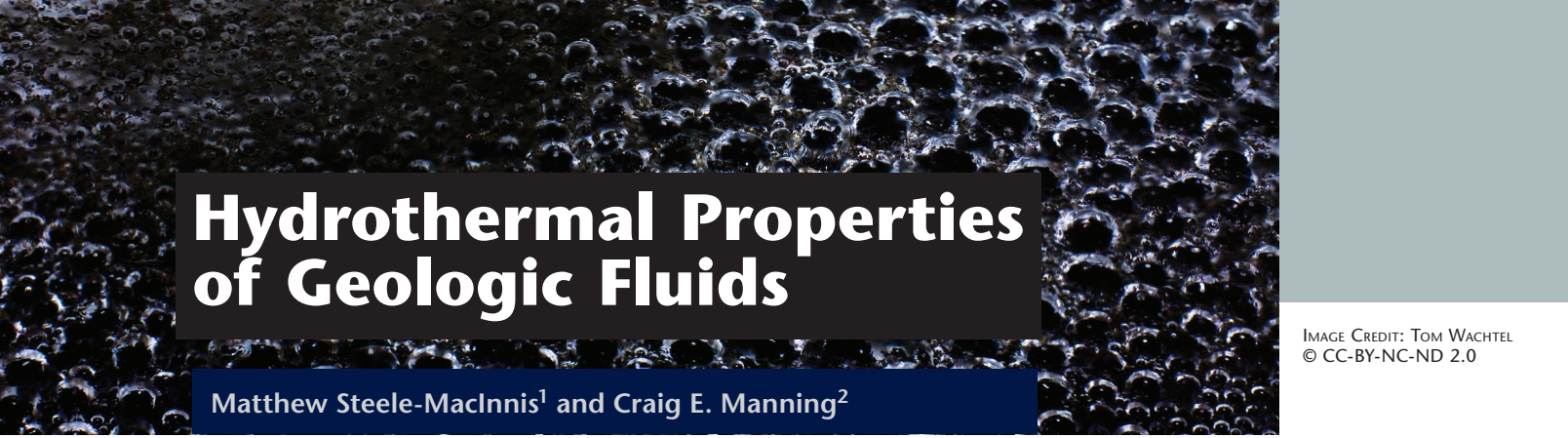




Hydrothermal Properties of Geologic Fluids

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Aqueous fluids are critical agents in the geochemical evolution of Earth's interior. Fluid circulation and fluid–rock reactions in the Earth take place at temperatures ranging from ambient to magmatic, at pressures from ambient to extreme, and involve fluids that range from nearly pure H₂O through to complex, multicomponent solutions. Consequently, the physical and chemical properties of hydrothermal fluids vary widely as functions of geologic setting; this variation strongly impacts fluid-driven processes. This issue will focus on the nature of geologic fluids at hydrothermal conditions and how such fluids affect geologic processes in some major settings.

KEYWORDS: Fluids, hydrothermal, phase equilibria, thermodynamics, geochemistry

INTRODUCTION

Earth is commonly referred to as “the water planet.” This epithet is mostly used to highlight the abundance of liquid water at Earth's surface, but it is worth emphasizing the outsized role that aqueous fluids play in Earth's interior. Geologic fluids affect and control tectonic, petrologic, and ore-forming processes from Earth's mantle to Earth's surface. Indeed, the vast majority of major geologic processes are strongly influenced or fundamentally driven by the actions of fluids.

