



Immiscible CO₂-H₂O fluids in the shallow crust

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[1] The significance of a single CO₂-H₂O fluid phase is well known for metamorphic systems, and CO₂-H₂O immiscibility is explicit in fluid inclusion literature, especially regarding hydrothermal ores. Complex multiphase CO₂-H₂O behavior exists over wide temperature and pressure ranges overlapping other important geochemical processes. The character and physical-chemical properties of multiple phases possible for CO₂ and H₂O, and the potential impact of these coexisting phases on geochemical processes in the crust, are not broadly appreciated. We propose that immiscible supercritical CO₂ fluid and a liquid rich in H₂O coexist in the shallow crust, to 400°C and 300 MPa, and that interactions among the two fluids and host rock are significant processes that produce recognizable geochemical and textural evidence. Supercritical CO₂ fluids bring potential complexity to fluid-rock systems by influencing aqueous reactions via carbonic acid equilibria, penetrating complex geometries inaccessible to aqueous fluid, and dissolving and redistributing metals as organometallic compounds. The distal margin of a contact metamorphic aureole is one example we discuss in which interaction between two disparate CO₂-H₂O fluids controls H₂O activity and the progress and distribution of metamorphic hydration reactions. In another example, supercritical CO₂ produces acidity, carbonate saturation, and silica supersaturation in brine. Separation and emplacement of this brine into a rock-dominated system buffered to neutral pH enhances precipitation of carbonates and quartz, chalcedony, or amorphous silica in veins. Other possible examples of CO₂-H₂O fluid immiscibility coupled with multiphase fluid-rock interactions are clay desiccation, diagenetic and postdiagenetic silicate reactions, origin and distribution of carbonate cements in sedimentary basin sandstones, fluid-mass transfer, and anthropogenic CO₂ sequestration.

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1. Introduction

[2] The potential significance of two fluid phases has been established for a limited number of geochemical processes occurring within the crust. The most important include CO₂-H₂O phase equilibria in low to moderate prograde metamorphism [Bowers and Helgeson, 1983b], flow and transport [Yardley and Bottrell, 1988] and veining [Sisson *et al.*, 1981] in metamorphic rocks, and fluid inclusions in hydrothermal ore deposits [Roedder and Bodnar, 1997]. Over a broad range of temperature and pressure within the shallow crust, up to 400°C and 300 MPa, multiple CO₂-H₂O phases exist in equilibrium. Yet, the character and physical-chemical properties of these multiple phases, and their potential impact on a broad range of geochemical processes in the crust, have not been evaluated or appreciated by the larger geologic community. Geochemical reaction models, for example, include CO₂ as a major ligand and precipitate, but have generally not included multiphase fluid constraints. Models that invoke extraction by and migration in supercritical CO₂ for the origin of atypical hydrocarbons and reduced carbon associated with alkaline igneous complexes, Archean and Carlin-type gold deposits, and mercury deposits [Gize and Macdonald, 1993] are relatively unknown (Table 1).

[3] We propose that immiscible supercritical CO₂ fluid and a liquid rich in H₂O coexist in many environments of the shallow crust, up to 400°C and 300 MPa. We suggest that the two fluids and host rock interact chemically and mechanically, and that the significance of these interactions awaits broad recognition. We further suggest that these multiphase fluid-rock interactions produce geochemical and textural evidence that may be interpreted within the paradigms we propose. Many potential

examples illustrate the inevitability of multiphase behavior for a host of common shallow geological environments (Table 1). Examples include effects on clay minerals and other silicates during and after diagenesis [Huang and Longo, 1994], origin and distribution of carbonate cements and veins in sedimentary basin sandstones, fluid-mass transfer in the crust, and developing issues of geologic sequestration of anthropogenic carbon [Kaszuba *et al.*, 2003, 2005]. We examine two systems here: origin of some quartz-carbonate veins and talc crystallization in a contact metamorphic aureole.

[4] While oxidation state plays an important role in the composition of these fluids, we limit our discussion to the CO₂-H₂O system and do not address CH₄. After H₂O, CO₂ is the most abundant volatile in the Earth's crust [Symonds *et al.*, 1994], and fluid inclusion data support the broad importance of CO₂-H₂O fluids as opposed to mixtures with CH₄ [Diamond, 2001]. A suitable treatment of the complexities of CO₂-H₂O fluids relative to CH₄-H₂O fluids in geologic environments requires a separate paper altogether. We begin this paper by assessing the relevant phase equilibria for CO₂ and H₂O in the shallow crust and examining the significance of CO₂-rich supercritical fluid behavior relative to a liquid rich in H₂O.

