

The Significance of Fluid Inclusions' Characteristics in Indicating the Evolution of Ore-Forming Fluids

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Abstract: Objective: Fluid inclusions are microfluids trapped within mineral crystals during their growth. These fluid droplets are the only direct observational samples which can invert the physicochemical condition and trace back its source as well as reveal the origin of mineral deposit. In order to comprehensively understand the petrographical, thermodynamic data on and compositional characteristics of the included fluids and what they imply for the history of mineralizing fluid evolution. Methods: To make a systematic and detailed division of fluids, use the petrographic division; analyze various microscopic thermometric data. Use laser Raman spectrum detection technology for detection, follow isotope tracing to track its movement, precipitation, etc., with the mass balance method, thermodynamic state equation method; Results: Temperature, Salinity Evolution of Inclusions has the same trend of uniform evolution, it is very accurate to display the mineralization dynamics process such as cooling, boiling (non-miscible), fluid mixing etc. in the fluid system; Volatile Components and Trace Element Composition can reflect the transport and precipitation way of metal complex. Conclusions: Fluid inclusion can play an important role of divide the stage of mineralizing, it also can be called "Mineralization Phase indicator" which give its microfluidic Dynamic evidence to prove at mining deep drilling when build a regional scale model of mineralized zone: It is inevitable that the site multiple scale and multiple method analyses of fluid inclusions, if we want to know about how these minerals form fluids evolves in the future.

Keywords: Fluid inclusions, Mineralizing fluids, Fluid evolution, Mineralization mechanism.

1. Introduction

In the current modern system of mineral deposit and geochemistry research, the ore forming fluid is the important connection between the deep material circulation of our planet and the shallow part where we find element concentrations. The entire mineralization process—from the initial extraction of metals from source rocks, through their long-distance migration along geological conduits, to their eventual precipitation under specific physico-chemical conditions—is intrinsically linked to the properties and dynamic evolution of ore-forming fluids [1]. But because of the un-reversibility and very long duration of geological processes, geologists cannot directly sample ancient ore-forming fluids. Luckily enough, when major rock mineral crystals or recrystallized quartz, calcite, fluorite and so on, they always bring some tiny cracks or lattice defects for very few liquid medium to occupy, thus forming the closed fluid inclusion [2]. And those inclusions were called "Microscopic Ancient Fluid Cells", and after that geological history, if the main mineral hasn't had great plastic deformity or advanced

metamorphosis, then the matter composition and overall density inside those inclusions should be basically constant.

2. Basic Types of Fluid Inclusions and Petrographic Characteristics

2.1. Classification of Inclusion Formation and Inclusion Age Indication

Inclusion formation classification is a requirement in order to do all the microscopic thermodynamic and composition analysis. The space distribution pattern of inclusion in mineral crystal is actually recording the sequence relationship between fluid activity time. As far as the origin is concerned, fluid inclusion is divided into primary inclusion, secondary inclusion, pseudo-secondary inclusion [3]. The Primary Inclusions are formed during the crystallization & Growth process of Minerals where the fluid got entrap into the growth face of crystals, Lattice defect or because of Uneven growth rate causing empty space. It mostly happens when they show up singly or in a line alongside certain growth areas of minerals.

Table 1. Classification of Fluid Inclusions Causes and Their Microscopic Discrimination Criteria

Inclusion Type	Spatial Distribution & Morphological Features	Temporal Relationship with Host Mineral Growth	Genetic and Metallogenic Significance
Primary	Isolated, randomly scattered; or clustered without preferred orientation; or aligned linearly along growth zones (e.g., oscillatory zoning, sector boundaries)	Trapped contemporaneously with crystal nucleation and growth; represent the in situ fluid during mineral precipitation	Preserve the composition, salinity, density, and temperature of the original ore-forming fluid, critical for reconstructing the main mineralization event
Pseudo-Secondary (or "Quasi-Secondary")	Linear arrays confined within the crystal interior, following narrow, healed microfractures that terminate before reaching crystal margins; often associated with growth bands or deformation lamellae	Formed by transient fracturing and rapid resealing during active crystallization, under tectonic stress or volume strain	Record fluid pulses coeval with mineral growth, reflecting episodic fluid influx, pressure fluctuations, or syn-mineralization deformation — key to understanding ore-fluid dynamics
Secondary	Bead-like or string-of-pearls alignment along well-defined, cross-cutting healed fractures; fractures commonly traverse grain boundaries, multiple crystals, or host-rock matrix	Generated after host mineral has fully crystallized and solidified; result from post-crystallization brittle deformation and subsequent fluid infiltration	Indicate late-stage hydrothermal overprinting, non-ore-related fluid circulation, or alteration events — useful for distinguishing primary mineralization from superimposed modification