Fluids play a central role in the Earth for several reasons. First, aqueous fluids are everywhere: from high in the atmosphere to deep in the planet's interior. This may seem like a trivial statement, but it has wide-ranging implications. Whereas other geologic materials, such as minerals and melts, are stable over specific, limited ranges of pressure and temperature, aqueous fluid persists across the whole spectrum accessible from surface to mantle. In fact, to our knowledge, aqueous fluids (along with volatile fluids such as CO₂) have a wider stability field in pressure–temperature space than any other common geologic material. Second, fluids are, by definition, capable of flow and can, therefore, move through fractures or along grain boundaries, thus bridging different geologic reservoirs. Third, fluids are endowed with a tremendous capacity to store and transport thermal energy and so can play a vital role in heat transfer within the Earth. Fourth, fluids are chemically reactive and capable of dissolving and precipitating minerals, thus driving mass fluxes, global geochemical cycles, and the formation of mineral deposits. Besides, fluids exert key controls on rheological properties, melting, and crystallization, as well as on mineral phase equilibria. Truly, “aqueous fluids make things happen inside the Earth” (Thompson 2010).

characteristics of such fluids and how they vary between geologic settings.

HISTORICAL PERSPECTIVES

The impact of hydrothermal fluids in geology is now widely recognized, but this was not always the case. Early interpretations of the rock record tended to be “lithocentric,” with fluids considered subordinate, or not considered at all (Yardley and Bodnar 2014). Perspectives on the presence and impact of hot aqueous fluids in the Earth evolved gradually. First came the accumulation of evidence for fluid circulation, through direct observation and analysis of the rock record. This led to a period (late 19th to early 20th centuries) during which hydrothermal fluids were commonly invoked as playing important roles, but the properties of such fluids were still essentially unknown. Next came empirical and thermodynamic descriptions of the bulk physical and chemical properties of fluids. Finally, in recent years, has come analysis of hydrothermal fluids at the molecular scale, such that our current understanding is rooted in fundamental, underlying controls.

Evidence for hot aqueous fluids within the Earth has been known since ancient times and was recorded in early historical descriptions of hot springs and sulfurous fumaroles. Most such descriptions through the Middle Ages focused on the therapeutic qualities of baths, but some early descriptions made explicit links between fumaroles and magmatism. During the 18th century in particular, recognition grew that vapors emanating from volcanoes and vents (Fig. 1A) are composed mostly of H₂O and other volatiles, and that degassing of vapor drives explosive eruptions (e.g., Spallanzani 1798).

Besides active hot springs and fumaroles, the other key line of evidence for hydrothermal fluids in the Earth was the occurrence of veins, especially in economic mineral deposits. As early as the 16th century, Georgius Agricola described mineralized veins and interpreted them as

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FIGURE 1 Early descriptions of hydrothermal geologic fluids and their record in the rocks. **(A)** In the early 19th century, fumaroles and hot springs provided evidence for a role of volatiles in magmatic settings. FROM DELLA TORRE (1805). **(B)** In the mid-16th century, Georgius Agricola described “veins, veinlets and seams in the rock” as being deposited by water that flowed through fractures. FROM AGRICOLA (1556).

products of hydrothermal fluids (FIG. 1B). He wrote that “the force of the water crushes and splits the brittle rocks” creating hydraulic fractures, and that “water runs and flows through them” (Agricola 1556). We now know that the majority of ore-forming settings are hydrothermal and that different ore deposit types represent distinct hydrothermal environments.

A key discovery that revealed direct evidence for fluids in Earth’s interior was the systematic description and interpretation of fluid inclusions made during the mid 19th century by Henry C. Sorby. Fluid inclusions are droplets of fluid trapped within a mineral, and, as such, they provide direct evidence that fluids were present when the mineral grew or when cracks in the mineral healed. Sorby (1858) realized that fluid inclusions record the physical and chemical conditions of the trapped fluid, and he differentiated various compositional types as well as relatively higher- versus lower-temperature fluids. Today, Sorby’s work is appreciated as remarkably prescient: most of his interpretations are regarded as essentially correct, and fluid inclusions are considered one of the best available tools to characterize hydrothermal fluids from the geologic past.

By the start of the 20th century, hydrothermal fluids were widely invoked in ore formation and other petrologic processes, but quantitative descriptions of the nature of the fluids were still mostly lacking. For example, in describing hydrothermal ore formation, Waldemar Lindgren wrote in 1907 that “at high temperature and pressure the behavior of the solutions changes in a marvellous degree,” and that “chemical reactions under ordinary surface conditions differ widely from those which prevail at great depths” (Lindgren 1907). But this view of hydrothermal fluids, as having anomalous—yet essentially unknown—properties was obviously frustrating. Hence, Norman Bowen later wrote that “to many petrologists a volatile component is exactly like a Maxwell daemon; it does just what one may wish it to do” (Bowen 1928). With the advent of hydrothermal experiments over the next decades, this situation changed dramatically.

