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Permalink
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Publication Date
2014

DOI
10.1016/j.precamres.2014.06.025

Peer reviewed
Brines at high pressure and temperature: Thermodynamic, petrologic and geochemical effects

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ARTICLE INFO

Article history:
Received 7 April 2014
Received in revised form 16 June 2014
Accepted 29 June 2014
Available online 7 July 2014

Keywords:
Brines
Metamorphic fluids
Granulites
High-grade metamorphism

ABSTRACT

A number of observations point to the participation of brines in high-grade metamorphic processes. These include findings of alkali and alkaline-earth halides as daughter crystals in fluid inclusions, appreciable concentrations of Cl measured in amphiboles, biotite, scapolite and apatite, and direct observations on high-temperature halides present in the intergranular space in high-grade rocks. This paper reviews some thermodynamic, petrologic and geochemical effects of these brines. Thermodynamic mixing properties of concentrated water–salt fluids at high pressure (P) and temperature (T) differ greatly from those of water–non-polar gas mixtures: the former are characterized by a large negative deviation from ideal solutions, while the latter exhibit positive deviation from ideality. The contrasting behavior has three major petrologic implications. First, compared to mixtures of water and non-polar gases, brines more strongly increase the melting temperature of quartzofeldspathic rocks and more strongly decrease dehydration temperature of water-bearing minerals. This allows a wide P–T window in which subsolidus deep-crustal metasomatism may take place at relatively low H2O activity (αH2O) via migrating fluids. In addition, above 2–3 kbar, brine-saturated solidi for simple granite melting show positive dPdT at constant H2O mole fraction (XH2O), favoring ascent of fluid-saturated liquids. Finally, a large miscibility gap exists in H2O–CO2–salt ternaries at lower crustal conditions, which may concentrate salts in a separate phase and help explain the common observation of CO2-rich inclusions in high-grade minerals. We discuss three geochemical consequences of high-grade brines. We report new experimental data on melting of a model granitoid liquid (69 wt% NaAlSi3O8, 31 wt% SiO2) at 2 kbar in the presence of aqueous NaCl solutions ranging in concentration from a salt mole fraction (XNaCl) of 0.1–0.3. The results show that Na preferentially partitions into the silicate liquid, enriching the coexisting fluid in HCl. This hydrolysis effect, known previously for granite melts equilibrated with dilute solutions, therefore also extends to more saline brines. Mineral solubilities depend strongly on salt concentration in the coexisting fluid. Below 5 kbar at 700 °C, quartz initially salts in with addition of NaCl to H2O, reaches a maximum, and then declines; however, it salts out at all XNaCl at higher P. At granite-facies P–T conditions, the solubilities of other oxide and silicate minerals (corundum, wollastonite, grossular) salt in and then either reach a plateau or salt out slightly at high XNaCl. In contrast, the solubility of Ca–salt minerals increases exponentially with rising XNaCl. The solubility patterns reflect variations in complexing and H2O activity in the brine. Partitioning of REE between rock forming minerals and brines, and between felsic melts and brines, differs strongly from that between minerals, melts and water ([± non-polar gas]). Brines extract REE from the melts much more efficiently, and LREE are extracted more efficiently than HREE. This effect may contribute to the decreased La/Yb ratio that accompanies the overall decrease in bulk REE concentration in leucosomes relative to their parental rocks (paleosomes) that has been documented from amphibolite- and granulite-grade migmatite complexes.

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1. Introduction

There is now abundant evidence for the participation of strongly saline fluids in high-grade metamorphic processes. The earliest indications came from the study of fluid and melt inclusions...
minerals of igneous and metamorphic rocks. Dolgov et al. (1977) described polyphase fluid inclusions containing alkali and alkaline-earth halides as daughter crystals along with liquid H2O and dense non-polar gases (mostly liquid CO2) in quartz from the lower-crustal migmates of the Aldan Shield, Eastern Siberia (Fig. 1). Touret (1985, 1995) reported apparently primary crystalline-salt-bearing fluid inclusions in minerals from the highest grade, Rb-depleted granulite facies zone of the Bamble region, S. Norway. He inferred that granulite-facies metamorphism was accompanied by a near-saturated supercritical brine and an immiscible CO2-rich phase. Findings of polyphase fluid inclusions with salt daughter crystals (chiefly chlorides) have now been reported in minerals from a variety of high-grade metamorphic settings (e.g., Xiao et al., 2001; Van den Berg and Huizenga, 2001; Nehring et al., 2009; Touret and Huizenga, 2011; Newton et al., 2014).

