



The solubility of rocks in metamorphic fluids: A model for rock-dominated conditions to upper mantle pressure and temperature



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ABSTRACT

Fluids exert a key control on the mobility of elements at high pressure and temperature in the crust and mantle. However, the prediction of fluid composition and speciation in compositionally complex fluid–rock systems, typically present in subduction zones, has been hampered by multiple challenges. We develop a computational framework to study the role of phase equilibria and complex solid-solutions on aqueous fluid speciation in equilibrium with rocks to 900 °C and 3 GPa. This is accomplished by merging conventional phase-equilibrium modeling involving electrolyte-free molecular fluids, with an electrostatic approach to model solute–solute and solute–solvent interactions in the fluid phase. This framework is applied to constrain the activity ratios, composition of aqueous solutes, and pH of a fluid in equilibrium with a pelite lithology. Two solvent compositions are considered: pure H₂O, and a COH fluid generated by equilibration of H₂O and graphite. In both cases, we find that the pH is alkaline. Disparities between the predicted peralkalinity of our fluid ($([Na] + [K])/[Al] \sim 6$ to 12 and results from independent mineral solubility experiments (~ 2) point to the presence of Na–K–Al–Si polymers representing ca. 60 to 85% of the total K and Al content of the fluid at 600 °C and 2.2 GPa, and to an important fraction of dissolved Ca and Mg not accounted for in present speciation models. The addition of graphite to the system reduces the relative permittivity by ca. 40% at elevated *T* and low *P*, triggers the formation of C-bearing anions, and brings the pH closer to neutrality by up to 0.6 units at low *T*. This ionic C pool represents up to 45 mol% of the fluid ligands at elevated *P*, and is dominant at low *P* despite the low ionic strength of the fluid (<0.05). The present study offers new possibilities for exploring redox–pH dependent processes that govern volatile, major and trace element partitioning between rocks and fluids in experimental or natural systems.

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1. Introduction

Metamorphic fluids exert a major control on rheology, reaction kinetics and the transport of heat and matter in the crust and mantle (e.g., Fyfe et al., 1978). Water, in particular, is a powerful solvent for transporting mass on and inside the Earth (e.g., Walther and Helgeson, 1980; Manning, 1994; Ague, 1994; Mott et al., 2004), participating in its long term differentiation. However, metamorphic fluids commonly contain a range of C-bearing species, characterized by no or low permanent dipole moment, that weaken their solvent property (e.g., Deul and Franck, 1991; Walther and Schott, 1988; Walther, 1992). Nevertheless, fluids

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rich in molecules such as CO₂, CH₄ and/or N₂ also contain dissolved solutes, e.g. Na⁺, K⁺, Cl[−], that may precipitate as daughter minerals in fluid inclusions upon decompression and cooling (e.g., Andersen et al., 1989; Philippot and Selverstone, 1991; Frezzotti et al., 2011; Ague and Nicolescu, 2014). Moreover, specific patterns of element gain-loss or isotopic systematics provide indirect geochemical evidences for COH fluid-mediated mass transfer, despite their less favorable solvent properties, in a wide range of metamorphic settings (e.g., Bebout and Barton, 1993; Penniston-Dorland and Ferry, 2008; Malvoisin et al., 2012; Galvez et al., 2013a, 2013b; Ague and Nicolescu, 2014).

Despite their importance as metasomatic agents, little is known about dissolution mechanisms, and electrolyte transport in COH fluids (e.g., Evans et al., 2009; Schmidt, 2014). Quantitative prediction of solute mobilization and transport by COH fluids hinges on accurate knowledge of the thermodynamic properties of solvents, solutes, minerals and their solution properties over a wide range of pressure (*P*) and temperature (*T*) conditions. Predic-