2.2. Classification of Inclusion Composition and Phase State

Phase compositions and volumes ratios of fluid inclusion at room temperature, which is generally about 20°C - 25°C. This is the most direct expression of the overall system's composition and the density of liquid. According to the phase characteristic of inclusions under RT, they are generally divided into liquid rich aqueous solution Inclusion, Gas-Rich Inclusions, Puregas/pureliquid Inclusions, multiphase inclusion and its parent minerals. As far as others are concerned, they account for most of them; mainly it involves systems where NaCl-H₂O has the dominant part of M-L salinity type [4]. As well as in Shallow Hydrothermal System which contains these types of Gold minerals and also near the surrounding of Porphyritic. In terms of gas inclusion, there are many rich gas inclusions (bubble volume > 70%) at the early stage of magmatic hydrothermal system or under strong boiling condition, and the main component is water vapor or some other volatile components such as CO₂, CH₄, etc.

3. Thermodynamic Parameters of Fluid Inclusions and Metallogenic Physical-Chemical Environment

3.1. Homogenization Temperature and Metallogenic Thermodynamics Background

Homogenization temperature (Th) is the most basic and important thermodynamic parameter in the microscopic temperature measurement of fluids inclusion. The minimum temperature of artificial heat so as to make it such that all is restored into 1 phase, the gas and all internal liquids and solids. Theoretically, if the ore-forming fluid is in the boiling state of coexistence of gas and liquid when captured, then the measured homogenization temperature in the laboratory is equal to the actual capture temperature of the ore-forming fluid (Tt). But mostly it is in one phase where fluid is captured

and the pressure at which the fluid was captured (Pt) needs to be more than the saturated vapor pressure of fluid at that temp. (Ph). Because the mineral's cooling contraction is much less than fluid's volume, so there is gas bubble appear in the fluid inside of inclusion when we cool down to room temperature [5]. Therefore, to obtain the actual ore-forming temperature, the homogenization temperature must be pressure-corrected. In terms of the thermodynamic deduction of the metallogenic physical-chemistry, it depends on this temperature and pressure for coordination. The simplest formula of pressure correction (Formula 1), we could write it like this: $P = P_h + (T_t - T_h) \cdot (dP / dT)_V$. Where P refers to the actual capture pressure of the fluid; P_h is the saturated vapor pressure of the fluid at the homogenization temperature; T_t is the actual capture temperature; T_h is the measured homogenization temperature; dP / dT V is the rate of pressure change for the fluid System with respect to Temperature at Constant Volume (Isochore Line). The salinity is an important parameter in fluid that determine the coordination forms, solubility and mobility of the metal element. It is generally given as the weight percent of sodium chloride equivalent (wt% NaCl eqv.) The salinity of fluid inclusions is estimated largely indirectly from the measurement of T_m or T_s of the ice and sub-micron minerals melted on a microscopic cold-hot stage [6]. For water solution inclusion without sub-minerals, the salinity is calculated by the classical thermodynamic empirical equations. For example, following the classic fluid inclusion salinity empirical formula put forth by Bodnar (Formula 2) Salinities can be determined from: $W = 0.00 + 1.78 \cdot T_m - 0.0442 \cdot T_m^2 + 0.000557 \cdot T_m^3$ W is salinity (wt %NaCl eqv.) When there's lots of CO₂ around to make cages, we need to melt those cage-like things and change the amount of salt to calibrate it. Get the uniform temperature and salinity, then get the overall density of the ore-forming fluid by combining with the state equation (EOS) of the H₂O-NaCl system. In terms of studying the evolution path of ore-forming fluid, and in all kinds of Th - Salinity scatter plots, it can be seen more clearly.

