy, Burnneau, and Dhamelincourt, 1987; Wopenka and Pasteris, 1987). However, as the critical point of the carbonic phase in low-XCO₂ inclusions is known from microthermometry (fig. 16), the accuracy may be checked independently by comparing the compositions calculated from the Raman spectra with the experimentally determined critical curve of the CO₂-N₂ system (Arai, Kaminishi, and Saito, 1971). Figure 18 shows close agreement between the two independent estimates of composition, and hence at least for the present case where the concentrations of N₂ are small, the variations of scattering cross sections with pressure are insignificant.
<table>
<thead>
<tr>
<th>VEIN/LEVEL</th>
<th>INCLUSION</th>
<th>GENERATION</th>
<th>TYPE</th>
<th>XNa</th>
<th>XCa</th>
<th>XCO2</th>
<th>XCO2</th>
<th>XCO2</th>
<th>XCO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>FENILLA</td>
<td>LD888-B7</td>
<td>Early Pseudo.</td>
<td>Low-XCO2</td>
<td>0.9686</td>
<td>0.0307</td>
<td>0.0007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LD888-B21</td>
<td>Late Pseudo.</td>
<td>Low-XCO2</td>
<td>0.9584</td>
<td>0.0407</td>
<td>0.0007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LD888-O15</td>
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<td>Low-XCO2</td>
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<td>0.0407</td>
<td>0.0002</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>LD888-O12</td>
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<td>High-XCO2</td>
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<td>0.0502</td>
<td>0.0013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BECHANZ</td>
<td>LD926-G2</td>
<td>Late Pseudo.</td>
<td>Low-XCO2</td>
<td>0.9273</td>
<td>0.0700</td>
<td>0.0027</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LD927-B1</td>
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<td>High-XCO2</td>
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<td>0.0281</td>
<td>0.0002</td>
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<td></td>
<td></td>
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<td></td>
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<td>Late Primary</td>
<td>Low-XCO2</td>
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<td>0.0458</td>
<td>0.0006</td>
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</tr>
<tr>
<td>ORBEITAZ</td>
<td>LD928-R1</td>
<td>Primary</td>
<td>Low-XCO2</td>
<td>0.9658</td>
<td>0.0342</td>
<td>&lt;0.0002</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>LD928-RG1</td>
<td>Late Pseudo.</td>
<td>Variable-XCO2</td>
<td>0.9578</td>
<td>0.0422</td>
<td>&lt;0.0002</td>
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<td></td>
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<tr>
<td></td>
<td>LD928-RG3</td>
<td>Late Pseudo.</td>
<td>Variable-XCO2</td>
<td>0.9455</td>
<td>0.0539</td>
<td>&lt;0.0002</td>
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<tr>
<td></td>
<td>LD928-RG3</td>
<td>Late Pseudo.</td>
<td>Variable-XCO2</td>
<td>0.9332</td>
<td>0.0659</td>
<td>0.0009</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$X_i = \text{mol fraction of species in supercritical carbonic phase at } 310^\circ \text{C. See figs. 4, 5, and 7 for the location of some of the inclusions.}$
As mineral stabilities suggest that the Brusson fluid inclusions formed below 300°C (see following discussion), that is, at or below the closure temperature of homogeneous equilibrium in the C–O–H system (Giggenbach, 1982; Diamond, ms), the Raman analyses are believed to be valid descriptions of the hydrothermal fluid at the time of vein formation.

Fig. 18. T–X plot comparing the experimentally determined critical curve of the CO₂–N₂ binary system (Arai, Kaminishi, and Saito, 1971) with the composition and homogenization temperatures of the carbonic phase of fluid inclusions analyzed by Raman spectroscopy. The low-XCO₂ inclusions homogenize via critical transitions or near-critical, bubble point transitions, and hence they plot on, or very close to, the experimental curve. The denser carbonic phases of the high-XCO₂ inclusions are spread through lower temperatures. The close match of the low-XCO₂ inclusions with the experimental curve confirms that the CO₂–N₂ binary may be used to model accurately the low-temperature P–V–T–X properties of the natural carbonic phases.
Bulk fluid inclusion solutions were extracted by crushing and leaching vein quartz and quantitatively analyzed for $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, and $SO_4^{2-}$ at the Centre de Recherches Pétrographiques et Géochimiques in Nancy, France, using the methods and laboratories described by Poty, Stalder, and Weisbrod (1974). Samples with the fewest solid inclusions and the most fluid inclusions were chosen for analysis from among the samples already investigated by microthermometry.

Approx 20 g of each sample were broken into chips, cleaned successively in HNO$_3$, pure water, and ion exchange resins, then sealed in stainless steel tubes, and crushed. The quartz powder was leached at 80°C with 40 ml pure water, and the resulting bulk solution was analyzed along with blanks for $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$ by atomic absorption (total uncertainty = $\pm 0.01$ ppm) and for $Cl^-$ and $SO_4^{2-}$ by colorimetry (total uncertainty = $\pm 0.05$ and $\pm 0.1$ ppm respectively). The procedure was replicated three or four times per sample, and the averaged results are given with the analytical uncertainties in table 3. Since the dilution factor of the leachates is unknown, the analyses have been recast as ratios of ion concentrations, normalized with respect to Na (table 3A).

Although solid inclusions within the quartz crystals provide a useful temporal reference for petrography, they are also potential contaminants of the bulk leachates. On the assumption that the degree of contamination varies randomly between replicates, the precision of analyses may be used to check on reliability. Replicates of sample LD875, for example, show poor reproducibility and high values of Ca/Na, Mg/Na, and SO$_4$/Na, suggesting contamination by dolomite and pyrite. Such suspect analyses are indicated by asterisks in table 3A. Note that the relative uncertainty in the ion ratios increases as concentrations approach the analytical detection limits, irrespective of contamination, for example, from 9 percent for Cl/Na to 200 percent for Mg/Na (table 3B).