Hydrothermal experiments kicked off at the start of the 20th century and ushered in a golden age in geochemistry and petrology. The center of this new field was the laboratory of Johannes van der Waals and colleagues in the Netherlands. New experimental labs spread rapidly into the geosciences. Already by the middle of the 20th century, experimental petrologists and physical chemists—including Bowen, George C. Kennedy, E. Ulrich Franck, George W. Morey and others—had laid the foundations for our current understanding of hydrothermal fluids. Their work provided fundamental data on the systematic relationships between pressure, temperature, fluid composition, and the physical properties such as density, heat capacity, and fluid-phase equilibria. These data fed thermodynamic models rooted in the statistical-mechanical insights of J. Willard Gibbs.

Today, as a result of experimental studies, we have extensive data on the hydrothermal properties of many “simple” (mostly binary) chemical systems (Valyashko 2008), though more complex systems are still generally not well studied and much remains to be done. One major obstacle that has become increasingly prominent in recent years is that our understanding of even “simple” chemical systems has commonly rested on descriptions of bulk fluid properties, whereas the identities of and reactions between actual chemical *species* in solution are less understood. The landmark Helgeson–Kirkham–Flowers equation of state for aqueous solutes (Helgeson et al. 1981) was a major advance in this regard, enabling modeling of fluid–rock reactions over wide ranges of temperature, although mostly at shallow-crustal pressures. This approach has now been extended to much higher pressures, into the deep crust, mantle, and subduction zones (Sverjensky et al. 2014). Nevertheless, in many cases, the chemical species that make up complex hydrothermal solutions remain elusive and uncharacterized.

At present, the study of hydrothermal fluid properties is undergoing another revolution: filling in the knowledge gaps at the molecular scale and, in the process, clarifying the factors that give rise to known bulk fluid properties. Analytical techniques that probe the molecular make-up and environment of solutes and their solvent include Raman spectroscopy and synchrotron X-ray techniques, such as X-ray absorption fine structure (XAFS) and X-ray absorption near-edge structure (XANES). Applications of these techniques to hydrothermal fluids, for example using the hydrothermal diamond-anvil cell, provides detailed revelations about the species present and how they reside within the solvent (Scholten et al. 2019). Molecular simulations provide complementary information and can be conducted at conditions that would be challenging or impossible by existing experimental techniques. As described below, the insights that we have obtained so far on fluid properties at

the molecular scale provide a clear framework for understanding what controls bulk fluid properties. As such, we are now in the era in which hydrothermal fluids should finally give up their secrets.

BASIC PROPERTIES OF HYDROTHERMAL FLUIDS

One of the main reasons that fluids play multiple key roles in geology is that the properties of fluids are extremely variable as functions of pressure (P), temperature (T), and composition. For example, at ambient T and P , liquid water is virtually incompressible; but as T and P approach the critical point of H_2O [the T and P at which properties of liquid and vapor converge, as discussed below] the compressibility diverges to infinity (!). Similarly, liquid water at ambient conditions is an excellent solvent for electrolytes but a rather poor solvent for nonpolar gases, whereas the opposite is true of water vapor. As such, even at equal T and P , the separation of H_2O into a higher-density liquid and lower-density vapor gives rise to radical contrasts in physical and chemical properties between fluid phases. For example, in boiling hydrothermal systems, a mineral such as quartz may be simultaneously precipitated by the liquid phase while being dissolved by the vapor phase (or vice versa) (Steele-MacInnis et al. 2012). Physical segregation of the two fluid phases—for example, by the greater buoyancy and lower viscosity of vapor compared to liquid—can, thus, disperse chemical components that are transported preferentially by vapor versus liquid, such as in the case of decoupling of gold from copper in hydrothermal fluids exsolved from magmatic melts (Heinrich et al. 2004).