2. CO₂-H₂O Phases in the Shallow Crust

[5] Geologically relevant fluids may exist in a supercritical state above a unique critical temperature and pressure. In this state, the fluid possesses properties of both gas and liquid. H₂O is a supercritical fluid above 374.2°C and 22.05 MPa, whereas CO₂ is a supercritical fluid at much lower conditions (31.1°C and 7.38 MPa). In mixtures of CO₂ and H₂O, single and multiple phases composed of gas-, liquid-, and supercritical-rich

Table 1. Geologic Environments With Immiscible Fluids^a

Geologic Environment	Examples	Process
Thermal aureoles in siliceous carbonate rocks	Alta Stock Aureole, Utah, US [<i>Cook and Bowman, 2000</i>]	CO ₂ -H ₂ O fluids segregate in outer aureole to control H ₂ O activity and tremolite- and talc-forming reactions [<i>Bowman and Pollington, 2004; Pollington et al., 2005</i>].
	Bufo del Diente aureole, Mexico	CO ₂ -H ₂ O fluids segregate in inner aureole and move separately, imposing different stable isotope patterns along flow paths [<i>Heinrich et al., 2004</i>].
Seafloor hydrothermal systems	JADE and CLAM sites, Okinawa Trough Back arc Basin	Formation and segregation of two fluids at submarine hydrothermal vent [<i>Sakai et al., 1990a, 1990b</i>] possibly due to CO ₂ -H ₂ O phase equilibria, not volcanic fluctuations or vesicle alteration in volcanoclastic rocks.
	Mariana Forearc	High pH of springs located on serpentinite mud volcanoes [<i>Mottl et al., 2004</i>] possibly due to loss of CO ₂ .
Degassing magma and fumarolic discharges	White Island Volcano, Taupo volcanic zone, New Zealand [<i>Giggenbach and Sheppard, 1989</i>]	Two fluid phases (brine and supercritical CO ₂) affect temporal evolution of fumarolic discharges and subsurface brine-vapor plumbing system within volcanic edifice
Sedimentary basins	Carbonate cements: Tertiary Sandstones, Northern Apennines, Italy [<i>McBride et al., 1995</i>] and Breathitt Formation, eastern Kentucky, US [<i>Milliken, 2001</i>]	Physical heterogeneity of two fluids controls spatial and chemical heterogeneity of calcite cement on a range of scales, from thin section to outcrop (to sedimentary basin?)
	Deep burial diagenesis, Kootenay Formation, southeastern British Columbia and southwestern Alberta	Pressure-temperature conditions of CO ₂ -H ₂ O fluid immiscibility and deep burial diagenesis overlap. Reactions between clay and carbonate minerals during deep burial diagenesis produce CO ₂ in quantities sufficient to produce fluid immiscibility [<i>Hutcheon et al., 1980</i>].
Economic mineral deposits	Quartz-carbonate veins, Coeur d'Alene district, US [<i>Rosenberg and Larson, 2000; Fleck et al., 2002</i>]	Supercritical CO ₂ buffers aqueous <i>f</i> CO ₂ , providing carbonate from small fluid volumes; concomitant brine acidity promotes silica supersaturation.
	Porphyry Cu deposits, Butte porphyry Cu, Montana, US	5 mol% CO ₂ in early magmatic-hydrothermal fluid [<i>Rusk et al., 2000</i>] leads to immiscibility as fluid evolves to lower pressure and temperature.
	“Gold-only” provinces and deposits	CO ₂ plays a critical role during gold transportation by buffering the fluid in a pH range where elevated gold concentration can be maintained by complexation with reduced sulphur. While not critical in transportation, CO ₂ -H ₂ O fluid immiscibility may be important to gold deposition [<i>Phillips and Evans, 2004</i>].
	Archean and Carlin-type gold deposits	Reduced carbon associated with Archean and Carlin-type gold deposits may result from CO ₂ -rich fluids interacting with host rock [<i>Gize and Macdonald, 1993</i>].
Oil and gas reservoirs	Hg deposits	Unusual hydrocarbons in Hg deposits are a manifestation of supercritical CO ₂ interacting with sedimentary organic matter [<i>Gize and Macdonald, 1993</i>].
	Lisbon field, Utah	Immiscible CO ₂ -H ₂ O fluids generated from interbedded, organic-rich shale at intermediate levels of thermal maturity [<i>Cappa and Rice, 1995</i>]
	Compositionally atypical hydrocarbons	Some hydrocarbons reported in igneous systems may contain a biogenic fraction resulting from CO ₂ -rich fluid extraction from country rock [<i>Gize and Macdonald, 1993</i>].