The speciation of ions in the leachates does not necessarily correspond to that of the unopened fluid inclusions. Sulfur, for example, regardless of its initial state in the inclusions, is oxidized to sulfate in the leachate prior to analysis. Although information on initial speciation is thus lost, the elemental ratios (S/Na) are considered representative of the average vein-forming hydrothermal solutions under the P-T conditions of inclusion entrapment. The solubility of the accidental solid inclusions, muscovite, dolomite, and pyrite, is very low. Thus their post-entrapment precipitation or dissolution within fluid inclusions is unlikely to have affected fluid compositions to an extent exceeding analytical uncertainty. Moreover, as the microthermometric and Raman spectroscopic data show that fluid compositions vary only slightly between generations of low-XCO$_2$ inclusions, and as the high-XCO$_2$
### Table 3
A. Leachate analyses of bulk fluid inclusion samples

<table>
<thead>
<tr>
<th>SAMPLE VEIN LEVEL</th>
<th>LD655E</th>
<th>LD655L</th>
<th>LD875</th>
<th>LD888A</th>
<th>LD907</th>
<th>LD659 FENILIA</th>
<th>FENILIA</th>
<th>FENILIA</th>
<th>FENILIA</th>
<th>BECHAZ</th>
<th>ORBEIL.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1670m</td>
<td>1670m</td>
<td>1648m</td>
<td>1690m</td>
<td>995m</td>
<td>1380m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**ION CONCENTRATIONS (ppm)**

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>Na</th>
<th>Ca</th>
<th>Mg</th>
<th>SO₄</th>
<th>Cl</th>
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<tr>
<td></td>
<td>0.09</td>
<td>0.08</td>
<td>0.33</td>
<td>0.16</td>
<td>0.16</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>1.22</td>
<td>1.85</td>
<td>3.29</td>
<td>2.85</td>
<td>1.71</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>0.11</td>
<td>14.3</td>
<td>0.28</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>0.004</td>
<td>0.002</td>
<td>0.359</td>
<td>0.031</td>
<td>0.003</td>
<td>0.007</td>
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<tr>
<td></td>
<td>0.10</td>
<td>0.13</td>
<td>5.31</td>
<td>0.14</td>
<td>0.12</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>3.67</td>
<td>3.56</td>
<td>4.30</td>
<td>3.96</td>
<td>2.80</td>
<td>4.85</td>
</tr>
</tbody>
</table>

**ION RATIOS**

<table>
<thead>
<tr>
<th></th>
<th>K/Na</th>
<th>Ca/Na</th>
<th>Mg/Na</th>
<th>SO₄/Na</th>
<th>Cl/Na</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.044</td>
<td>0.027</td>
<td>0.058</td>
<td>0.035</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>0.027</td>
<td>0.032</td>
<td>2.494*</td>
<td>0.043*</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>0.003</td>
<td>0.001</td>
<td>0.103*</td>
<td>0.012*</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>0.021</td>
<td>0.016</td>
<td>0.379*</td>
<td>0.018</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>2.047*</td>
<td>1.285</td>
<td>0.848</td>
<td>0.912</td>
<td>1.068</td>
</tr>
<tr>
<td>±</td>
<td>-0.98*</td>
<td>-0.19</td>
<td>+6.96*</td>
<td>+0.22</td>
<td>-0.001</td>
</tr>
</tbody>
</table>

Results for each sample are averages of 3 or 4 replicates. Orbeil. = Orbeillaz Vein. Sample LD665 includes an early quartz fraction (LD655E) and a late fraction (LD665L). * = Contamination suspected on basis of poor reproducibility of replicates. ± = charge balance: Σ (zCᵢ/gfw), where for the ith ionic species, z is the charge, Cᵢ is the concentration (ppm by wt), and gfw is the gram formula weight.

### B. Uncertainties of bulk leachate analyses

<table>
<thead>
<tr>
<th>UNCERTAINTIES</th>
<th>K/Na</th>
<th>Ca/Na</th>
<th>Mg/Na</th>
<th>SO₄/Na</th>
<th>Cl/Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average deviation</td>
<td>0.004</td>
<td>0.002</td>
<td>0.004</td>
<td>0.008</td>
<td>0.042</td>
</tr>
<tr>
<td>Precision (2σ)</td>
<td>0.001</td>
<td>0.001</td>
<td>0.0002</td>
<td>0.001</td>
<td>0.056</td>
</tr>
<tr>
<td>Total uncertainty</td>
<td>0.005</td>
<td>0.003</td>
<td>0.004</td>
<td>0.009</td>
<td>0.098</td>
</tr>
<tr>
<td>Relative uncert.</td>
<td>11%</td>
<td>18%</td>
<td>200%</td>
<td>50%</td>
<td>9%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INDIVIDUAL SAMPLES</th>
<th>ALL UNCONTAMINATED SAMPLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>0.042</td>
</tr>
<tr>
<td>Uncertainty (2σ)</td>
<td>0.03</td>
</tr>
<tr>
<td>Relative deviation</td>
<td>71%</td>
</tr>
</tbody>
</table>
inclusions are less saline and vastly less abundant than the low-XCO₂ type, the average composition obtained from bulk leachate analysis should also approximate closely the composition of individual low-XCO₂ fluid inclusions.

In all uncontaminated leachates the relative molar concentrations of ions follow the order: \( \text{Na} \approx \text{Cl} \gg \text{K} > \text{Ca} \approx \text{S} > \text{Mg} \), where \( \text{Na} \) is three orders of magnitude more concentrated than \( \text{Mg} \). This result is consistent with the high apparent eutectic temperature of the aqueous phase of the inclusions. The differences between samples in \( \text{K}/\text{Na}, \text{Ca}/\text{Na} \), and \( \text{Cl}/\text{Na} \) are significantly larger than the relative uncertainty of individual analyses, presumably because of variations in wallrock composition. Nevertheless, the respective ranges of all five ratios listed in table 3 are less than an order of magnitude. Thus both the relative order and magnitude of the ion ratios attest to uniform fluid compositions in the Brusson area.