Bulk Fluid Properties

Even in the “simplest” case of a single chemical component, such as pure H_2O , fluids exhibit remarkable variability of physical properties as functions of T and P . To some extent, this variability is qualitatively described by the ideal gas law, especially when temperature is high and pressure is low. But forces of attraction and repulsion, and other chemical interactions between molecules in the fluid, give rise to additional complexity, such as liquid–vapor immiscibility and criticality.

Density (or molar volume) is a fundamental property of the fluid and is strongly correlated to many other properties, including dielectric constant, viscosity, and the solubility of minerals. The ideal gas law tells us that fluid density decreases with increasing T and increases with increasing P : this gives rise to the general disposition of fluid *isochores* (contours of fluid density) (Fig. 2A) in P – T space. To these basic rules, we add insights from empirical observation: a liquid at ambient conditions is nearly incompressible but expands with increasing T ; a vapor at ambient conditions is highly compressible. In light of this, we can make two basic predictions. First, isochores of liquid and vapor must intersect one another, causing liquid–vapor immiscibility. Second, at some elevated T and P , the densities of liquid and vapor must ultimately converge. This T and P represents the *critical point*, where not only density but all physical and chemical properties of liquid and vapor become exactly equal, and the distinction between liquid and vapor ceases to exist. In a one-component system, the critical point is also the terminus of the *liquid–vapor curve*, or boiling curve, along which liquid and vapor coexist immiscibly (Fig. 2A).

From a geometric point of view, the main consequence of adding a component is to increase the thermodynamic variance (i.e., adding a “degree of freedom”) of each feature on the phase diagram. Hence, the liquid–vapor curve becomes an area of P – T space in a system of two components. Similarly, with an added component, the

critical point becomes a *critical curve*, which extends from the critical point of the first end-member component to the critical point of the second end-member component. In detail, the latter effect differs markedly depending on the type of solute added: electrolyte (salt) solutes tend to produce a critical curve with a shallow dP/dT slope that projects towards high temperatures, whereas nonelectrolyte solutes (e.g., molecular gases, or neutral, non polar species such as dissolved silica) produce a critical curve with a nearly vertical dP/dT slope (Figs. 2B and 2D). In addition, solutes directly affect all the physical properties of the resulting solution, including density, viscosity, and solubility of minerals. These effects can only be understood with attention to the molecular scale.

Fluid Properties at the Molecular Scale

At the molecular scale, the lower-density vapor phase is distinguished from the higher-density liquid by weaker intermolecular forces. In the vapor phase, each molecule is essentially independent, free-floating, and affected only by occasional collisions with its neighbors (Fig. 2A). In contrast, molecules in the liquid phase are highly interactive and, at ambient conditions, closely packed (Fig. 2A). A crucial feature of H_2O is the strong polarity of each molecule, which confers a strong intermolecular attraction between nearby molecules. Based on this, the behavior of added components and their effect on the properties of the fluid can be rationalized in terms of how these substances interact with H_2O (and other) molecules in solution. The closely packed molecules of the liquid phase are able to tightly shield charged particles in solution, which explains the great propensity of liquid water for dissolving electrolytes. In contrast, water vapor is a poor solvent for electrolytes because these solutes are ineffectively shielded, but it is an excellent solvent for nonpolar gases which prefer a spacious environment.