^aSupercritical CO₂ and a liquid rich in H₂O.

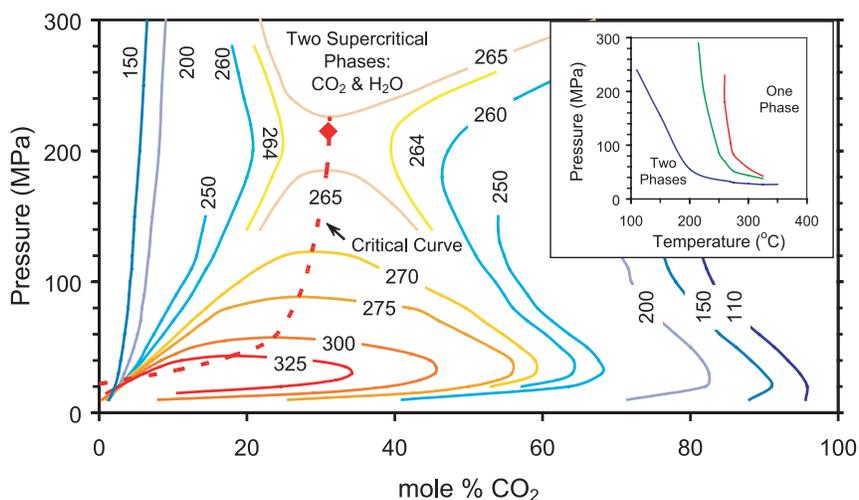


Figure 1. Pressure- X_{CO_2} diagram depicting fluid compositions for the system CO_2 - H_2O , including critical curve (dashed red line) and consolute curves for 110 to 325°C [after *Takenouchi and Kennedy*, 1964]. The data of *Takenouchi and Kennedy* [1964] were selected as internally consistent for these pressures and temperatures, as discussed by *Blencoe et al.* [2001]. Bifurcation or saddle point (diamond) marks a division in phase behavior. Solvii below this point mark regions where two phases (a supercritical fluid rich in CO_2 and a liquid rich in H_2O) exist, whereas two supercritical fluids occupy regions above this point (i.e., at higher pressure). Inset presents same data in pressure-temperature coordinates for 20 (red line), 10 (green line), and 5 (blue line) mol% CO_2 . It is widely believed that CO_2 in hydrothermal solutions rarely exceeds 20 mol% [*Holland and Malinin*, 1979]. Early fluids in the Butte, Montana, magmatic-hydrothermal system contained ~ 5 mol% CO_2 , as evidenced by aqueous fluid inclusions [*Rusk et al.*, 2000].

regions can exist in equilibrium. For the CO_2 - H_2O system (Figure 1), critical points and phase relationships have been independently established [*Takenouchi and Kennedy*, 1964; *Sterner and Bodnar*, 1991; *Blencoe et al.*, 2001; and references therein]. A notable feature of the system is the saddle or bifurcation point (265°C and 215.0 MPa), where a division in phase behavior occurs. Saddle points commonly occur when the critical properties of the two mixture components differ substantially [*Van Konynenburg and Scott*, 1980].

[6] At low to moderate temperatures below the saddle point, both branches of the two-phase envelope rise steeply with increasing pressure (e.g., 150 through 264°C in Figure 1), then diverge at very high pressures. The two phases that coexist within the envelope are a supercritical fluid rich in CO_2 and a liquid rich in H_2O . As the temperature of the system is further increased, the two-phase envelope becomes a closed dome. A single-phase CO_2 - H_2O supercritical fluid exists outside this region. If pressure is subsequently increased above the saddle point, the single fluid phase encounters another two-phase envelope. This envelope contains two supercritical fluids, a behavior known as gas-gas phase equilibrium [*Gordon*, 1972], though the phrase is perhaps misleading.