Table 2. Methods for Estimating Microscopic Thermodynamic Parameters of Fluid Inclusions and Geological Significance

Thermodynamic Parameter	Measurement or Estimation Method	System Constraints	Geological Significance for Ore-Forming Fluid Evolution
Homogenization Temperature (Th)	Observed microscopically as the temperature at which vapor bubbles (or daughter minerals) fully homogenize into the liquid phase during heating on a calibrated heating–freezing stage	Valid only if inclusions retain original trapping conditions; requires absence of post-entrapment leakage or re-equilibration	Constrains the minimum trapping temperature; maps thermal evolution of hydrothermal systems and identifies cooling trends across mineralization stages
Salinity (wt% NaCl equiv.)	Derived from measured ice-melting temperature TM , clathrate dissociation temperature, or gypsum dissolution temperature using empirical calibrations and phase diagrams	Applicable to H ₂ O–NaCl, H ₂ O–CO ₂ –NaCl, or multi-component brine systems; accuracy declines beyond ~25 wt% NaCl or with complex volatile content	Tracks ligand availability (e.g., Cl ⁻ , CO ₂) critical for metal complex stability; discriminates between mixing (e.g., meteoric–brine), boiling, or evaporation events
Fluid Density (g/cm ³)	Computed by inputting Th and salinity into experimentally validated equations of state (e.g., PVTx models for H ₂ O–NaCl or H ₂ O–CO ₂ –NaCl)	Assumes fluid inclusion volume remains constant (isochoric behavior) since entrapment; sensitive to correct EOS selection and compositional assumptions	Reflects buoyancy forces driving fluid migration; constrains paleo-fluid pressure gradients and estimates minimum ore-forming depth (via density–pressure–depth relationships)
Trapping Pressure (Pt, MPa)	Determined by intersecting calculated isochores (from Th–salinity–EOS) with independent geobarometric constraints (e.g., coexisting mineral equilibria) or via boiling-curve fitting where applicable	Requires reliable estimate of true formation temperature (Tt) or confirmation of boiling behavior; invalid if inclusions experienced stretching or necking	Reconstructs paleo-fluid overpressure conditions; distinguishes lithostatic vs. hydrostatic regimes—key for evaluating structural control on fluid focusing and vein formation

4. Characteristics of Fluid Inclusion Components and Their Indications for Ore-Forming Mineral Sources

4.1. Raman Spectroscopy of Gas-Liquid Components and Group Composition Analysis

The ore-forming fluid is not an aqueous solution, it's a super-critical fluid or a hydrothermal system which contains various volatile substances like CO₂, CH₄, N₂, H₂S, and also a lot of ore-forming metal complexes. With the introduction of laser raman spectroscopy (LRM) we can now do non-destructive qualitative and almost semi-quantitative analysis on what is in an individual micrometer-sized inclusion. In the fluid inclusion of orogenic gold deposit, Raman frequently sees extremely high amount of CO₂ and trace quantity of CH₄ as well as N₂ in the rich gas phase. It shows that this low-saline CO₂-filled fluid has some characteristics similar to that it is fingerprint of typical deep metamorphic fluids which have big influence on maintenance and steady situation of Au's S-H bond compound Au (HS)₂. Fluid quickly rises towards the fracture zone and a large drop in pressure is observed. Due to the massive release of CO₂, there will be an extreme fluctuation in pH value of the fluid, this directly results in a fast precipitation of gold [7]. In addition to this, by applying the group inclusion extraction method together with GC-MS or IC analysis, one can get a sense of how much each kind of ion like halide (F⁻, Cl⁻, Br⁻) and sulfate is present in your fluid. Because there is an obvious difference in Cl/Br ratio from various fluid sources like magmatic water, basin forming water etc., so such a small amount element indicator could be an important chemical probe to distinguish between the origins of initial ore-forming fluids and track the evolution

route of fluid-rock reactions.