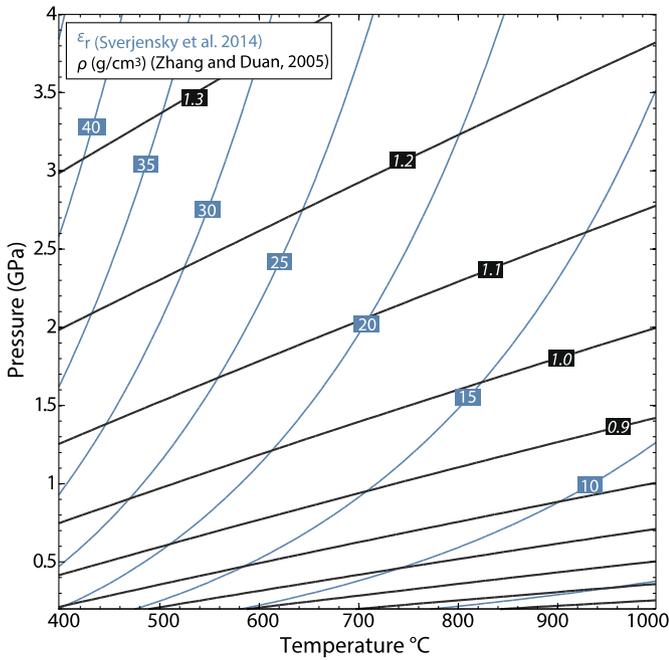


Fig. 1. Contour plot of the static relative permittivity of H₂O (ϵ_r)_{H₂O} (EoS developed by Sverjensky et al., 2014) along with density values from Zhang and Duan (2005). There is an increase of (ϵ_r)_{H₂O} with density increase along isotherms, and with temperature decrease along isochores over the P – T conditions of interest. This can be explained by a combination of bulk and microstructural factors (e.g., Kirkwood, 1939; Yoshii et al., 2001): With increasing temperature along isochores, higher kinetic energies of water molecules induce partial breakage of the hydrogen bond network between water dipoles, progressively annihilating the intermolecular orientational correlation contribution to the overall polarization (for relatively constant dipole moment of individual molecules) and, induce a drop in (ϵ_r)_{H₂O}. With isothermal density increase the tight packing of water molecules and increased hydrogen bonding of H₂O invariably favors an increase of (ϵ_r)_{H₂O} (cf. Appendix A). (For interpretation of the references to color in the figure legends of this paper, the reader is referred to the web version of this article.)

tion of how rock-forming chemical components are redistributed between mineral and fluids has depended chiefly on independent models of the thermodynamic properties of aqueous electrolytes (e.g., Helgeson and Kirkham, 1976; Helgeson et al., 1981; Wolery, 1992) and have been hampered by two main challenges. The first challenge is that there have been limitations to assessing the solvent properties of H₂O beyond the P – T range of the commonly used Helgeson–Kirkham–Flowers (HKF) equations of state: In this model, the partial molal Gibbs free energy of hydration $\Delta G_{\text{sol},j}$ of an ion in a solvent follows the Born equation (Helgeson et al., 1981):

$$\Delta G_{\text{sol},j} = \omega_j \left(\frac{1}{\epsilon_r} - 1 \right) \quad (1)$$

where ϵ_r is the relative permittivity of the solvent at P and T , and ω_j is the absolute Born coefficient of the species j . The Born coefficient is an ion-specific function of the ionic charge Z_j , of the effective electrostatic radius (a function of P and T , see Appendix B), and of the vacuum permittivity. The conventional Born coefficient used is defined as $\bar{\omega}_j = \omega_j - |Z_j|\omega_{\text{H}^+}$. Expressions for the relative permittivity of pure water, (ϵ_r)_{H₂O}, as a function of density and temperature were long restricted to <0.5 GPa (e.g., Archer and Wang, 1990). However, quantification of (ϵ_r)_{H₂O} has now been extended to ca. 6 GPa, and ca. 1000 °C (Fernandez et al., 1997; Pan et al., 2013; Sverjensky et al., 2014, and Fig. 1). Building on these fundamental advances, this paper explores the new opportunity for integrating petrologic models of rock systems with models of electrolyte chemistry to high P and T .