[7] Several studies examine the effect of NaCl on the CO_2 - H_2O system [*Anovitz et al.*, 2004; *Duan et al.*, 2006, and references therein], but only a limited range of pressures, temperatures, and compositions have been experimentally evaluated. In general, NaCl (and other salts) in the fluid shift consolute curves to higher temperature and pressure [e.g., *Takenouchi and Kennedy*, 1965; *Bowers and Helgeson*, 1983a, 1983b; *Gehrig et al.*, 1986; *Joyce and Holloway*, 1993], expanding the stability field at which two fluids coexist. Pressure has the opposite effect, decreasing the size of the CO_2 - H_2O solvus (Figure 1). The theoretical work of *Bowers and Helgeson* [1983b] evaluates both NaCl and pressure effects on the interactions between silicate reactions and CO_2 - H_2O equilibria at temperatures in excess of 400°C and 200 MPa.

[8] The significance of a single-phase CO_2 - H_2O fluid is well-known for metamorphism and hydrothermal ore genesis [e.g., *Labotka*, 1991; *Sterner and Bodnar*, 1991]. However, important geochemical processes also take place at temperatures, pressures, and CO_2 concentrations where two phases, supercritical CO_2 fluid and a liquid rich in H_2O , exist (Figure 2). Supercritical CO_2 , with its distinctive physical and chemical properties, pro-

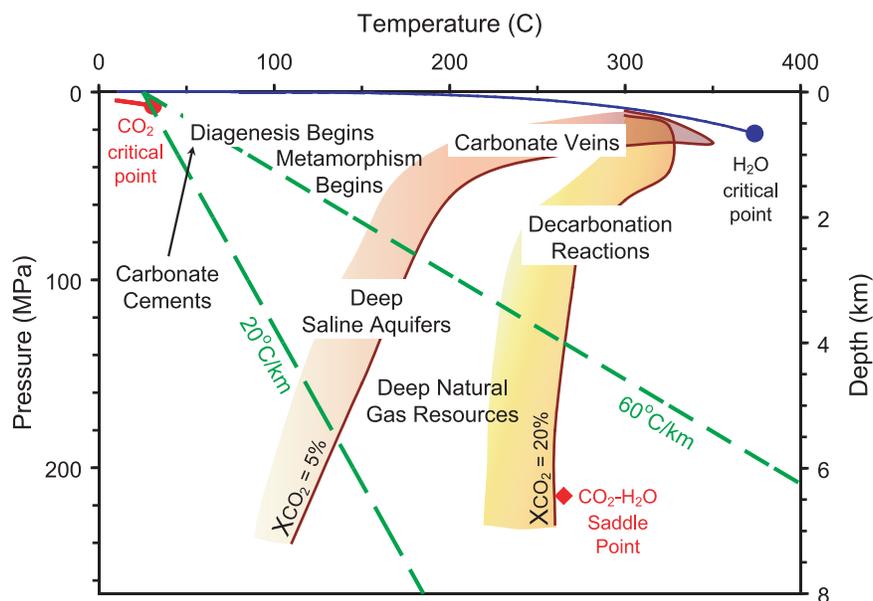


Figure 2. Pressure-temperature diagram depicting critical curves and points for pure CO₂ (31°C, 7.38 MPa) and H₂O (374°C, 22.05 MPa). Saddle point for binary system CO₂-H₂O (diamond) is plotted as a point of reference to Figure 1. Geothermal gradients for basins exhibiting normal (20°C/km) and high (60°C/km) heat flows are plotted (dashed lines), and approximate regions at which important geochemical processes begin to occur are labeled. The 5 and 20 mol% CO₂ curves from Figure 1 (inset) are reproduced to illustrate the broad range of geologic conditions at which immiscible supercritical CO₂ and a liquid rich in H₂O may exist together (regions extending to the left of each curve and its shading).

vides added complexity with important implications for geologic and geochemical processes.

3. Special Geochemical Properties of Supercritical CO₂

[9] The density of supercritical CO₂ varies continuously (approximately 0.1 to 1.1 g/cm³) over a broad range of geologically relevant temperatures (to 400°C) and pressures (to 300 MPa) [Clifford, 1999]. Supercritical CO₂ density decreases with temperature and increases with pressure, exhibiting gas-like to liquid-like characteristics. To a first approximation, the ability of a solvent to dissolve compounds is related to its density. High, liquid-like densities achievable in supercritical CO₂ permit substantial solubilities [Clifford, 1999]. In addition to liquid-like density and solvent strength, supercritical CO₂ possesses gas-like transport properties of viscosity and diffusivity [McHugh and Krukonis, 1994] that strongly contrast with a coexisting liquid rich in H₂O. With a viscosity 1/10 that of H₂O, supercritical CO₂ will penetrate matrices of low permeability more readily than a liquid rich in H₂O. Additionally, low viscosity leads to considerably higher diffusivity of solutes in supercritical CO₂ than in H₂O [Hitchen and

Dean, 1993]. The viscosity and diffusivity exhibited in supercritical CO₂ result in faster diffusion of solutes into or out of complex pore geometries of sedimentary and metamorphic rocks compared to analogous aqueous systems.