Elevated Cl concentrations often measured in magmatic and high-grade metamorphic hydrous minerals such as amphibole, biotite, scapolite and apatite (e.g., Henry, 1988; Mora and Valley, 1989; Nijland et al., 1993; Kullerud, 2000; Faryad, 2002; Xiao et al., 2005; Harlov et al., 2006; Hansen and Harlov, 2007; Hammerli et al., 2014) may also be considered as evidence for chloride-rich metamorphic fluids. This is because of the strong partitioning of Cl into the fluid phase relative to hydrous minerals (e.g., Munoz, 1981; Zhu and Sverjensky, 1991, 1992; Kullerud, 1996).

Compelling evidence for the involvement of highly saline fluids in the petrogenesis of the lower crust also comes from the observation of high-temperature halides in the intergranular space of high-grade rock samples (Trommsdorff et al., 1985; Markl and Bucher, 1998; Markl et al., 1998). Such reports are rare, presumably because of the conventional preparation of thin sections using water as a lubricant, thus leaching soluble intergranular materials. Nevertheless, these findings clearly indicate that a brine or hydrosaline melt was involved in the generation of the sample assemblages, and motivate more careful search for these grain-boundary features in high-grade rocks elsewhere.

Regional magnetotelluric soundings and/or electrical conductivity measurements offer further evidence for the existence of lower crustal fluids with salinity at least as high as that of seawater (e.g., Unsworth and Rondenay, 2012). For example, horizontal reflectors and large, regional-size conductive layers in tectonically active areas and extensional basins (Wannamaker et al., 1997, 2002) are interpreted to signal the presence of large volumes of deep saline fluids.

The observation of halide daughter minerals in fluid inclusions from high-grade metamorphic rocks places a simple constraint on the salinity levels attained by the fluids. Halite saturation at room temperature is 26.8 wt% NaCl, or XNaCl = 0.1 (where XNaCl is the molar NaCl/(NaCl + H2O) ratio). Therefore salt concentrations in the included fluids must exceed these values; i.e., they are strongly saline. We use the term “brine” to refer to any solution with salinity in excess of the 26.8 wt% NaCl equivalent required to produce halide daughter minerals in fluid inclusions at ambient conditions.

High concentrations of halite salts have a significant impact on the thermodynamic and transport properties of natural deep-seated fluids, on the dissolution of minerals and metasomatic alteration, and on dehydration and melting reactions and compositions of resulting magmas. The purpose of the present paper is to discuss some major thermodynamic, petrologic and geochemical effects relevant to the action of brines in the lower crustal environment. In this paper we review the activity–composition relations in water–salt mixtures, their petrologic implications, and the geochemical consequences of high salinity lower crustal fluids. We focus chiefly on alkali-chloride salts because they are the subject of most experimental and theoretical work; however, the behavior of other salt systems (e.g., KCl, CaCl2 or NaF) is noted where relevant data exist.

Fig. 1. Polyphase inclusions in quartz from migmate leucosomes, Aldan shield, Siberia (photomicrographs courtesy of Anatoly Tomilenko). LH2O, aqueous solution; LCO2, liquid CO2; Cr, solid phases (mostly NaCl, KCl, rare carbonates). Note different proportions of LH2O and LCO2 in the two inclusions.

2. Sources of salinity in high P–T brines

Yardley and Graham (2002) reviewed the sources of salinity in metamorphic fluids. They identified three mechanisms by which saline fluids can be generated in metamorphic systems: connate pore fluids derived from sedimentary protoliths, dissolution of evaporitic salt minerals, and preferential partitioning of H2O relative to halide during hydration reactions. Only the latter is likely to be relevant to high-grade metamorphism because any saline fluids generated by the first two mechanisms are likely to be lost during the prograde history.

Magmatic fluids should also be recognized as an additional source of salinity in metamorphic systems (e.g., Yardley, 2013). Mantle-derived magmas behave as open systems when they stall near the Moho or transit the crust (e.g., Annen et al., 2006). High Cl solubility makes mafic magmas potentially effective agents of CI delivery. When mafic magmas crystallize in the lower crust, volatile components separate and interact with the metamorphic host rocks. By this mechanism, elevated concentrations of Cl along with CO2 and S, can be generated in deep fluids.

The especially low solubility of Cl (and CO2 and S) in silicic magmas (Stolper et al., 1987; Webster and Holloway, 1988; Papale, 1999; Newman and Lowenstern, 2002; Webster et al., 2002; Webster, 2004; Aranovich et al., 2013a) also means that, where fluid-saturated melting occurs in the middle and lower crust, the melt will strongly partition H2O relative to chloride and promote formation of a residual saline fluid. Most conceptual models of fluid-saturated melting focus solely on the role of H2O. If the fluid at the solidus is pure H2O, it is likely to be completely consumed by the silicate liquid because of high H2O solubility and low rock porosity. However, the lower solubility of Cl (as well as CO2 and S), if present in the fluid, will lead to differential partitioning between fluid and melt. In this case, the fluid phase may not be completely consumed by melting. Instead it becomes enriched in Cl and other components with lower affinity for the silicate liquid than H2O.