**Quantitative Estimation of Fluid Composition and Density**

The analytical results presented above show that the fluid inclusions contain at least the following 10 components: \( \text{H₂O}, \text{CO₂}, \text{CH₄}, \text{N₂}, \text{S}, \text{Cl}, \text{K}, \text{Na}, \text{Ca}, \text{Mg} \). A computational algorithm has been developed to estimate quantitatively, in terms of these components, the composition and bulk molar volume (and thus density) of each fluid inclusion generation (Diamond, ms). The algorithm integrates phase equilibrium data on model experimental systems with the following ten variables measured by microthermometry, Raman spectroscopy, and leachate analysis: \( T_{\text{m}_{\text{CLA}}}, T_{\text{CAR}}, T_{\text{TOT}}, X_{\text{N₂}}, X_{\text{CH₄}} \) in the carbonic phase; \( \text{K}/\text{Na}, \text{Mg}/\text{Na}, \text{Ca}/\text{Na}, \text{Cl}/\text{Na}, \) and \( \text{S}/\text{Na} \) in the aqueous phase. Bulk salinity is calculated using a statistical mechanics model of clathrate stability in the system \( \text{CO₂}–\text{N₂}–\text{CH₄}–\text{H₂O}–\text{NaCl} \) (Ng and Robinson, 1976, 1977) and resolved into concentrations of \( \text{NaCl}, \text{KCl}, \text{CaCl₂}, \) and \( \text{MgCl₂} \) after the method of Weisbrod and Poty (1975).

As it has been demonstrated that the fluid inclusions are overwhelmingly dominated by \( \text{CO₂}, \text{H₂O}, \) and \( \text{NaCl} \), the volume-corrected \( P–V–T–X \) experimental data of Gehrig (1980) on parts of the \( \text{CO₂}–\text{H₂O}–\text{NaCl} \) system are assumed to represent realistically the fluid inclusion properties at high pressures and temperatures. Thus \( \text{N₂} \) is treated as equivalent to \( \text{CO₂} \), and all electrolytes are treated as equivalent to \( \text{NaCl} \). Based on this model, the bulk compositions and molar volumes of the inclusions have been calculated from equations that relate \( T_{\text{TOT}} \) to the compositions and molar volumes of the carbonic and aqueous phases at \( T_{\text{CAR}} \).

The compositions of low-XCO₂ inclusions calculated in this way are probably accurate to within 1 percent relative. For high-XCO₂ inclusions, however, the optically-estimated volume fraction of the carbonic phase must be substituted for \( T_{\text{TOT}} \) in the algorithm, and therefore the
bulk V-X parameters of these inclusions are subject to large errors (Roedder, 1979). Consequently, the compositions of high-XCO₂ inclusions are accurate to only ±10 percent relative and the bulk molar volumes to approx ±15 percent.

Table 4 presents the calculated bulk compositions and molar volumes of selected fluid inclusions typical of the various generations. Input data required to calculate these parameters are given in the appendix. The salinity of the aqueous phase of low-XCO₂ inclusions ranges from 4.5 to 6 equivalent wt percent NaCl and total chloride in the bulk inclusions amounts to 1.2 to 1.9 mol percent (0.75–1.15 molal). CO₂ is 3 to 4 times more concentrated than the salts, ranging from 4.6 to 6.4 mol percent (2.8–4 molal). Total Cl in the high-XCO₂ inclusions is less than 0.5 mol percent, and CO₂ makes up approx 65 to 75 mol percent of the fluid. Based on leachate analyses, total sulphur in the low-XCO₂ inclusions is around 0.02 mol percent (0.015 molal), a value that coincides exactly with the maximum sulfur content predicted from the H₂S detection limit of the Raman microprobe. This result again emphasizes the consistency found in this study between inclusion analyses obtained by independent techniques.

**EVIDENCE FOR FLUID IMMISCIBILITY**

In view of the extensive liquid + vapor field in CO₂–H₂O–NaCl fluids (Takenouchi and Kennedy, 1965; Gehrig, 1980), it is clearly important to test the inclusion assemblages identified in this study for any immiscibility relationships that could have existed during vein formation.

The rare occurrences of variable-XCO₂ assemblages (figs. 6 and 7) prove that the hydrothermal fluid that filled cross-cutting fractures reached a state of immiscibility at some time in its history (Roedder and Bodnar, 1980: Ramboz, Pichavant, and Weisbrod, 1982). However, the significance of this fact for ore deposition hinges on whether the state was attained (1) in the bulk vein fluid during inclusion entrapment and mineral precipitation, or (2) in fluid sealed within fractures undergoing necking-down, possibly well after mineral precipitation had ceased. As both processes may produce identical P–V–T–X and textural characteristics in pseudosecondary inclusions, it is impossible to distinguish, alone from the variable-XCO₂ assemblages, exactly when phase exsolution took place.