[10] Dissolution of metals by “neat” (i.e., no dissolved H₂O or other compounds) supercritical CO₂ is inefficient because of a charge neutralization requirement and weak solute-solvent interactions [Smart et al., 1997; Wai and Wang, 1997; Wang et al., 2003]. Dissolution of polar molecules in nonpolar supercritical CO₂ is enhanced by dissolved H₂O (Figure 1) acting as a modifier or “cosolvent”. Dissolved H₂O also affects the density and viscosity of supercritical CO₂. For example, the density of supercritical CO₂ fluid containing 0.3 mol% H₂O changes between 1% to as much as 10% from that of pure CO₂, depending on pressure and temperature [Zhang et al., 2001]. The general affect of dissolving any polar cosolvent in supercritical CO₂ is to shift the solubility, density, and viscosity characteristics of the supercritical CO₂ toward that of the polar fluid.

[11] Organic ligands functioning as chelating agents that form organometallic complexes also enhance solubility and extraction of alkali metals,

transition metals, and lanthanides with supercritical CO₂ [Wai *et al.*, 1997; Burford *et al.*, 1999; Mochizuki *et al.*, 2000]. In the Earth's crust, organic matter may react with metals to form organometallic compounds that are soluble in supercritical CO₂ [Darr and Poliakoff, 1999]. The potential importance of organometallic compounds is well known for some hydrothermal solutions, especially sedimentary basin waters and oilfield brines [Seward and Barnes, 1997]. But while the geologic community has evaluated qualitative aspects of organic solubility by supercritical CO₂ [Landais and Gize, 1997], quantitative evaluation has only begun. Acetyl acetone, for example, effectively complexes and dissolves metals into supercritical CO₂ [Lagalante *et al.*, 1995]. Acetate (ethanoate) is a common ligand in ore fluids as well as sedimentary basin and oilfield brines [Giordano, 1994; Lewan and Fisher, 1994]. Acetate has a hydroxyl group which is readily deprotonated/protonated depending on fluid pH. Acetyl acetone undergoes tautomerization [Park and Turner, 2006] to produce a structure similar to acetate with the ability to deprotonate one of the oxygens. The term tautomerism designates a rapid and reversible interconversion of isomers by the actual movement of electrons as well as one or more hydrogen atoms. Both structures produce a similar bidentate ligand structure that can complex with metals. The efficacy of acetate to complex and dissolve metals in supercritical CO₂ is unknown.

[12] The synergy of H₂O cosolvent and organometallic complexes in supercritical CO₂ is illustrated in a laboratory study evaluating metal extraction efficiencies in supercritical CO₂ [Heltai *et al.*, 2000]. Lake sediments containing heavy metals and 8.8% organic matter were reacted with neat supercritical CO₂ at 80°C and 27.0 MPa, temperature-pressure conditions consistent with those found in oilfield reservoirs and deep sedimentary basins. Neat supercritical CO₂ extracted and dissolved ppm levels of the geochemically important elements Al, Fe, Mg, Ca, Pb, Ni, Cr, Zn, and Ba. With H₂O added, extraction and dissolution of Fe, Mg, Ca and Zn into supercritical CO₂ increased by factors of 2 to 10. Extraction and dissolution of Pb, Ni, Cr, Mo and especially Al was greatest in neat supercritical CO₂.

[13] Possibly the most significant impact of a supercritical CO₂ fluid is the potential to affect chemical equilibria in coexisting aqueous systems via carbonic acid equilibria. A decrease of 1 to 2 pH units was observed in brine reacted with supercrit-

ical CO₂ and rock in hydrothermal experiments [Kaszuba *et al.*, 2003, 2005]. Supercritical CO₂ fluid provided a reservoir for generating carbonic acid and buffering aqueous carbonate fugacity that is orders-of-magnitude greater than comparable volumes of CO₂ gas. Subsequent discharge of CO₂ increased pH in the brine by ~3 units, with potential consequence for mineral precipitation.