The dissolution of solutes—be they electrolytes, molecular gases, or silicate components—into an aqueous solution also has a significant impact on the molecular structure of the solvent, and, hence, on the properties of the fluid itself. The addition of electrolytes induces local constrictions of the solvent, as H_2O molecules cluster to form tight hydration shells, whereas addition of nonpolar gases causes the solvent to dilate as H_2O molecules are shouldered aside (Fig. 2B). These divergent effects of electrolyte versus nonpolar solutes essentially explain the divergent critical curves of water–“salt” versus water–“gas” systems: when electrolytes are added to an already dense liquid, the local hydration domains have a similar density to, and sit comfortably within, the surrounding liquid. In contrast, addition of electrolytes to a low-density vapor creates local hydration domains that are highly dissimilar to their surroundings in the vapor. Only a limited number of such domains can be sustained before physically separating as droplets of high-salinity liquid (Fig. 2B). In other words, the addition of salt causes condensation of liquid from an initially homogeneous vapor. As such, liquid–vapor immiscibility in a water–“salt” system occurs at relatively low pressures and up to high temperatures, overlapping with the region of vapor-like densities in the pure H_2O system (Fig. 2B).

In the case of nonpolar (gas) solutes, the opposite situation unfolds: addition of nonpolar solutes to the vapor is straightforward because the particles are already widely spaced. But addition of nonpolar solutes to the liquid creates cavities, as polar H_2O molecules are pushed aside to accommodate the standoffish solute. Again, the liquid is only capable of sustaining a limited number of such cavities before they coalesce to nucleate bubbles of vapor

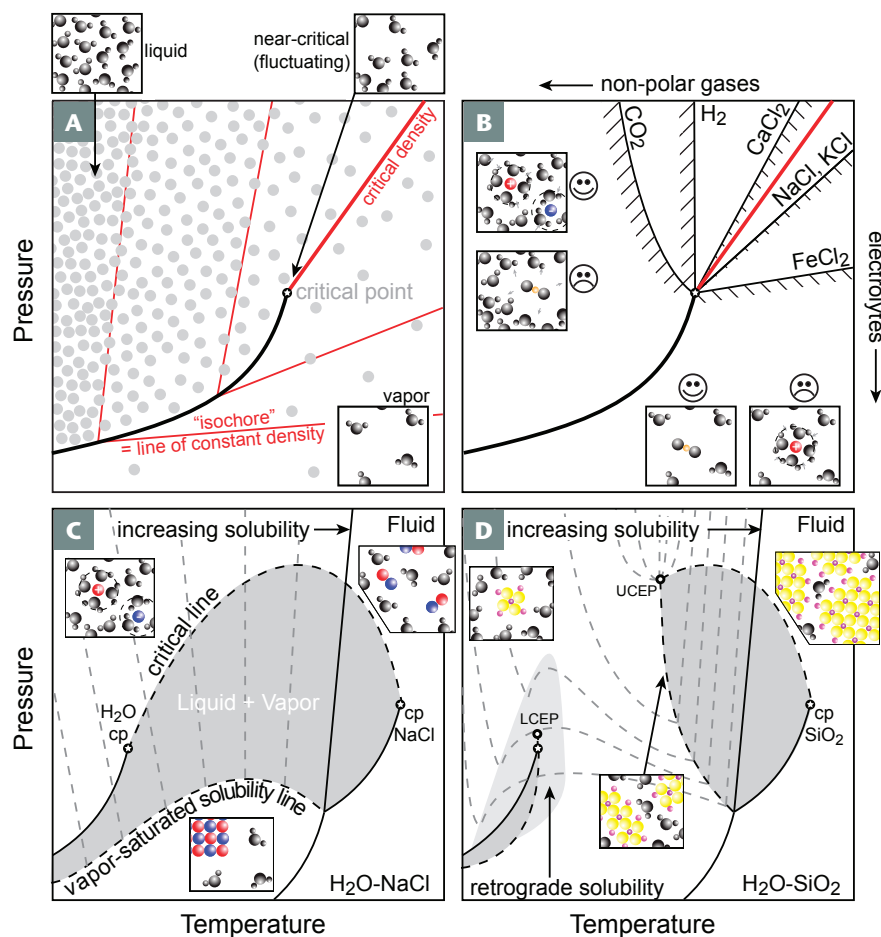


FIGURE 2 Properties of hydrothermal fluids, their relationship to molecular-scale phenomena, and the resulting phase equilibria of multicomponent fluids. **(A)** Schematic phase diagram for H₂O showing the liquid-vapor critical point, and particle density represented by grey circles. **INSET PANELS** show the general molecular environment in the liquid, the vapor and near the critical point. **(B)** Divergent critical curves of different binary water-salt and water-gas systems. For each, the hatched side of the line represents the two-phase (liquid + vapor) side. **INSETS** show the rationale: The liquid phase is a good solvent for electrolytes but struggles to dissolve molecular gases, giving rise to a steep critical curve and immiscibility at low T and high P . The vapor phase can readily dissolve gases but struggles to accommodate electrolytes,