Thus, there are likely three main pathways to increasing salinity in fluids associated with high-grade metamorphism. The preferential extraction of H2O during hydration reactions will enrich the fluid phase in salt components. Externally derived salts may be introduced from magmatic volatiles. And finally, salt concentration may be enriched in a residual fluid during fluid-saturated melting.

3. Activity–composition relations and petrologic consequences of high P–T brines

Thermodynamic mixing properties of concentrated water–salt fluids at high P–T differ greatly from those of mixtures of water and non-polar gases. According to experimental data (Aranovich
and Newton, 1996, 1997; Shmulovich and Graham, 1996), H$_2$O activity ($a_{H_2O}$) in H$_2$O–NaCl, H$_2$O–KCl and mixed H$_2$O–(Na,K)Cl brines strongly depends on pressure (at a given temperature and salt concentration), decreasing sharply from almost ideal molecular solution relation $a_{H_2O} = x_{H_2O}$, approximately valid at relatively low pressure of ~2 kbar, to a nearly ideal ionic solution with $a_{H_2O} = x_{H_2O}^2$ at 10 kbar (Fig. 2a). That the presence of dissolved NaCl substantially decreases the activity of water has been confirmed at pressures of up to 45 kbar (Tropper and Manning, 2004; Mantegazzi et al., 2013).

In contrast to its behavior in water–salt solutions, $a_{H_2O}$ in mixtures of water and non-polar gas is greater than $x_{H_2O}$ at high pressures (Fig. 2b; e.g., Kerrick and Jacobs, 1981; Aranovich and Newton, 1999; Haefner et al., 2002; Aranovich, 2013; Bali et al., 2013). This difference has three major petrologic implications. First, compared to water–non-polar gas brines, brines more strongly increase the melting temperature of quartzofeldspathic rocks and decrease dehydration temperature of water-bearing minerals (at a given pressure and water mole fraction). Fig. 3 illustrates these features at 7 kbar using isobaric T–X$_{H_2O}$ sections of simple granite melting according to experimental data of Aranovich et al. (2013a; Fig. 3A) and the dehydration reaction

$$\text{phlogopite + quartz} = \text{enstatite + K feldspar + H}_2\text{O}$$  (1)

(Aranovich and Newton, 1998; Fig. 3B). At X$_{H_2O}$ = 0.5, simple granite melting occurs at ~800 °C in the presence of brine, but 80° lower (~720 °C) in the presence of H$_2$O–CO$_2$ fluid. The temperature of dehydration also differs dramatically. At the same X$_{H_2O}$ of 0.5, reaction (1) proceeds to the right at ~775 °C if the fluid is H$_2$O–KCl, but 100 °C higher (~875 °C) if the fluid is H$_2$O–CO$_2$. Notably, at the temperature of 875 °C required in an H$_2$O–CO$_2$ fluid, the product assemblage is metastable relative to the K feldspar + quartz + melt. There is thus a substantial P–T range over which subsolidus deep-crustal metasomatism may take place at relatively low $a_{H_2O}$ via migrating fluids. In the above example, the granulite-facies assemblage orthopyroxene + K feldspar + quartz could form at the expense of phlogopite + quartz due to interaction with a brine of X$_{H_2O}$ = 0.5 without producing any melt over a 40 °C temperature range. This temperature range becomes even greater at higher pressure (Aranovich et al., 2013a).
addition, brine metasomatism may increase alkalis, CaO and SiO₂ in the mid-crust and thus condition it for anatexis (Aranovich et al., 2014). Brine-assisted anatexis differs greatly from rock melting in pure H₂O or in H₂O–CO₂ fluids. Large changes in feldspar composition in equilibrium with melts can result from small shifts in fluid compositions (Aranovich et al., 2013a). The presence of brines during high-grade metamorphism may help resolve the “granulite paradox”: extensive dehydration without wholesale melting in numerous examples of these rocks (Aranovich et al., 2014).

The second petrologic consequence of the mixing thermodynamics of water–alkali chloride systems is that contours of constant X₁₂₃ in the fluid at granite minimum melting have strongly positive dP/dT slopes above 2–3 kbar (Fig. 4; Aranovich et al., 2013a). At even modest X₁₂₃, the slopes are shallower than model adiabatic (Johannes and Holtz, 1991) or isothermal ascent paths for haplogranite. Assuming X₁₂₃ = 0.5 and a closed system free of crystals, a brine-saturated magma formed at 7 kbar and ~720 °C can rise to shallow crustal levels because X₁₂₃ required to remain above the solids decreases along this path (Fig. 4). In contrast, a magma saturated with a H₂O–CO₂ fluid of the same composition forms at 7 kbar and ~720 °C, but it cannot rise because the amount of H₂O required to remain entirely liquid continuously increases as the liquid decompresses along an adiabatic ascent path (Fig. 4). Moreover, aH₂O in salt solutions increases strongly with decreasing P at constant H₂O–salt composition (Aranovich and Newton, 1996, 1997). The increasing aH₂O in the fluid accompanying the rising magma can promote further melting of the country rocks. These results offer an explanation for mid-crust migmatization and granite production: rising hot brines may cause rocks to melt at some threshold of decreasing depth in the range 15–20 km (Aranovich et al., 2014). Because of their enhanced capacity for metasomatism, leading to eventual melting at appropriate conditions of T, P and aH₂O, concentrated brines may be important agents in crustal evolution.