4. Supercritical CO₂ and Immiscible H₂O in Geologic Environments

[14] A few experimental studies provide evidence of geochemical reaction among supercritical CO₂, H₂O, and rocks of the shallow crust. Examination of smectite and chlorite formation at pressures and temperatures of deep sedimentary basins (100 to 200°C and at least 100 MPa, Figure 2) suggests that chlorite may crystallize at high XCO₂ and in the presence of two fluids, supercritical CO₂ and a liquid rich in H₂O, whereas smectite crystallizes at low XCO₂ [Huang and Longo, 1994]. The diagenetic implications of this observation remain unexplored. Evaluation of processes relevant to geologic sequestration of anthropogenic carbon indicates that supercritical CO₂ is a buffering reservoir for aqueous carbonate, a process that may also be important in the generation of large amounts and heterogeneous distributions of calcite cement in some sandstones and veins [Kaszuba *et al.*, 2003]. Given this experimental evidence for multiphase interaction, reexamination of relevant natural systems for evidence of like processes of geochemical reaction, material transport, and phase stability is appropriate (Table 1). Textural evidence may include heterogeneous or anomalously distributed mineralization, such as metamorphic dehydration reactions in distal margins of thermal aureoles and cements in clastic sedimentary rocks. Potential geochemical evidence may include mass transfer in veins and fractures and anomalous distributions of stable isotopes and trace elements due to partitioning between two fluids. We discuss two examples that we believe display some of these aspects, origin of some quartz-carbonate veins and talc mineralization in a contact metamorphic aureole, in order to explore potential implications for previously unrecognized CO₂-H₂O phase equilibria.

4.1. Quartz-Carbonate Veins

[15] Quartz veins are present in a considerable number of geologic environments, including metamorphic rocks from all levels of the crust, pegma-

tites, hydrothermal systems, structurally deformed rocks, and sedimentary basins. Veins are evidence of mass transfer and form by a variety of processes. In regionally metamorphosed rocks, for example, they form by large scale fluid flow through regional fracture systems, local diffusion through stagnant pore fluids, and local fluid flow from wallrocks to fractures [Ague, 2005]. In the classic case with hydrothermal fluids, quartz precipitates in veins because silica solubility decreases in fluid that cools and depressurizes along a fracture flow path [Fyfe *et al.*, 1978].

[16] Concomitant with carbonate mineralization in experimental acidic brine-supercritical CO₂ systems, aqueous SiO₂ concentrations doubled from about 3 millimole/kg (near quartz saturation) to greater than 6 millimole/kg (above chalcedony saturation) [Kaszuba *et al.*, 2005]. Aqueous SiO₂ concentrations increased via dissolution of silicates and apparent inhibition of quartz (and other silicates) precipitation. Silica super-saturation and inhibition of quartz precipitation were also noted for the mixing of hydrothermal solutions with seawater at mid-ocean ridge vents [Janecky and Seyfried, 1984]. These phenomena were attributed to kinetics of silica polymerization and precipitation under acidic conditions, assumptions consistent with recent experimental results [Icopini *et al.*, 2005]. Phase separation and subsequent emplacement of an acidic, carbonate saturated, and silica super-saturated brine into a rock-dominated system buffered to more neutral pH may enhance precipitation of carbonates and quartz, chalcedony, or amorphous silica as veins or cements, depending on the permeability structure of the host rock. Similarly, CO₂ loss or phase separation with decreasing pressure can substantially increase pH and result in massive vein or scale formation that greatly exceeds the amount possible due to aqueous carbonate solubility.

4.2. Contact Metamorphic Aureoles

[17] The thermal aureole of the Alta stock is a classic example of a granitic intrusion providing heat and water to metamorphose silicious dolostones into marbles [Moore and Kerrick, 1976; Cook and Bowman, 2000]. A prograde isograd sequence of talc, tremolite, forsterite, and periclase is observed in the carbonate rocks of the Alta thermal aureole with proximity to the igneous contact. These minerals are produced by decarbonation reactions such as



that yield calcite marble and generate copious amounts of CO₂. Decarbonation reactions, fluid composition, and fluid infiltration are well understood in the marbles close to the igneous contact of the Alta stock (i.e., the forsterite and periclase zones) [Bowman *et al.*, 1994; Cook and Bowman, 1994, 2000; Cook *et al.*, 1997]. Processes and mechanisms controlling fluid composition and mineral reaction in the inner aureoles of other contact metamorphic systems like the Alta aureole are generally well-understood [e.g., Ferry, 1994; Ferry *et al.*, 2002].