4.2. Isotopic Geochemistry and Fluid Source Tracing

Hydrogen(H) and Oxygen(O) in fluid inclusion has been preserved and it's the most authoritative geo-chemical basis of tracing the origin of ore-forming fluid up till now. The mineral lattice generally consists only of O elements and there is no H element, so we can directly determine the water in quartz, other minerals and so on through the hydrogen isotope ratio(δD) of the sample by vacuum crushing; while the oxygen isotope ratio(δ¹⁸O_{fluid}) of the fluid is generally derived from the oxygen isotope ratio(δ¹⁸O_{mineral}) of the main minerals measured and combined with the temperature of mineralization obtained from the fluid inclusion temperature measurement[8]. The oxygen isotope balance fractionation equation of the quartz-water system (Equation 3) is usually expressed as: $1000\ln\alpha = A * (10^6 / T^2) + B$. α is the fractionation factor, T is the thermodynamic absolute temperature K, A and B are calibration constants determined experimentally. By drawing our calculated δ¹⁸O_{fluid} values and the real measurements for d onto the hydrogen–oxygen (H-O) isotope standard correlation chart we can readily discern if the fluid in question originates with the primary magmatic water, metasedimentary dehydration, atmosphere or deep ocean circulation of seawater. And more importantly, if this point deviates from the typical end member point on the figure and has an obvious trend of moving closer to another end member (such as a strong 'oxygen isotope drift' phenomenon), then it clearly indicates that the ore-forming fluid has undergone intense water-rock isotope exchange reactions with the surrounding rock or a large amount of fluid from various sources have mixed for a long time.

Table 3. Typical Hydrogen-Oxygen Isotope Characteristic Reference Values of Different Source Ore-Forming Fluids

Fluid Source Endmember	$\delta^{18}\text{O}$ fluid (‰, SMOW)	δD (‰, SMOW)	Key Indicators of Fluid Evolution and Material Exchange
Magmatic Water	+5.0 to +9.0	-80 to -40	Reflects derivation from late-stage magmatic crystallization; typically transports primary metal loads from crystallizing intrusions.
Metamorphic Water	+5.0 to +25.0	-60 to -20	Signals devolatilization during regional metamorphism; strongly associated with orogenic gold systems in accretionary or collisional belts.
Meteoric Water	< 0 (latitude-dependent)	< -50 (typically follows global meteoric water line, GMWL)	Suggests significant infiltration and shallow-circulation mixing; commonly induces rapid cooling, dilution, and salinity drop—triggering metal precipitation.
Formation Brine (Basinal Brine)	0 to +10.0	-80 to -20	Represents high-salinity fluids expelled from compaction and dewatering of deep sedimentary sequences; enriched in Cl^- , metals, and often linked to Mississippi Valley-type (MVT) and basin-hosted deposits.

5. Ore-Forming Fluid Evolution Mechanism Discussion

5.1. Evidence of Fluid Boiling and Incompatible Interaction from Inclusion Evidence

Fluid boiling (also called immiscibility effect or phase separation): It is the most important trigger mechanism for the large scale precipitation and re-removal of metals from hydrothermal system: Deep and warm fluid flows out from the fault zone. When the static water pressure, static rock pressure changes suddenly or the flow-out process is too violent, there may be a chance that the liquid can undergo a decompress boiling. In the microfacies research, it is the definite proof for fluid boiling: in the same mineral growth zone or in the same microcrack there exist the closely-related gas-rich and liquid-rich inclusions (even halite sub-mineral inclusion). During microthermo, these two kinds of inclusions have basically the same uniform temperature, but the way of this uniformity is quite different: The liquid-rich inclusion is uniformly distributed for the liquid, and the gas-rich inclusion is uniformly distributed for the gas [9]. This fact undeniably proves that the major minerals formed in a boiling fluid where there is both gas and liquid. The significance of fluid boiling for the evolution of ore-forming fluids is very great. Boiling will make many acidic volatiles, such as H_2S , CO_2 and so on transferred into the gas phase and escape from the system, thus greatly increasing the pH value of the remaining liquid; meanwhile, the evaporation of water molecules in the liquid phase will cause a rapid increase in the concentration of coordination groups like Cl^- but at the same time reduce its total flow volume. Such huge changes in physical and chemical surroundings will destroy the stability of metal complexes such as chloride complex or hydrogen sulfide complex, which will result in a large amount of metal sulfide

precipitating extremely fast but confined in some small area.