The third consequence of H₂O–CO₂ and H₂O–NaCl activity relations is an extensive region of immiscibility in H₂O–CO₂–salt ternaries at lower crustal conditions (e.g., Heinrich, 2007; Liebscher, 2010; Manning et al., 2013). Most work has been conducted at low pressure (Gehrig et al., 1979; Aranovich et al., 2010; Anovitz et al., 2004), but extension of these results to lower crustal conditions (Frantz et al., 1992; Johnson, 1991; Kotelnikov and Kotelinkova, 1990; Shmulovich and Graham, 1999, 2004; Joyce and Holloway, 1993; Gibert et al., 1998) yields a ternary miscibility gap between NaCl–H₂O–rich brine and CO₂–H₂O–rich vapor. Equations of state for ternary systems describe the highly non-ideal behavior over a range of P and T (Bowers and Helgeson, 1983; Duan et al., 1995; Aranovich et al., 2010). The system CaCl₂–CO₂–H₂O behaves similarly (Shmulovich and Graham, 2004; Zhang and Frantz, 1989).

Immiscibility in H₂O–CO₂–salt ternary systems is a mechanism for further concentration of salt components in the separate brine phase relative to the bulk fluid composition. It may explain granulite terranes in which field and petrologic data require presence of a low-aH₂O fluid phase capable of metasomatizing major and trace elements. The CO₂-rich fluid inclusions often found in high-grade rocks led Newton et al. (1980) to suggest that dilution of H₂O by CO₂ may explain reduced aH₂O; however, this is not consistent with petrologic observations (e.g., Lamb et al., 1987). Brine and vapor immiscibility may offer a better explanation (Touret, 1983; Newton et al., 1998; Newton and Manning, 2010) because the wetting properties of the CO₂–rich vapor phase lead to preferential entrapment as fluid inclusions relative to the brine phase (Gibert et al., 1998). In addition, the brine component can generate significant metasomatism (see below), while the requirement of reduced aH₂O is satisfied.

4. Geochemical effects of high P–T brines

The presence of alkali chlorides, either dissolved in a felsic melt or in a separate fluid phase, leads to a number of geochemical effects unexpected for mixtures of H₂O and non-polar gases. These include hydrolysis accompanying phase separation, significantly different mineral solubilities and solubility patterns, and trace-element partitioning.

4.1. Hydrolysis

Shmulovich et al. (1995) and Bischoff et al. (1996) reported significant accumulation of HCl (up to 0.1 mole/kg H₂O) in the vapor phase in the experiments on boiling curves in the systems H₂O–alkali/alkali earth chlorides at high P–T conditions. They related it to the forward progress of a hydrolysis reaction of the form

\[
\text{MeCl}_n + n\text{H}_2\text{O} = \text{Me(OH)}^{+}_n + \text{nHCl}^- \quad (2)
\]

where Me = Na, K, Ca or Mg, and n equals 1 or 2 depending on the formal charge of the metal. The HCl formed by this reaction preferentially accumulates in the less dense vapor phase (ν), while the hydroxide prefers the denser liquid phase (l).

A similar effect was discovered some 40 years ago in the experiments on granite melting in presence of relatively dilute NaCl-bearing fluids (Holland, 1972; Ryabchikov, 1975) and was attributed to accumulation of Na(OH) in the melt and HCl in the fluid phase. As Cl solubility in felsic melts is restricted to a few tenths of a weight per cent (e.g., Webster, 2004; Aranovich et al., 2013a) and partitioning of Cl between melt and fluid favors the fluid phase, relative Cl enrichment may be expected in the fluid that separates from a felsic magma at the early stages of crystallization.