In contrast to the variable-XCO₂ assemblages, unequivocal evidence of fluid immiscibility during vein formation may be found in spatially separate, contemporaneous assemblages of inclusions that exhibit uniform liquid/vapor ratios, that is, uniformly low-XCO₂ on the one hand and uniformly high-XCO₂ on the other (fig. 5). In such cases, the confusion with products of necking-down is avoided, because it may be confidently assumed that the respective inclusion assemblages
<table>
<thead>
<tr>
<th>TYPE</th>
<th>LOW-XCO₂ FLUID INCLUSIONS</th>
<th>HIGH-XCO₂ FLUID INCLUSIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>VEIN SAMPLE INCLUSION ASSEMBLAGE GENERATION</td>
<td>ORBEILLAZ BECHAZ FENILIA BECHAZ FENILIA FENILIA ORBEILLAZ</td>
<td>FENILIA BECHAZ ORBEILLAZ ORBEILLAZ</td>
</tr>
<tr>
<td></td>
<td>LD928 LD927 LD888 LD927 LD888 LD888 LD928</td>
<td>LD888 LD926 LD928 LD928</td>
</tr>
<tr>
<td></td>
<td>R1 R2 B7 B1 O15 B21 RG8</td>
<td>012 G2 RG1 RG3</td>
</tr>
<tr>
<td></td>
<td>Uniform Uniform Uniform Uniform Uniform Uniform Variable</td>
<td>Uniform Uniform Variable Variable</td>
</tr>
<tr>
<td></td>
<td>Primary Late- Primary Early- Pseudo. Early- Pseudo. Late- Pseudo. Late- Pseudo. Late- Pseudo. Late- Pseudo.</td>
<td>Late- Pseudo. Pseudo. Pseudo. Pseudo. Pseudo.</td>
</tr>
<tr>
<td></td>
<td>Mol% H₂O 90.4 90.7 91.8 91.7 92.2 92.4 92.0</td>
<td>24.2 23.4 22.8 22.3</td>
</tr>
<tr>
<td></td>
<td>CO₂ 6.4 6.1 5.3 5.4 4.6 4.9 5.1</td>
<td>71.5 70.8 72.7 72.2</td>
</tr>
<tr>
<td></td>
<td>N₂ 0.16 0.20 0.11 0.11 0.12 0.13 0.14</td>
<td>3.8 5.3 4.1 5.1</td>
</tr>
<tr>
<td></td>
<td>CH₄ &lt;0.002 0.002 0.003 &lt;0.002 &lt;0.002 0.003 &lt;0.002</td>
<td>0.1 0.2 0.05 0.07</td>
</tr>
<tr>
<td></td>
<td>K 0.03 0.07 0.05 0.07 0.06 0.04 0.03</td>
<td>- - - -</td>
</tr>
<tr>
<td></td>
<td>Na 1.28 1.41 1.41 1.28 1.58 1.27 1.11</td>
<td>0.2 0.15 0.15 0.14</td>
</tr>
<tr>
<td></td>
<td>Ca 0.01 0.02 0.04 0.02 0.05 0.04 0.01</td>
<td>- - - -</td>
</tr>
<tr>
<td></td>
<td>Mg 0.003 0.002 0.003 0.002 0.003 0.003 0.003</td>
<td>- - - -</td>
</tr>
<tr>
<td></td>
<td>Cl 1.17 1.53 1.29 1.39 1.44 1.16 1.49</td>
<td>0.2 0.15 0.15 0.14</td>
</tr>
<tr>
<td></td>
<td>S 0.03 0.02 0.03 0.02 0.03 0.02 0.02</td>
<td>- - - -</td>
</tr>
<tr>
<td>Wt% NaClₑq</td>
<td>4.5 4.5 5.0 4.5 5.5 4.5 4.0</td>
<td>2.5 2.0 2.0 2.0</td>
</tr>
<tr>
<td>Density</td>
<td>0.90 0.90 0.93 0.92 0.95 0.93 0.92</td>
<td>0.75 0.83 0.83 0.86</td>
</tr>
<tr>
<td>V_TOT (cm³)</td>
<td>22.4 22.2 21.3 21.6 20.6 21.0 21.5</td>
<td>49.5 42.3 45.2 43.6</td>
</tr>
</tbody>
</table>

Most of the inclusions belong to assemblages in which relative volumetric ratios of phases are uniform. Also listed are three inclusions from a late-pseudosecondary, variable-XCO₂ assemblage (inclusion LD928-RG8 represents the low-XCO₂ extreme composition whereas LD928-RG1 and LD928-RG3 represent the high-XCO₂ extreme: fig. 7). Wt% NaClₑq = total salinity of the aqueous phase (exclusive of CO₂) expressed as equivalent wt percent NaCl. Density in g/cm³. V_TOT = total molar volume of inclusion.
formed via entrapment of chemically dissimilar, locally homogeneous fluids.

The principles of phase equilibrium provide criteria to judge whether two given fluids, under fixed P-T conditions, constitute stable immiscible phases. Thus, four criteria derived by Ramboz, Pichavant, and Weisbrod (1982) for isochoric-isoplethic systems may be used to test the possibility that the late-pseudosecondary assemblages of low-XCO$_2$ and high-XCO$_2$ inclusions represent, respectively, coexisting “liquid” and “vapor” (the quotation marks again refer to the relative densities of the homogenized inclusions):

Criterion (1): The two inclusion types should be closely related in time and space: both high-XCO$_2$ and low-XCO$_2$ assemblages within individual quartz crystals are clearly late-pseudosecondary, but there is no hard evidence for the length of time separating their entrapment.

Criterion (2): The contrasting densities of the two inclusion types should lead to opposite modes of total homogenization: one via the bubble-surface, the other via the dew-surface transition. It has been noted above that all low-XCO$_2$ inclusions homogenize via a bubble-surface transition, and all high-XCO$_2$ inclusions tend toward a dew-surface transition upon heating.

Criterion (3): The bulk molar volumes of the liquid of vapor inclusions must be compatible with equilibrium coexistence at a unique value of Th$_{TOT}$. As a consequence, the inclusions should also have the same internal pressures of total homogenization (Ph$_{TOT}$) or should decrepitate at broadly similar temperatures if they are similar in size and shape. Ph$_{TOT}$ has been predicted from the experimentally determined positions of solvi in the model subsystem, CO$_2$–H$_2$O–NaCl (Gehrig, 1980), using the calculated inclusion compositions (table 4) and Th$_{TOT}$ data (fig. 17H) for the low-XCO$_2$ fluid inclusions. For high-XCO$_2$ inclusions the bulk molar volumes and compositions (table 4) are used to predict Th$_{TOT}$, as no direct measurements could be made. With the additional constraint that Th$_{TOT}$ lies above the highest decrepitation temperature, these calculations yield a possible Th$_{TOT}$ range of 200$^\circ$ to 270$^\circ$C. This range in turn permits possible Ph$_{TOT}$ values to be obtained from the solvi data.

Figure 19 superimposes Th$_{TOT}$ and Ph$_{TOT}$ of late pseudosecondary low-XCO$_2$ and high-XCO$_2$ inclusions on a P-T projection. Because of uncertainties in estimating composition and volume, the possible homogenization conditions of each inclusion type describe a volume within the P–T–X space of the model ternary fluid, and this volume projects onto an area of the P-T diagram. The predicted bubble points of the low-XCO$_2$ inclusions describe a relatively small segment on figure 19, whereas the less well defined dew points of the high-XCO$_2$ inclusions define a much larger area. As the areas on figure 19 do not overlap, it appears that the two fluid inclusion types were trapped under different P-T conditions—in contradiction to criterion (3).
Fig. 19. Comparison of homogenization conditions of late-pseudosecondary fluid inclusions, based on the H₂O–CO₂–NaCl model system (Gehrig, 1980). The bubble points of low-XCO₂ inclusions are tightly constrained by direct measurements of TH₂TOT and by relatively certain predictions of PH₂TOT, but the dew points of high-XCO₂ inclusions are predicted entirely from low-temperature measurements (see text). Owing to the resulting uncertainties, the possible dew points of high-XCO₂ inclusions define a large field in P–T space, constrained on its low temperature boundary by the highest observed decrepitation temperature. As the two fields do not overlap, it appears that the low-XCO₂ inclusions were trapped under different P–T conditions.