5.2. Fluid Mixing and Its Trigger Mechanism for Metal Precipitation

Another very common mineralization process: Fluid Mixing is pretty common for porphyres and shallow-forming low-temps, it's a good fit for siliciclastics too. In the shallow part of the earth's crust there is an extremely large underground groundwater circulation system due to seepage from atmospheric rainfall. When the high temperature, high salt, magma hydrothermal fluid moves out from the deep part to the shallow part of the crust, necessary huge volume of mixing with those atmospheric precipitation is unavoidable [10]. In the thermodynamic diagram of inclusions, the mixing is shown by the perfectly positive correlation linear progression relationship with temperature and salinity. Fluid mixing is an equilibrium process between mass and energy; therefore, we can describe it using the simple mass balance equation: Equation 4) $M_{\text{mix}} * C_{\text{mix}} = M_{\text{a}} * C_{\text{a}} + M_{\text{b}} * C_{\text{b}}$ (M is fluid mass; C is temp., salinity or conc. Of a certain element; a & b are end member fluids; mix means mixture) Fluid mixing indicating mineralization evolution has significance because when there is an influx of a large amount of low-temperature cold water, the temperature of the deep hydrothermal system will suddenly fall, thereby decreasing the solubility limit of metal complexes; also due to the dilution effect of the water body on the outside, the activity of complexing ions such as Cl^- in the fluid is greatly reduced, which can also promote the dissociation of metal complexes. Also it will cause atmospheric precipitation to have higher oxygen fugacity which can oxidize the reducing sulfur in hydrothermal fluid and make system Eh be changed. Due to the effect of cooling and dilution, etc., the mineralization elements in the liquid quickly lose their activity and precipitate as mineral form.

Table 4. Key Fluid Evolution Mechanisms Triggering Metal Deposition and Their Inclusion Identification Indicators

Fluid Evolution Mechanism	Core Inducing Factors	Changes in Fluid Physical and Chemical Properties	Typical Inclusion Identification Indicators
Fluid Cooling and Condensation	Thermal dissipation due to distance from heat source and conductive heat loss	Solubility of metal complexes declines exponentially with decreasing temperature	Homogenization temperature (Th) exhibits a gradual, continuous decrease; salinity remains relatively stable; absence of coexisting vapor- and liquid-rich inclusions
Pressure-Driven Boiling / Fluid Immiscibility	Structural dilation or uplift-induced pressure reduction	Volatile exsolution elevates pH abruptly; residual brine salinity exceeds solubility limits	Vapor-rich and liquid-rich inclusions with identical Th occur in close spatial association but display distinct morphologies and phase ratios
Mixing of Two End-Member Fluids	Fracture opening linking deep hydrothermal and shallow meteoric or formation fluids	Rapid cooling, ligand dilution, and shift in oxidation-reduction potential (Eh)	Linear positive correlation between Th and salinity; systematic isotopic shifts (e.g., $\delta^{18}\text{O}$, δD , $\delta^{34}\text{S}$) across inclusion populations
Fluid-Rock Interaction	Fluid migration along permeable pathways and pervasive wall-rock alteration	H^+ consumption drives acid neutralization; dissolution releases rock-bound metals and alters fluid composition	Inclusions enriched in lithophile elements (e.g., Al, K, Rb, Li) characteristic of host rock; spatial and textural association with alteration minerals (e.g., chlorite, sericite, epidote)

6. Conclusion

Microanalytical data obtained from fluid inclusions provide critical geochemical evidence for deciphering the deep crustal evolution of mineralizing fluids. Dissection inclusion distribution based on petrology as well Microthermodynamic Parameters (uniform temp and salt density) of petrology regarding volatile Components Isotopic Components at every mineralised phase together would give us a full life-cycle migration route picture - From the start of magma or Metamorphism dehydroxylation up till Reduction Pressure Boiling point, and then after that Fluid remixing Cooling Precipitation: The large changes in all kinds of physical and chemical parameters have become a testing method for fluid dynamic methods (boil, mix, water-rock reaction). They are also the most basic keys to explain why many minerals are enriched and where their spatial zoning pattern is.

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