To determine whether a hydrolysis effect holds in the brine-granite liquid system, several melting experiments were carried on the model granitoid composition 69 wt% NaAlSi₃O₈ and 31 wt%
SiO$_2$ in the presence of aqueous NaCl solutions ranging in concentration from $X_{\text{NaCl}} = 0.1$ to 0.3. Experimental conditions were 800 °C and 2 kbar. The starting synthetic glass was prepared by melting carefully mixed proportions of reagent grade Al$_2$O$_3$, SiO$_2$ and Na$_2$CO$_3$ in a closed, unsealed Pt crucible at 1280 °C for 10 h. This procedure was repeated twice to ensure homogenous starting material. Reagent grade NaCl and distilled and doubly deionized H$_2$O completed the starting materials. The starting glass/solution ratio in this series of runs was 5:1 by mass. All experiments were carried out in a vertically mounted, internally heated argon pressure vessel, for 5 days duration. Temperature was controlled automatically to within ±5 °C with sheathed Cr–Al thermocouples positioned at the top and the bottom of the Cu-capsule holder. Pressure was measured with a Bourdon tube gauge and is accurate to ±0.1 kbar. For comparison, two capsules in the same series were loaded with pure H$_2$O as a fluid phase. All experiment products contained glassy chunks and balls of the quenched granite melt, a solution, and some quenched NaCl. The pH of the quenched materials was measured qualitatively with universal indicator paper. The pH of the NaCl-bearing solutions was found to vary from 2 to 3 without clear correlation with the starting NaCl concentration, while the runs with pure H$_2$O showed quench pH values between 5 and 6, thus indicating that the shift in pH resulted from the hydrolysis reaction rather than dissolution of the granite material. The experiments demonstrate that the hydrolysis effect can be extended to concentrated salt solutions at the investigated pressure of 2 kbar. It seems likely that the effect persists to higher pressure because of the low solubility of Cl relative to H$_2$O (Aranovich et al., 2013a). The production of HCl by this mechanism will promote wall-rock metasomatism driven by neutralization of the acid, though its magnitude is probably lower at high P where HCl is a substantially weaker acid than at ambient conditions (Manning, 2013).

4.2. Solubility of minerals

Elevated concentrations of alkali halides have a profound affect on the solubilities of rock forming minerals in deep-crustal fluids. Experimental studies reveal that the magnitudes and mechanisms of solubility in brines depend strongly on mineral composition and structure (e.g., Newton and Manning, 2010). The primary distinction in solubility behavior is between simple oxides and silicates on the one hand, and ionic salt minerals on the other.

4.2.1. Oxide minerals

4.2.1.1. Quartz. At quartz saturation, the concentration of SiO$_2$ in otherwise pure H$_2$O increases with rising P and T such that, at halite-grade conditions of 800 °C and 7 kbar, quartz-saturated H$_2$O contains ~1 m SiO$_2$ (~6 wt% Anderson and Burnham, 1965; Manning, 1994). Addition of dissolved alkali-halide salts changes quartz solubility behavior. At low pressures and constant temperature, quartz solubility rises with increasing concentration of NaCl at low total salinity (Fig. 5; Novgorodov, 1977; Xie and Walther, 1993; Newton and Manning, 2000). Solubility reaches a maximum at modest salinity (e.g., $X_{\text{NaCl}} = 0.1$ at 700 °C, 2 kbar; Newton and Manning, 2000) and then it declines to higher salinity. Thus, at these conditions, quartz salts in at low salinity but salts out at high salinity. This behavior contrasts with that at moderate to high pressure (e.g., above ~5 kbar at 700 °C; Newton and Manning, 2000), where quartz salts out at all $X_{\text{NaCl}}$ (Fig. 5).

The transition from salting-in to salting-out behavior of quartz solubility varies significantly with the type of salt (Fig. 6; Shmulovich et al., 2006; Newton and Manning, 2010). At 5 kbar and 800 °C, quartz salts out at all $X_{\text{salt}}$ if the salt is CaCl$_2$ or NaCl, but exhibits initial salting-in to a maximum before salting out if the salt is KCl or CsCl. The salt concentration and relative solubility enhancement at the maximum also differ with salt type (Fig. 6). Hypotheses explaining this behavior include changes in solvent properties (Xie and Walther, 1993; Shmulovich et al., 2001, 2006) and complexing of salt components with silica (Anderson and Burnham, 1967; Evans, 2007). However, as noted by Newton and Manning (2010), neither is fully satisfactory and the modeling of quartz solubility in saline solutions at deep-crustal conditions remains empirical (Fournier et al., 1982; Fournier, 1983; Shibue, 1996; Akinfiev and Diamond, 2009).

A key observation is that although quartz salts out over a wide range of lower crustal conditions, the decrease in concentration for a given reduction in $a_{\text{H}_2\text{O}}$ is significantly less than for CO$_2$ (Newton et al., 2010).
Thus, low-\(\text{H}_2\text{O}\) salty fluids are substantially better solvents for silica than equivalent-\(\text{H}_2\text{O}\) fluids containing \(\text{CO}_2\). Of the two fluid phases produced by unmixing in the \(\text{H}_2\text{O}–\text{CO}_2–\text{NaCl}\) ternary, the brine phase is capable of dissolving and transporting more \(\text{SiO}_2\) than the coexisting \(\text{H}_2\text{O}–\text{CO}_2\) phase.