The second challenge is that there have also been limitations in the extension of the HKF model to geologically complex solvents

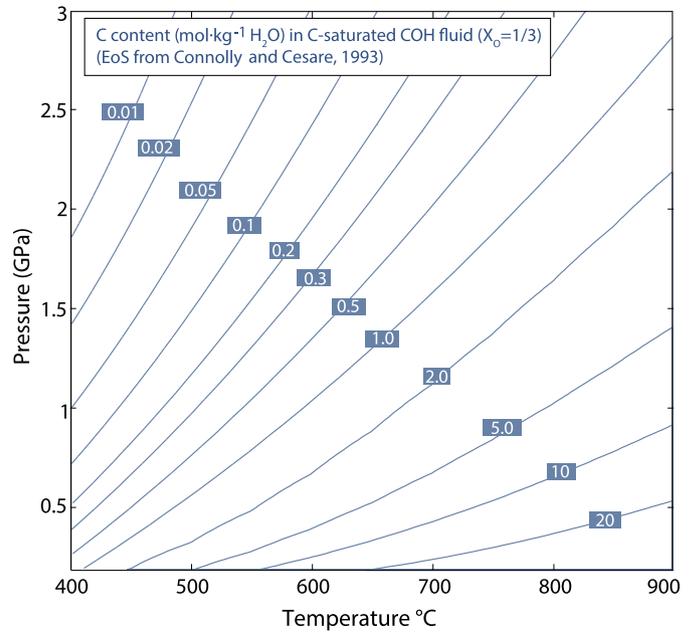


Fig. 2. Contour plot of C molality ($\text{mol}\cdot\text{kg}^{-1}$ H₂O) in a C-saturated (graphite) COH fluid at $X_0 = 1/3$. The EoS used is from Connolly and Cesare (1993), and it assumes that the solid C phase is perfectly crystalline graphite, refer to Appendix B for details. The C molality spans a large range (10^{-3} to >10 molal) and reaches the highest values at elevated T and lower P as can be expected from the weakly polar nature of H₂O at these conditions, i.e. where (ϵ_r)_{H₂O} is lowest (Fig. 1). The $\log f(\text{O}_2)$ of this fluid ranges between -2.5 (elevated T and low P) and 0 log units (elevated P and low T) below the fayalite–magnetite–quartz (FMQ) equilibrium $\log f(\text{O}_2)$. Interestingly, the solubility of CaCO₃ in pure H₂O (Caciagli and Manning, 2003) displays comparatively limited variations around 0.01 to 0.3 molal in this P – T range, and only equals or exceeds that of C at the high P and low T conditions typical of the blueschist–lawsonite facies (cf. Fig. 4) where (ϵ_r)_{H₂O} is highest (Fig. 1). This geochemical feature is noteworthy given the dramatically different structure, properties and kinetics of dissolution of these important C-bearing minerals.

that contain, in addition to H₂O, species such as CO₂ and CH₄ (e.g., Connolly and Cesare, 1993). C concentrations may reach tens of molal in such fluids at elevated T and P and $X_0 = 1/3$ (Fig. 2) ($X_0 = n_{\text{O}}/(n_{\text{O}} + n_{\text{H}})$), and the molar fraction of carbon-bearing species may even exceed that of H₂O during metamorphism of some carbonate lithologies. In such mixed-volatile mixtures, the density and solvent properties, e.g. (ϵ_r)_{mix}, deviate from those of pure H₂O (Fig. 1). Although changes to the ion-solvation energetics (Eq. (1)) can nominally be derived using predictions of the relative permittivity of mixtures between molecules of geological interest (e.g., Looyenga, 1965; Kirkwood, 1939; Wang and Anderko, 2001), this has only rarely been attempted for metamorphic fluids, and, to our knowledge, only to 0.5 GPa (e.g., Walthier, 1992; Evans et al., 2006). These two challenges have prevented the application of the HKF model to fluid speciation at lower-crustal and subduction-zone conditions.

An alternative approach to fluid speciation exploits the empirical observations of log–log linear relationships between the dissociation constants of aqueous complex, (ϵ_r)_{H₂O}, and $\rho_{\text{H}_2\text{O}}$ at elevated P and T (e.g., Marshall and Franck, 1981; Manning, 1998; Dolejš and Manning, 2010; Dolejš, 2013) to alleviate the need for values of (ϵ_r)_{H₂O} beyond its range of calibration. However, this method remains largely empirical and does not provide insight into key solvent and solute properties. Moreover, this approach is cumbersome to include with accurate, comprehensive description of the changing compositions of complex mineral solid-solutions that occur in realistic petrological systems over the wide range of P and T relevant to metamorphism, which may include shallow magma-hydrothermal systems, orogenic belts or subduction zones. In contrast, while petrological modeling generally account for com-

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