Criterion (4): The relative concentration of chemical components in the liquid and vapor should be appropriate to equilibrium fractionation at TH₂TOT and PH₂TOT. Low-pressure hydrothermal fluids show the following order of equilibrium distribution coefficients between liquid and vapor in the system CO₂–N₂–CH₄–H₂O–NaCl (Ellis, 1979):

\[
K_D(\text{NaCl}) < K_D(\text{H}_2\text{O}) < K_D(\text{CO}_2) < K_D(\text{CH}_4) < K_D(\text{N}_2)
\]

where \( K_D(i) = \left( \frac{X_i^{\text{VAP}}}{X_i^{\text{LIQ}}} \right)_{P,T} \)

Not all these constants are known under the PH₂TOT and TH₂TOT conditions of the fluid inclusions in this study, but their relative trend serves as a qualitative test of immiscibility.
Table 5 and figure 20 show the chemical fractionation between two pairs of inclusions that serve as models of the hypothesized "liquid" and "vapor". It is clear that the five fluid components show the distribution trend expected for immiscible fluids at equilibrium, except that the relative positions of CH$_4$ and N$_2$ are reversed. In the absence of appropriate experimental data it could be speculated that a cross-over of CH$_4$-N$_2$ fractionation coefficients occurs at the high pressures considered, or alternatively, the calculated ratios do indeed contradict criterion (5). The significance of this inconsistency in partitioning is uncertain, however, as the concentrations of CH$_4$ in the "liquid" inclusions lie near the detection limit of the Raman microprobe (table 2). Fractionation in the CO$_2$-H$_2$O-NaCl subsystem (fig. 20B) fits closely with the experimental results of Gehrig (1980).

According to this test the fluid inclusions satisfy only three of the four criteria for immiscibility; criterion (3) is not fulfilled if the laws of phase equilibrium are interpreted strictly. Although Th$_{TOT}$ values of the two inclusion types are compatible within error, Ph$_{TOT}$ estimates are not. The pressure difference shown on figure 19 (150–800 bars) may be due to unrecognized errors in the predictive calculations or to inadequacies of the assumed model ternary system. For example, the precise effect of N$_2$ on P–V–T properties in the CO$_2$–H$_2$O–NaCl system is unknown. On the other hand, the pressure difference may be real and even expectable in inclusions trapped in a vein environment. For example, in a vein fluid undergoing simultaneous unmixing and P-T evolution, a time delay between entrapment of the liquid and vapor phases—unrecognizable from petrographic evidence—conceivably could produce the observed pressure discrepancy.

<table>
<thead>
<tr>
<th>INCLUSION PAIR</th>
<th>K$_D$(NaCl)</th>
<th>K$_D$(H$_2$O)</th>
<th>K$_D$(CO$_2$)</th>
<th>K$_D$(CH$_4$)</th>
<th>K$_D$(N$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD8880–15 (VAP) LD8880–12 (LIQ)</td>
<td>0.12</td>
<td>0.26</td>
<td>16</td>
<td>&gt;100</td>
<td>32</td>
</tr>
<tr>
<td>LD926–G2 (VAP) LD927–B1 (LIQ)</td>
<td>0.23</td>
<td>0.26</td>
<td>13</td>
<td>&gt;100</td>
<td>48</td>
</tr>
<tr>
<td>GEOTHERMAL FLUIDS</td>
<td>&gt;180</td>
<td>&gt;800</td>
<td>&gt;1200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The distribution coefficients (K$_D$), calculated from data in table 4, reflect liquid-vapor fractionation of the gold-bearing fluid at 230°C, 600 bar. Because of the procedure adopted to calculate the bulk compositions in table 4, the K$_D$ values of CO$_2$ and H$_2$O are not mutually independent. Samples LD926 and LD927 are adjacent quartz crystals from the Bechaz mine. Gas distribution coefficients for salt-free, geothermal fluids at 230°C, 30 bar are shown for comparison (Ellis, 1979; Giggenbach, 1980). Consideration of salting-out would increase the values shown for the low pressure geothermal fluids.
of hydrothermal solutions in Late-Alpine gold-quartz veins

Fig. 20. Compositions in mol percent of two pairs of coexisting, late-pseudosecondary fluid inclusions (squares; conjugate "liquid" and "vapor" joined by tie lines), and a typical primary low-XCO₂ inclusion (star). (A) Subsystem CH₄-CO₂-N₂. No phase equilibrium data are available to test if these compositions fit the hypothesized process of fluid unmixing at 230°C, 600 bars, but the trend of component fractionation agrees with low pressure data. (B) Subsystem CO₂-H₂O-NaCl, showing phase boundaries at 230°C, 600 bars (Gehrig, 1980). Despite having been trapped under slightly different pressures (see fig. 19), the conjugate "liquid" and "vapor" inclusions plot on the bubble curve (liquid/liquid + vapor boundary) and dew curve (vapor/liquid + vapor boundary), respectively, as required of immiscible phases. The primary low-XCO₂ inclusion (star), which falls close to the tie lines within the liquid + vapor field, likely represents the composition of the hydrothermal vein fluid prior to unmixing.

Do the above data permit an alternative explanation to immiscibility? Several of the criteria could be satisfied by fluids that are miscible or partly miscible at the pressure and temperature of inclusion entrapment; by coincidence, two fluids that have never been in mutual contact could form inclusions of approximately the same age that homogenize at the same temperature via opposite phase transitions. Such miscible fluids would also contradict a strict interpretation of criterion (3), as observed in the present case. Consideration of criterion (4), however, especially applied to multi-component systems, allows unequivocal discrimination between the alternatives; only conjugate immiscible fluids conform to chemical equilibrium fractionation. Therefore there is little
doubt that immiscibility was attained in the Brusson veins at approx
230°C and 600 bars fluid pressure (fig. 19).