giving rise to a shallow critical curve and immiscibility at high T and low P . **(C)** Basic phase equilibria of water-salt systems in which the salt is highly soluble, such as NaCl. The dashed lines represent solubility of the salt in the aqueous liquid, and solubility increases monotonically with increasing T . Abbreviation: cp = critical point. **(D)** Basic phase equilibria of a water-salt or water-rock system, in which the salt or silicate is sparingly soluble in H₂O. The dashed lines represent solubility, and solubility overall increases with increasing T , but there is a region of P - T space in which solubility decreases with increasing T (labeled retrograde solubility). Abbreviations: cp = critical point; LCEP = lower critical endpoint; UCEP = upper critical endpoint.

(or, at higher pressures, a second liquid). In other words, the addition of a nonpolar gas causes exsolution of an initially homogeneous liquid (Fig. 2B). Hence, immiscibility in the water-gas systems occurs at relatively low temperatures and up to very high pressures, in the region of liquid-like densities of H₂O.

Besides the differences in initial trajectory of the critical curve, the other key difference between solute types is the continuity—or lack thereof—of the critical curve. This feature is correlated to the trends in solubility of a solute, and, hence, to the strength of attraction (or repulsion) with H₂O. In the case of highly soluble salts such as NaCl, solubility increases monotonically with T and the critical curve extends unbroken from the critical point of H₂O to that of NaCl (Fig. 2C). This continuity seems to reflect the fact that as H₂O becomes a less effective solvent for ions with increasing T it can still dissolve NaCl comfortably and progressively in the form of neutral solute species.

In contrast, in the case of some salts (e.g., Na₂SO₄) or silicate components (e.g., SiO₂), solubility decreases with increasing T , especially in the vicinity of the critical point of H₂O (Fig. 2D). This behavior, which is at odds with a general

trend of increasing entropy with increasing T , reflects the fact that mineral solubility is commonly highly dependent on solvent density, and density decreases strongly with increasing T in the vicinity of the critical point (Brooks and Steele-MacInnis 2019). As a result, the critical curve is intersected by the solubility curve, resulting in two critical endpoints and a bipartite immiscibility field comprising regions of liquid-vapor and liquid-liquid immiscibility. The specific molecular-scale phenomena that control this behavior are only partially understood, but evidence suggests that polymerization or clustering of solutes in the aqueous phase (i.e., the formation of species that resemble the molten salt or silicate melt) is a precursor to the onset of liquid-liquid immiscibility (Manning et al. 2010; Reimer et al. 2015).

In the case of fluids at or near the critical point, the statistical-mechanical view is that properties vary and fluctuate widely between shifting microdomains of different densities (Fig. 2A). This gives rise to extreme variability in the behavior of solutes, and the effect of solutes on fluid properties, when the system is subjected to even very minor changes in temperature or pressure (Driesner 2013).

Along the critical curve of a binary system, the variation of physical properties is somewhat subdued compared to the single-component critical point, but the region of anomalous physical properties may be greatly expanded. This gives rise to wide swaths of P - T space in which hydrothermal fluids exhibit a heightened ability to drive heat and mass flux (Klyukin et al. 2016). In systems with a discontinuous critical curve, such as H_2O - SiO_2 , the upper critical endpoint (UCEP) (Fig. 2D) also confers anomalous properties to the fluid (Hunt and Manning 2012), resulting in unexpected and unintuitive properties of deep fluids compared to those at ambient or even at relatively shallow hydrothermal conditions (Manning 2018).