The pH of quenched salt solutions in experiments on quartz solubility provides important qualitative insights into the relative roles of NaCl and \(\text{H}_2\text{O}\) in dissolving silica. This is because the solutes rapidly precipitate during quench. Assuming minimal back reaction between precipitated solutes and fluid, the quench pH probes whether there was fractionation of Na from Cl in the experiments. An excess in Na in the quench fluid (Cl fractionation into the solute) will yield alkaline pH, whereas an excess in Cl will yield acidic pH. Newton and Manning (2006) found that the quench pH of a \(\text{H}_2\text{O}–\text{NaCl}\) fluid equilibrated with quartz at 800 °C and 10 kbar was neutral at ambient conditions. Thus, the silicate solute component does not preferentially partition either Na or Cl at high \(P_H\) and \(T_H\) and pH upon quench is neutral. This implies that the higher solubility of quartz in \(\text{H}_2\text{O}–\text{NaCl}\) fluids than in \(\text{H}_2\text{O}–\text{CO}_2\) fluids does not arise from formation of Na-silicate complexes. A possible explanation was suggested by Evans (2007), who proposed a stable \(\text{SiO}_2\)(\(\text{NaCl}\))\(_{0.5}\) aqueous species.


4.2.1.2. Other oxide and silicate minerals. Experimental studies of the solubilities of other oxide minerals at high P in \(\text{H}_2\text{O}–\text{NaCl}\) reveal behavior similar to that of quartz at <5 kbar (Fig. 5). Fig. 7 compares experimental results on the variation in the solubilities of corundum (\(\text{Al}_2\text{O}_3\)), wollastonite (\(\text{CaSiO}_3\)) and grossular (\(\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_7\)) with NaCl concentration at 800 °C, 10 kbar (Newton and Manning, 2006, 2007, 2008). Fig. 7 gives results in terms of solute mole fractions in a fully dissociated \(\text{H}_2\text{O}–\text{NaCl}\) solution (Newton and Manning, 2010, Eq. (5)). This is preferred to the often-used molality scale, which gives concentration relative only to one component of the solvent (\(\text{H}_2\text{O}\)). As with quartz at low pressure (Fig. 5), corundum and wollastonite both salt in at low NaCl concentrations, reach maxima, and then salt out. However, this behavior is exhibited at higher pressure, and \(X_{\text{NaCl}}\) at the maxima are greater than seen in quartz (Figs. 5 and 6). Grossular, an intermediate phase on the corundum–wollastonite binary, shows evidence of attaining a maximum, though salting-out behavior was not observed even at the highest \(X_{\text{NaCl}}\) of 0.4. Notably, the addition of NaCl enhances the solubility of grossular relative to pure \(\text{H}_2\text{O}\) to a substantially greater degree than is the case for either component oxide alone. Moreover, grossular dissolves congruently at all studied fluid compositions along the \(\text{H}_2\text{O}–\text{NaCl}\) join; that is, for every 3 moles of Ca in solution there are 2 moles of Al and 3 moles of Si. This nominally refractory mineral is quite readily dissolved by saline solutions, suggesting surprising capability for metasomatic transport of otherwise insoluble elements such as Al. Less pronounced enhancements have been observed for andradite garnet (\(\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}\); Wykes et al., 2008). The variations in relative solubility enhancements and solubility maxima imply that the observed behavior is controlled by a varying combination of \(\text{H}_2\text{O}\) activity and solute complexing, involving chloride with metal cations and Na with polymerized aluminosilicate components (e.g., Manning, 2007; Newton and Manning, 2008; Manning et al., 2010).

As with quartz, insights into the dissolution mechanisms of other oxide and silicate minerals can be gained from measurements of quench pH in solubility experiments. Newton and Manning (2006) found that quench fluids in experiments on corundum solubility in \(\text{H}_2\text{O}–\text{NaCl}\) solutions were neutral at ambient conditions, similar to results of experiments on quartz solubility. Evidently, aluminite solute species do not preferentially partition Na or Cl, and Na-aluminate or Al-chloride species are not present above detection limits. In contrast, quench pH is highly alkaline in wollastonite–\(\text{H}_2\text{O}–\text{NaCl}\) experiments, but highly acidic in experiments on corundum–quartz–\(\text{H}_2\text{O}–\text{NaCl}\) (Newton and Manning, 2006, 2008). This implies that the dissolution of wollastonite yields hydrous sodium-silicate complexes, Ca chloride and OH− solute products, whereas dissolution of aluminosilicates yields sodium-aluminosilicate and HCl solute products (Newton and Manning, 2010). The latter is similar to equilibration between model granitoid magma and NaCl discussed above. \(\text{H}_2\text{O}\) and NaCl may play very different roles in mineral dissolution depending on the nature of the component rock-forming components, just as is seen in their interactions with silicate liquids.