In the light of this conclusion and of the relative ages of the various
inclusion generations (table 1), it is probable that at least some of the
variable-XCO₂ assemblages were indeed produced via entrapment of
inhomogeneous fluids, that is, as mechanical mixtures of high-XCO₂
“vapor” and low-XCO₂ “liquid”. For example, the most CO₂-rich and
CO₂-poor inclusions shown in figure 7 have compositions and bulk
molar volumes that closely match those of the high-XCO₂ and low-
XCO₂ assemblages, respectively (compare data in table 4).

Given that final-stage boiling was widespread, however, the rarity
of variable-XCO₂ assemblages is noteworthy. In fact, assemblages with
wide variations in composition (fig. 6) are even rarer than bimodal
assemblages such as in figure 7. Thus it appears that in the final stage of
hydrothermal activity, when the vein fluid was no longer supersaturated
with respect to quartz, fractures healed slowly enough to allow most
trapped mixtures of liquid and vapor to differentiate in response to
wetting and buoyancy effects, into almost endmember low-XCO₂ and
high-XCO₂ inclusions.

THE PROCESS LEADING TO IMMISCIBILITY: PARTIAL MIXING VERSUS UNMIXING

Having demonstrated that immiscibility was attained during vein
formation, attention may be turned to the process that led to this state.
Two simple possibilities are considered: (1) the “liquid” and “vapor”
phases were produced via exsolution from a single, homogeneous parent
fluid as its path of P-T evolution intersected a solvus surface; (2) the
“liquid” and “vapor” phases resulted from the partial mixing of two
originally unrelated, partly miscible, homogeneous fluids. There is no
evidence to support partial mixing, as inclusions with compositions
appropriate to precursor fluids have not been found. In contrast, the
primary and early pseudosecondary inclusions fit well the prerequisites
of a parent fluid as envisaged in process (1): they are demonstrably older
than the late pseudosecondaries, and their compositions and bulk molar
volumes fall on tie-lines between the “liquid” and vapor” (fig. 20).

Figure 20B shows that the composition of the “parent” primary
inclusions is very close to that of the exsolved “liquid”. Although it is
possible that the primary inclusions are themselves the exsolved product
of an immiscible system, no early high-XCO₂ assemblages have been
found as proof. Rather, the observed sequence of fluid inclusion
assemblages is interpreted to record the onset of retrograde boiling as
the P-T trajectory of an originally homogeneous fluid (represented by
the primary fluid inclusions) penetrated the bubble-surface of a liquid-
vapor field.

The compositional similarity between the inferred parent fluid and
the exsolved liquid suggests that boiling initiated in response to a
gradual P-T evolution of the vein fluid: no dramatic decreases in fluid
pressure or temperature need be invoked to explain the observations.
Furthermore, the compositional similarity implies that the extent of boiling was minimal; there are no "liquid" fluid inclusions that show anything but very minor degrees of chemical evolution. Indeed, whether by coincidence or not, the boiling event comes at the close of hydrothermal activity in the Brusson vein system. Thus more prolonged boiling appears to have been prevented simply by the halt of fluid flow. The cessation of flow in turn may have been caused by changes in the local tectonic regime, by changes in the fluid source region, or even by self-sealing of the fluid conduits by mineral precipitation.

In all three mines examined in detail, the same temporal progression of fluid inclusion types is found. Ubiquitous late pseudosecondary assemblages of high-XCO₂ and low-XCO₂ inclusions show that boiling took place in the Fenilia, Bechaz, and Orbeillaz veins irrespective of variations in wallrock composition (fig. 1). Thus, although it may have been short-lived, fluid unmixing was evidently a widespread phenomenon in the vein swarm.

CORRELATION OF FLUID P–T–X EVOLUTION WITH MINERAL PRECIPITATION

The possible pressure-temperature conditions of main-stage vein formation are limited by the stability of phase assemblages found in the veins and in their metasomatic envelopes. Thermodynamic calculations of mineral-fluid equilibria (Diamond, 1986) show that the tightest constraints on formation conditions are provided by the absence of talc in hydrothermally altered metaserpentinite wallrocks that contain magnesite + quartz + low-XCO₂ fluid inclusions (fig. 21).

Isochores for the entire range of primary and early pseudosecondary inclusions have been derived from their calculated bulk compositions and molar volumes (such as listed in table 4) by interpolation of the experimental data of Gehrig (1980). Although isochoros are rapidly obtained from the equation of state of Bowers and Helgeson (1983), their equation does not reproduce Gehrig's (1980) data with sufficient accuracy in the P–T–X region of interest for this study (Diamond, ms).

As the primary and early pseudosecondary inclusions formed from homogeneous solutions, the main-stage vein minerals (table 1) must have precipitated somewhere within the band of isochoros shown on figure 21, at P–T conditions above the respective bubble points (240°–260°C, 600–750 bar) and below the intersection with the stability field for talc (300°–310°C, 1100–1350 bar).

A possible evolution path that fits the P-T constraints for the vein-forming fluid is shown on figure 21. The path passes successively through isochoros of the primary, late-primary, and early-pseudosecondary inclusion generations and terminates at the P-T point (marked by a star) at which the fluid is inferred to have boiled. There is no evidence that compels the P-T path to drop in temperature or pressure between the respective isochoros of the primary, late-primary, and early-pseudosecondary generations: a straight trajectory indicating a steady decrease in P and T has been chosen, because it fits the qualitative scenario of
Fig. 21. Pressure-temperature evolution path of vein formation at Brusson. A possible trajectory for the hydrothermal fluid is indicated by the small arrows (black for the entrapment of primary inclusions and white for pseudosecondaries). The stippled regions show bands of isochoires corresponding to the indicated fluid inclusion generations. A very speculative path for the vein wallrocks (lithostat), in thermal equilibrium with the fluid, is shown by the large white arrows. The constraints used in defining the fluid path are described in the text.
continuing uplift and cooling during vein formation, as deduced from
the local geochronology and regional geology (Diamond and Wieden-
beck, 1986; Diamond, ms). In detail, however, many small fluctuations
in fluid pressure are likely to have occurred as each new pulse of
hydrothermal solution entered the veins via hydrofracturing or fault
displacement.