[18] New field, petrologic and analytical data from the outer Alta aureole (i.e., the talc and tremolite zones) indicate that it differs significantly from the inner aureole [Bowman and Pollington, 2004; Pollington *et al.*, 2005]. For example, the distribution and abundance of talc is very heterogeneous on several scales, does not define a regular isograd surface (unlike the inner forsterite and periclase zones), and appears controlled by stratigraphy at several scales (<1 meter stratigraphic interval), not bulk composition. Preliminary measurements indicate that extent of reaction (that is, reaction progress) in the talc zone is less than 10% [Bowman and Pollington, 2004], a value much less than is measured in the other zones. The distinct heterogeneity in the distribution and abundance of talc (independent of bulk composition) indicates significant heterogeneity in the XCO₂ values of pore fluids on several scales in the talc zone that are not related to distance from the igneous contact. These heterogeneities in pore fluid composition are more important than temperature and bulk composition in determining the distribution of talc in the outer aureole. Consequently, the processes and mechanisms responsible for heterogeneities in pore fluid composition at the lower temperature conditions of the outer aureole may be fundamentally different from those in the inner aureole.

[19] Conventional thought attributes these phenomena to primary depositional and/or diagenetic processes that produced lithologic heterogeneity in the dolostone. Bowman and Pollington [2004] suggest that heterogeneous talc abundance and distribution are due to heterogeneity in pore fluid XCO₂ within the talc zone and provide three plausible mechanisms: (1) down-temperature fluid flow, in which stratigraphic layers control variations in progress of higher grade reactions, inducing variations in XCO₂ of fluids flowing from the igneous intrusion and into the talc zone; (2) up-temperature flow, in which stratigraphic layers control variations in

permeability, allowing a liquid rich in H₂O to flow toward the igneous intrusion; and (3) in situ generation of a liquid rich in H₂O by fluid immiscibility as high XCO₂ fluids generated in the inner aureole

flow away from the igneous intrusion and cool and/or decrease in fluid pressure.

[20] The third hypothesis is in line with paradigms we advocate. The CO₂-H₂O fluid in the outer aureole [Cook and Bowman, 2000] was of a composition (38 to 95 mol% CO₂ emanating from the tremolite zone), temperature (less than 375°C in the talc zone), and pressure (at least 75 MPa) consistent with formation of a two-phase CO₂-H₂O fluid (Figures 1 and 3). We suggest that separation of these two fluid phases changed H₂O activity, and, indirectly, controlled the progress and distribution of metamorphic hydration reactions of the outer aureole in which a two-phase CO₂-H₂O fluid formed and flowed. Our model links the transition from a one- to a two-phase CO₂-H₂O fluid with the temperature-XCO₂ chemographic relationships of tremolite- and talc-forming reactions in the Alta aureole (Figure 3). No talc crystallizes at ~375°C in the presence of a one-phase CO₂-H₂O fluid containing greater than ~50 mol% CO₂ (i.e., a composition to the right of the invariant point in Figure 3a). With modest quantities of NaCl (and other salts) in the fluid (Figure 3b), the CO₂-H₂O solvus emerges near these temperatures and intersects talc- and tremolite-producing reactions. Higher quantities of salt (Figure 3c), such as those found in other contact aureoles as well as in deep saline aquifers and basinal brines, further expand the CO₂-H₂O solvus. Development of a liquid rich