4.2.2. Salt minerals

The solubilities of several Ca salt minerals have been extensively studied in \(\text{H}_2\text{O}–\text{NaCl}\) solutions. Investigated minerals include calcite (\(\text{CaCO}_3\)), anhydrite (\(\text{CaSO}_4\)), fluorite (\(\text{CaF}_2\)) and apatite (\(\text{Ca}_5(\text{PO}_4)_3\)) (Fig. 8; Newton and Manning, 2002, 2005; Tropper and Manning, 2007; Antignano and Manning, 2008). The dependence of solubility on NaCl concentration is similar in all cases: it increases exponentially with rising salinity to halite saturation. Salting-in behavior is seen over the entire range of fluid compositions; there are no maxima and no compositions at which salting out is observed. Preliminary data suggest that, at least for calcite, similar behavior is seen for other salts (e.g., KCl, LiCl: Eguchi et al., 2013). Thus, the solubility patterns of simple ionic salts in salt solutions differ fundamentally from those of oxide minerals. Solubilities may become extreme in highly saline brines. Indeed, Newton and Manning (2002) note that \(\text{H}_2\text{O}–\text{NaCl}–\text{CaCO}_3\) solutions may be fully miscible over the entire ternary system above \(\sim 1000\) °C at 10 kbar, except along the NaCl–\(\text{CaCO}_3\) binary.

The mechanism for the strong solubility enhancements seen in salt minerals is again complexing between Cl− and the metal mineral component, and Na+ and the anionic mineral component. That is, the dissolution of these minerals is controlled by the salt component in the solution, as in

\[
\text{CaCO}_3 + 2\text{NaCl}_{\text{aq}} = \text{CaCl}_2_{\text{aq}} + \text{Na}_2\text{CO}_3_{\text{aq}}
\]

(3) calcite.
(Newton and Manning, 2002, 2010). This interpretation is consistent with the observed exponential increase in solubility with rising NaCl concentration.

In summary, the presence of saline fluids during lower crustal metamorphism can be expected to yield high to extreme solubility of carbonates, sulfates and phosphates. Substantial mobilization of these minerals should be anticipated, and evidence for their precipitation down solubility gradients should be sought.

4.3. Brines and redox effects

Several high-grade terranes exhibit unusually high oxidation states (Griffin et al., 1978; Currie and Gittins, 1988; Harlov, 1992, 2000; Harlov and Förster, 2002a,b; Harlov et al., 1997). This may result from interaction with brines carrying SO₂ exsolved from underplated magmas (Cameron and Hattori, 1994; Harlov et al., 1997). Newton and Manning (2005) proposed that dissolved calcium sulfate in high-grade brines, derived from magmatic SO₂, could be an effective oxidative agent. For example, the interaction of externally derived, calcium sulfate-bearing solutions with reduced granulate-facies assemblages could drive forward progress of a reaction such as

\[
\text{CaSO}_4 + 2\text{FeSiO}_3 = \text{FeS} + \text{CaFeSi}_2\text{O}_6 + 2\text{O}_2
\]

Elevated initial CaSO₄ concentrations may be attained because of the very high solubility of anhydrite in high P-T brines (Newton and Manning, 2005). The proposed reaction is consistent with the stability of pyrrhotite at high oxygen fugacity. Brines rich in dissolved CaSO₄ could yield significant oxidation at the relatively low fluid/rock ratios typically inferred from stable-isotope geochemistry.

4.4. Rare-earth element partitioning

Partitioning of REE between rock-forming minerals and brines, and felsic melts and brines differs strongly from that between minerals, melts and water (± non-polar gas) (e.g., Flynn and Burnham, 1978; Keppler, 1996; Reed et al., 2000). La and Yb are representative of the light and heavy REE, respectively. Fig. 9 shows experimental results indicating that both La and Yb become more compatible in the fluid with increasing Cl concentration (present mostly as alkali chlorides). For Cl concentrations of the experimental solutions above 3 M (which corresponds to X_MCl = 0.052), La partitions preferentially into the fluid phase (i.e., K_D,La becomes greater than 1). Slight extrapolation of the experimental data leads to K_D,Yb > 1 at the Cl concentration just over 4 M (X_MCl = 0.07). Importantly, the difference between K_D,La and K_D,Yb also increases with increasing chlorine concentration (Yang, 2012).

Tropper et al. (2011) experimentally determined the solubility of CePO₄ monazite and YPO₄ xenotime in H₂O–NaCl solutions at 800 °C, 10 kbar. Their results indicate that, as in the work of Reed et al. (2000), the solubility of both Ce and Y increase with rising X_NaCl. Moreover, for a hypothetical fluid saturated in both monazite and xenotime, the Ce/Y ratio increases with increasing NaCl concentration. However, whereas La/Yb > 1 at all Cl concentrations in the experiments of Reed et al. (2000), Ce/Y > 1 only at X_NaCl > 0.3. Although both studies may have encountered problems at the lowest salinities, it is nevertheless the case that if Y is taken to be geochemically similar to Ho, the most saline solutions exhibit a strong preference for LREE over HREE. Note that Tropper et al. (2013) found that NaF solutions yielded even stronger increases in Ce/Y concentration with rising salt concentrations, but that Ce/Y < 1.0 for all studied NaF concentrations.