The change in mineralogy from the main stage to the final stage
paragenesis (table 1) coincides with the formation of fluid inclusions
diagnostic of boiling. Thus boiling was presumably the trigger for
widespread deposition of minor galena, tetrahedrite, and calcite. Not
only are muscovite, dolomite, rutile, and pyrite missing during the final
stage, but quartz as well: the only fracture traces in vein quartz that bear
fluid inclusion evidence of boiling are those that intersect crystal
boundaries.

Much of the gold at Brusson precipitated during the main stage of
mineralization, but at least at the Fenilla and Orbeillaz mines, some gold
also overlapped with the final-stage paragenesis (table 1). None of the
samples examined, however, contains high-XCO₂ inclusions and gold in
a textural relationship that proves directly the contemporaneity of
boiling and gold precipitation. Nevertheless, the broad temporal coinci-
dence of gold and immiscible fluids, deduced from indirect petrographic
relationships, strongly suggests that some gold precipitated from the
boiling fluid. Observations of gold are too sparse, however, to generalize
on the relative total quantities of main- versus final-stage gold.

Based on this timing relationship and by analogy with modern
geothermal systems, in which boiling drastically lowers gold solubility
(Brown, 1986; Seward 1989), one could infer that boiling actively
promoted the late precipitation of gold at Brusson. Yet, whereas fluid
inclusion evidence for boiling is ubiquitous in all studied veins, local
wallrock composition strongly controls the spatial distribution of both
early and late gold. Recall, for example, that the Fenilia vein is aurifer-
ous where it passes through metagranites and metasediments but is
barren where it passes through metacarbonates and metaserpentinites
(Reinhold, 1916). Moreover, at the Bechaz mine there is ample evidence
of final-stage boiling, but all the gold apparently is earlier—associated
with main-stage pyrite. These observations argue for gold precipitation
mechanisms that, rather than being dependent on boiling, are domi-
nantly controlled by fluid-wallrock reactions.

The analogy with boiling in modern geothermal systems fails
presumably for two reasons. First, the rate of boiling at Brusson
evidently was low enough to allow fluid-wallrock reactions to compete
with vapor separation in influencing gold solubility. Second, because of
the less pronounced chemical fractionation between liquid and vapor in
the Brusson veins, compared to their low pressure geothermal counter-
parts (table 5), the extent of boiling at Brusson was too limited to affect
gold solubility significantly.
TECTONIC AND METAMORPHIC CONTEXT OF GOLD MINERALIZATION AT BRUSSON

The P-T evolution of the vein fluids and their modest compositional evolution via boiling, were determined apparently by regional tectonic events in the Western Alps. Local Meso-Alpine compressional metamorphism reached 425° to 450°C and 3 to 5 kb (Frey and others, 1976) approx 38 Ma ago (Hunziker, 1970; Frey and others, 1974). Subsequent rapid uplift and erosional unloading of the nappe pile was accompanied by regional extension, by widespread emplacement of lamprophyric dikes, and by intrusion of syeno-monzonitic stocks (Biella) on the internal margin of the Western Alps, some 18 km east of Brusson (Dal Piaz, Hunziker, and Martinotti, 1972; Gosso and others, 1979; Laubscher, 1983). At the same time—around 32 Ma ago—uplift and extension at Brusson (fig. 22) produced normal faults and joint sets and permitted lamprophyric dikes to intrude (Diamond and Wiedenbeck, 1986). The deep auriferous fluids tapped by these faults cooled, depressurized, and finally boiled as they rose through the crustal level now exposed at Brusson. The P-T—t path on figure 22 suggests that hydrothermal activity lasted less than 2.2 Ma.

Ubiquitous wallrock alteration attests to chemical disequilibrium between the vein fluids and all lithologic units at Brusson (Diamond, ms). In the Central Alps, however, fluid inclusions with comparable major-element compositions were apparently in chemical equilibrium with structurally deeper amphibolite facies rocks (Poty, Stalder, and Weisbrod, 1974). None of the occurrences is auriferous, and as Meso-Alpine metamorphism in the Central Alps outlasted that in the Western Alps, they are also much younger (8–18 Ma; Poty, Stalder, and Weisbrod, 1974). Nevertheless, the similarity in compositions suggests that fluid evolution in the Central Alps during the Miocene may have been analogous to that below Brusson in the mid-Oligocene.

Hypothetical processes that could have produced ore-bearing fluids below Brusson include devolatilization reactions driven by prograde regional metamorphism (note, however, that metamorphism was retrograde at the level of gold deposition) or driven by intrusion of equivalents of the coeval Biella syenite. Alternatively, the faults that host veins at Brusson may have released deep fluids trapped much earlier under the Meso-Alpine compressional tectonic regime.

CONCLUSIONS

The auriferous veins at Brusson formed in active normal faults and dilatent joints during rapid uplift and cooling of the Western Alps, approx 32 Ma ago. At this time, regional metamorphism was waning after a local greenschist-facies peak, some 4 to 8 Ma earlier. The many pulses of auriferous fluid that ascended along the faults therefore passed through the structural level of Brusson at successively lower temperatures and pressures—spanning the interval between 300°C, 1300 bars and 240°C, 650 bars. Although the density of the ore-bearing fluid progressively increased throughout this interval, its major-element
Fig. 22. Approximate temporal evolution of pressure and temperature at Brusson. The shaded fields represent P–T–t conditions attending the Meso-Alpine phase of regional metamorphism (Frey and others, 1976). Gold mineralization occurred well after the peak in metamorphism, during an episode of rapid decompression and cooling caused by regional uplift and erosional unloading of the Western Alps (Diamond and Wiedenbeck, 1986). The precise course of the P–t evolution is uncertain, but the T–t path is constrained by fission-track annealing ages in apatites from metagranite correlatives of the Arcesa-Brusson unit: the northern Gran Paradiso (Carpena, 1984) and southwestern Monte Rosa massifs (Wagner, Reimer, and Jaeger, 1977). As Brusson lies midway between these two units, the T–t path has been drawn between the respective data points.