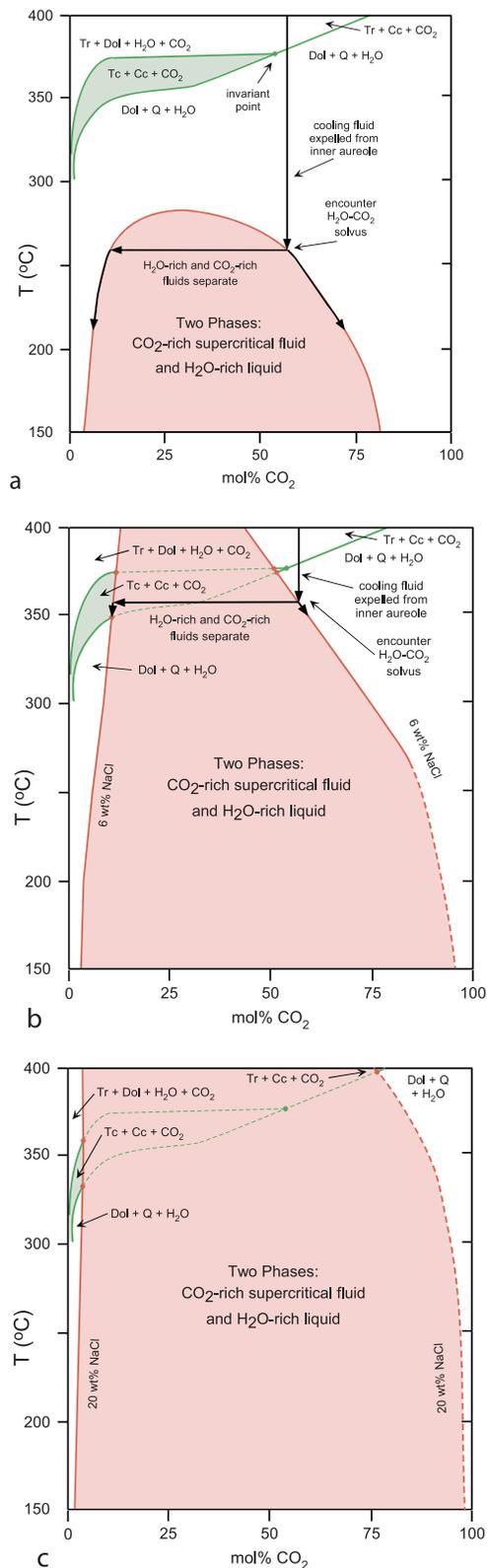


Figure 3. Schematic diagrams for reactions in the outer thermal aureole of the Alta stock. Silicate reactions and invariant point (green lines and points) are based on Cook and Bowman [2000] (lithostatic pressure is 150 MPa; fluid pressure is 75 MPa; Cc, calcite; Dol, dolomite; Q, quartz; Tc, talc; Tr, tremolite). Figure 3a depicts the physicochemical evolution of a single-phase CO₂-H₂O fluid as it is expelled from the inner thermal aureole and intersects the CO₂-H₂O solvus (red lines, based on the experimental data of Takenouchi and Kennedy [1964]). Figures 3b and 3c depict the evolution of a fluid containing 6 wt% (1 mole per kilogram) and 20 wt% (3.4 mole per kilogram) NaCl, respectively. The CO₂-H₂O solvus in these latter two diagrams is based on the experimental data of Takenouchi and Kennedy [1965] and Gehrig *et al.* [1986] (red lines, dashed where inferred). Chemographic intersections of silicate reactions with CO₂-H₂O solvus are denoted by red dots, and metastable extensions of silicate reactions are marked by dashed green lines. Fluids in the thermal aureole of the Alta stock probably contained between 5 and 10 wt% NaCl.

in H₂O and CO₂-rich supercritical fluid, and the concomitant increase in H₂O activity, provide a mechanism for talc crystallization. Note that fluid-dominated controls of talc crystallization are both chemical and spatial (physical, fluid dynamic) in character, in that fractionation of the two fluids promotes independent development of H₂O activity and potentially heterogeneous crystallization of talc in the rock matrix.

[21] Besides talc crystallization, the potential for fluid immiscibility and multiphase fluid-rock interactions in outer contact aureoles of carbonate rocks may have wide applicability to a variety of shallow crustal environments, from low grade metamorphism to diagenesis in deeper parts of sedimentary basins. Low-grade hydrothermal systems developed in these contact metamorphic environments are fossil records of the production, transport and storage of CO₂ at timescales on the order of 10³ to 10⁵ years [Jaeger, 1964; Hanson, 1995]. The long end of these timescales overlaps those of processes operating in sedimentary basins, such as cementation and dissolution that impact porosity and permeability. The short end of these timescales overlap those required for geologic carbon sequestration to be effective at managing anthropogenic carbon.

5. Summary and Conclusions

[22] The behavior of CO₂-H₂O fluids has been the focus of field, experimental and theoretical geologic investigations for decades, particularly with respect to single-phase CO₂-H₂O fluids in metamorphism and hydrothermal systems. Yet, with all that we know about the nonideality of CO₂-H₂O fluid behavior, remarkably little study and thought address shallow crustal environments (up to 400°C and 300 MPa) where nonideal behavior and fluid immiscibility may be especially prevalent. The inevitability of multiphase behavior in a host of common shallow geological environments is apparent. We propose that immiscible CO₂-H₂O fluids and host rock interact geochemically and geomechanically, and implications for these interactions merit serious study. This topic is timely and appropriate because of international scientific and social interest in the carbon cycle, climate change, and the management of anthropogenic carbon. It is time to examine conceptual models for a broad range of crustal geosystems in light of the physical-chemical properties of these two fluid phases (e.g., what happens

to CO₂-rich metamorphic fluids discharged from a thermal aureole?).

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