Much of how solutes affect the physical and chemical properties of fluids can be rationalized in terms of molecular-scale interactions. In the case of electrolytes, constriction of the solvent generally renders a saline solution higher in density and viscosity, whereas molecular gas solutes have the opposite effects. Dissolved molecular gases also generally render the solvent less effective at dissolving metals and silicate minerals. Electrolyte solutes have mixed effects on mineral solubility: chloride is a highly effective ligand for mobilizing many metals, and saline fluids commonly show enhanced solubilities of rock-forming minerals (Brooks and Steele-MacInnis 2019). But, some minerals, such as quartz, also show decreasing solubility with increasing salinity because dissolved ions compete with silica for any available H_2O (Brooks and Steele-MacInnis 2019). In the case of deep fluids, dissolved silica can strongly influence the physical properties of the solution as a result of polymerization. And, dissolved silica can itself function as a ligand, enhancing the solubility of other components such as the high field-strength elements that are nominally insoluble in dilute H_2O (Manning et al. 2008).

FLUIDS IN THE EARTH

Geologic fluids include a range of compositional types, which circulate over different ranges of temperature and pressure in the Earth. In general, geologic fluids in the near-surface environment have been categorized according to source region as meteoric, seawater, basinal (connate), metamorphic, and magmatic (Yardley and Bodnar 2014) (Figs. 3A, 3B). Each of these five fluid types is capable of

circulating into Earth's interior and over a range of P and T , but major differences exist between these ranges for different fluid types. Each fluid type also contributes to the formation of distinct hydrothermal ore deposit types.

Meteoric Water

Meteoric water has interacted recently with the atmosphere and includes that derived from precipitation at Earth's surface, as well as fresh surface water. The composition is generally very dilute [relative to dissolved salt content]. Meteoric water is commonly heated in geothermal settings up to $\sim 350^\circ\text{C}$, usually limited by the brittle-ductile transition of felsic rocks and the approach to the critical temperature of a dilute aqueous solution ($\sim 375^\circ\text{C}$); heating to supercritical temperatures sometimes occurs (Chambefort and Stefánsson 2020 this issue). Boiling of meteoric water in geothermal settings is commonplace. Ore deposits in which meteoric water plays a key role include many epithermal Au and/or Ag deposits.

Seawater

Seawater is that from Earth's oceans and is modestly saline. Seawater, with a somewhat higher critical temperature as a result of higher salinity, circulates to $>400^\circ\text{C}$ in submarine hydrothermal settings and undergoes immiscibility in the deep roots of such systems (Schwarzenbach and Steele-MacInnis 2020 this issue). These hydrothermal systems commonly give rise to a class of ore deposit called volcanogenic massive sulfide (VMS) deposits.

Basinal or Connate Water

Basinal or connate water, sometimes referred to simply as "saline groundwater," is that which has resided in rock or sediment over long duration and has acquired a higher solute load through evaporative concentration and/or dissolution of minerals. Basinal brines mostly reside in rocks of relatively lower temperatures but are occasionally drawn into higher-temperature systems through convection, such as when magma is emplaced into sedimentary country rocks. Circulation of the latter three fluid types is generally limited to pressures of a few tens of mega-Pascal (MPa). Basinal brines are the key ore-forming fluid in the carbonate-hosted Pb-Zn deposits called Mississippi Valley Type (MVT).

Metamorphic Fluids

Metamorphic fluids are derived from devolatilization reactions and tend to be only moderately saline but are enriched in molecular gases, particularly CO_2 . Metamorphic fluids are generated over a wide temperature range by progressive devolatilization (Evans and Tomkins 2020 this issue), most voluminously from greenschist through middle amphibolite facies. Pressures of metamorphic fluid release and circulation range up to at least 1 GPa, and the elevated concentrations of molecular gases in these fluids are key to enabling immiscibility in metamorphic settings. Metamorphic fluids are widely invoked in the formation of a diverse family of orogenic Au deposits.