Composition remained almost constant: (avg in mol percent, see table 4) 90.9 H₂O, 5.9 CO₂, 1.47 Cl, 1.47 Na, 0.15 N₂, 0.06 K, 0.02 S, 0.02 Ca, 0.003 Mg, 0.002 CH₄.

The main-stage mineral assemblage, composed of quartz + ferroan dolomite + muscovite + rutile + pyrite + chalcopyrite + gold, precipitated from this “low-XCO₂” fluid in response to the cooling and depressurization imposed by regional uplift and in response to metasomatic interaction with the various countryrocks affected by faulting. Hence gold occurs in all but the segments of veins enclosed by serpentinite or metacarbonate wallrocks.

Further P–T decreases forced the last of the ascending fluids through their miscibility boundary, at approx 230°C and 600 bars. Gold continued to precipitate during retrograde boiling, but the other main-stage minerals were locally replaced by minor amounts of calcite, tetrahedrite, and galena. Although the exsolved vapor phase was enriched in volatiles and depleted in chloride salts, there is no indication
that boiling induced rapid precipitation of gold, as is known to happen in lower pressure geothermal environments. The compositional evolution of the fluid that resulted from vapor separation was evidently slow enough to allow fluid-wallrock reactions to continue controlling the spatial distribution of gold. In fact, late gold is absent from some veins that show convincing evidence of late boiling. Fluid flow ceased before the composition of the residual liquid had changed appreciably. In all, hydrothermal activity lasted less than 2.2 Ma.

The evidence for fluid immiscibility during final-stage mineral precipitation is compelling. It is drawn from coexisting, contemporaneous assemblages of fluid inclusions that contrast in composition and density, but that were each formed from locally homogeneous vein fluids: assemblages of exclusively low-XCO₂ “liquid” on the one hand and assemblages of exclusively high-XCO₂ “vapor” on the other. The state of immiscibility between the assemblages has been rigorously tested against the thermodynamic requirements of phase equilibrium in the system H₂O–CO₂–N₂–CH₄–NaCl. Temporal relationships show that immiscibility was attained via retrograde boiling. Based on this result, some of the rare variable-XCO₂ assemblages also are interpreted to have formed during boiling.

This case study demonstrates that, although all fluids with CO₂ contents typical of mesothermal lode deposits must eventually unmix if they rise to shallow enough crustal levels, and although gold may precipitate continuously, the mere occurrence of boiling is not a guarantee that ore will be formed. Rather, in the relatively high pressure mesothermal environment, where chemical fractionation between liquid and vapor is only moderate, the boiling fluid must first lose large amounts of vapor before gold solubility is significantly reduced.

ACKNOWLEDGMENTS

This study is part of a doctoral thesis submitted to the Swiss Federal Institute of Technology (ETH), Zurich. I thank Volkmar Trommsdorff, Alan Thompson, and Jean Dubessy for their supervision of this work and Martin Engi for valuable discussions. Bernard Charoy of the Centre de Recherches Pétrographiques et Géochimiques and Jean Dubessy of the Centre de Recherches sur la Géologie de l’Uranium (CREGU), both in Nancy, France, kindly made the leachate and Raman spectroscopic analyses, respectively, and Michel Cuney (CREGU) introduced me to microthermometry. Thanks are due to H. Stalder (Naturhistorisches Museum, Bern) and E. Curti for providing access to their gold-bearing vein samples and to Y. Riaño for assistance with drafting. This research was supported by a Swiss Federal Scholarship and an ETH-Assistenzstelle (Trommsdorff). I am grateful to George Skippen and to two anonymous journal reviewers whose comments greatly aided in clarifying the text.
### APPENDIX

<table>
<thead>
<tr>
<th>VEIN SAMPLE INCLUSION</th>
<th>LOW-XCO₂ FLUID INCLUSIONS</th>
<th>HIGH-XCO₂ FLUID INCLUSIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ORBEILAZ</td>
<td>BECHAZ</td>
</tr>
<tr>
<td>TmCLA (°C)</td>
<td>8.6</td>
<td>8.1</td>
</tr>
<tr>
<td>ThCAR (°C)</td>
<td>28.3</td>
<td>27.4</td>
</tr>
<tr>
<td>PhCAR (bar)</td>
<td>79.0</td>
<td>80.0</td>
</tr>
<tr>
<td>ThTOT (°C)</td>
<td>256.0</td>
<td>250.0</td>
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<tr>
<td>mCO₂/AQ</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td>vCO₂/AQ(cm³)</td>
<td>51.0</td>
<td>49.0</td>
</tr>
<tr>
<td>VAQ (cm³)</td>
<td>18.03</td>
<td>18.03</td>
</tr>
<tr>
<td>VCAR (cm³)</td>
<td>90.3</td>
<td>90.0</td>
</tr>
<tr>
<td>F̂ CAR</td>
<td>0.19</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Input parameters for calculation of the fluid inclusion compositions and molar volumes in table 4. In addition to these parameters, the calculations incorporate the Raman spectroscopic data in table 2 and the ion ratios from leachate analyses given in table 3.

- $m_{CO₂/AQ}$ - molality of CO₂ in the aqueous phase at $Th_{CAR}$ and $Ph_{CAR}$, obtained from the data of Wiebe and Gaddy (1940), and corrected for salting-out effects using the coefficients of Malinin and Savelyeva (1972) and Malinin and Kurovskaya (1975).
- $v_{CO₂/AQ}$ - partial molar volume of CO₂ in the aqueous phase at $Th_{CAR}$ and $Ph_{CAR}$ (Parkinson and de Nevers, 1969).
- $V_{AQ}$ - molar volume of the H₂O-NaCl portion of the aqueous phase at $Th_{CAR}$ and $Ph_{CAR}$ (Rogers and Pitzer, 1982).
- $V_{CAR}$ - molar volume of the carbonic phase at $Th_{CAR}$ and $Ph_{CAR}$ (Arai, Kaminishi, and Saito, 1971).
- $F_{CAR}$ - volume fraction of carbonic phase: values for high-XCO₂ inclusions are approximate optical estimates; values for low-XCO₂ inclusions are calculated from the parameters listed in this table.
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