Magmatic Fluids

Magmatic fluids are those exsolved from melts and exhibit a wide range of compositions from gas-rich in deeper and more mafic settings through to aqueous and saline in shallower and more felsic settings. Magmatic fluids are degassed at magmatic temperatures up to $>1,000^\circ\text{C}$, and pressures ranging from surficial up to a few hundred MPa; again, the elevated concentrations of electrolyte solutes result in widespread liquid-vapor(-melt) immiscibility in these settings. Magmatic fluids are a key ingredient in the formation of porphyry-type ore deposits of Cu, Mo and/or Au (Audétat and Edmonds 2020 this issue).

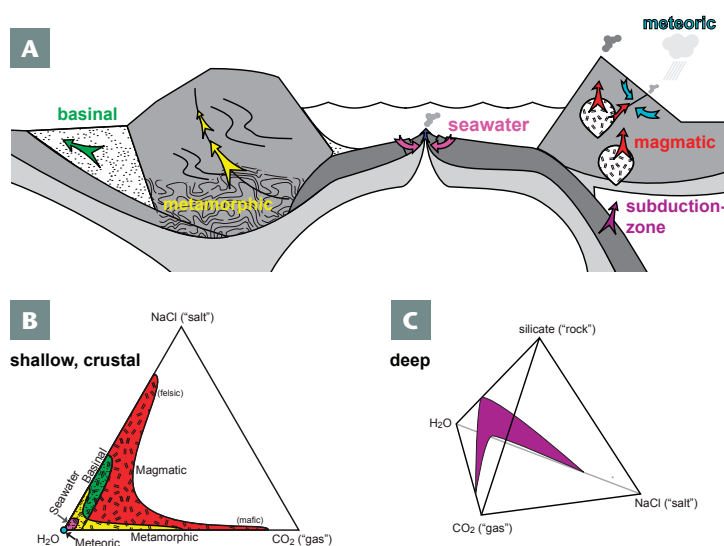


FIGURE 3 Fluids in the Earth. (A) Schematic cross section, not to scale, showing some of the main geologic settings of the major fluid types. (B) Ternary water–"salt"–"gas" space showing the compositional types of crustal fluids. AFTER YARDLEY AND BODNAR (2014). (C) Quaternary diagram of water–"salt"–"gas"–"rock" space, showing the general nature of deep fluid compositions enriched in silicate components. AFTER MANNING (2018).



FIGURE 4 Hydrothermal veins.

(A) Crosscutting quartz veins with K-feldspar alteration haloes hosted in diorite from the Ray porphyry copper deposit (Arizona, USA). (B) Quartz veins with muscovite envelopes hosted in metapelitic schist from the Panasqueira tungsten deposit (Portugal). In both A and B cases, the veins represent hydraulic fractures produced by overpressured magmatic hydrothermal fluids.

Both of the two latter fluid types (metamorphic and magmatic) are generated in situ, and, thus, are capable of generating high fluid overpressures, causing hydraulic fracturing and thereby creating fluid pathways through otherwise low-permeability rocks (Fig. 4).

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Fluids Deep Within Earth

Deeper within the Earth, hydrothermal fluids include those of primitive (mantle) origin, and fluids generated by dehydration reactions in subduction zones (Manning and Frezzotti 2020 this issue). The latter may be considered a subtype of the metamorphic category but are distinctive in terms of physical and chemical properties, because of the enhanced solubility of the rock-forming minerals (Fig. 3C) and the anomalous fluid properties that are imparted by the upper critical end-point (Hunt and Manning 2012; Manning 2018) (Fig. 2D) at the extreme pressures encountered deep in Earth's interior. For example, aqueous fluids at the conditions of subduction zones may dissolve enough silicate components to have major impacts on the physical properties of the solution (Audétat and Keppler 2004), and may even become completely miscible with silicate melts (Shen and Keppler 1997). At such conditions, our intuition regarding properties of fluids based on shallower veins deteriorates, and deep fluids must be regarded as fundamentally distinct from their shallower counterparts.

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