The experimental results highlight two key features of REE geochemistry: the extraction of felsic melt from the lower crust in the presence of a chloride brine. First, partial melting in the presence of a brine should result in a noticeable depletion in the bulk REE concentration compared to parental rocks. Such patterns are evident in well-studied exposures of the amphibolite–granulate transition (e.g., Tamil Nadu: Harlov, 2012). In addition, there should be a significant decrease in the LREE/HREE ratio in the residual rock from which the melt was extracted. Neither of these effects is expected for dehydration melting in the absence of a fluid phase, so their presence may signal anatexis in the presence of a brine.
Fig. 10. REE patterns of zircons from oceanic-plagiogranite migmatites (opg), normalized to REE content of zircon in the host gabbro (gb) (Aranovich et al., 2013b). If oceanic plagiogranites were formed by dehydration melting of the amphibole-bearing gabbro, the zircons should be enriched in REE. The observed preferential depletion in light and middle REE might result from melting in presence of concentrated brine.

In a study of zircon from the gabbroic rocks containing segregations of oceanic trondhjemites and tonalites, referred to here as plagiogranites, Aranovich et al. (2013b) found that the zircons contained melt inclusions, indicating crystallization from a magma. The zircons are depleted in REE, especially LREE, relative to those in the host gabbro (Fig. 10). This result closely matches what might be expected if the plagiogranites formed by partial melting of gabbro in the presence of a salt-rich aqueous fluid that preferentially extracted LREE from the felsic melt.

A decrease in the La/Yb ratio, accompanied by the overall decrease in the bulk REE concentration in leucosome relative to parental rocks (palaeosome), has been documented in amphibolite- and granulite-grade migmatite complexes (e.g., Watt and Harley, 1993; Nabelek, 1999; Mengel et al., 2001; Milord et al., 2001; Nehring et al., 2009; Acosta-Vigil et al., 2012). Examples of the protolith–leucosome relationships of this type are shown in Fig. 11 for three thoroughly studied complexes – Black Hills, South Dakota, USA (upper-amphibolite grade, metapelitic protoliths; Nabelek, 1999); Turku area, Southwestern Finland (granulite grade, metapelitic to semi-pelitic protoliths; Mengel et al., 2001) and St. Malo Terrane, Armorican Massif, France (upper-amphibolite grade, mostly metagreywacke protoliths; Milord et al., 2001).

Only the most segregated leucocratic diatexite and leucosome compositions from the latter work (Milord et al., 2001) are plotted in Fig. 11, as they seem to best represent the partial melt itself. The patterns of decreasing La concentration and La/Yb ratio may be caused by several factors, including variable degrees of melt-residuum non-equilibration and separation, fractional crystallization of the melt phase, and variable mode and degree of accessory mineral involvement in the melting reactions (e.g., Watt and Harley, 1993; Bea, 1996; Milord et al., 2001; Acosta-Vigil et al., 2012). All of these have been considered within the framework of dehydration melting or pure water-assisted melting models. However, efficient, preferential light REE extraction by the fluid might also be an important factor if brine-assisted anatexis is considered (Fig. 9; Aranovich et al., 2014).

5. Concluding remarks

Most experimental studies of brines focus on simple systems, chiefly H2O–NaCl. However, natural high-grade brines are complex multi-component solutions comprised of a range of rock-forming cations. They are likely dominated by chloride, but other ligands such as fluoride, carbonate and sulfate may also be present in subordinate concentrations. The petrological and geochemical effects of these additional components remain largely unexplored, but they may be significant. For example, it should be anticipated that common-ion effects may modify mineral solubilities significantly. In addition, the little work that has been carried out on NaF vs. NaCl brines suggests that even a small amount of F could profoundly affect REE redistribution.

Nevertheless, it remains clear that brines have potentially significant geochemical and petrological consequences for high-grade processes. This arises largely from the different activity–composition relations in H2O-brine systems relative to H2O–CO2 and other water–non-polar gas systems. The opposite signs of the departures from ideality along these two types of binaries means that, when brines are present, crustal melting temperatures will be higher than in the presence of H2O or H2O–CO2. In addition, the isopleths of salt mole fraction at brine-saturated minimum melting (Fig. 4) favor the upward transport of crustal melts produced during brine infiltration. The presence of CO2 in modest concentrations leads to phase separation in multicomponent saline fluids. The H2O–CO2 component of this two-fluid system is well represented in fluid inclusions, but brines are not due to their wetting properties (e.g., Touret, 1985; Newton et al., 1998). Yet the brine component is likely responsible for much of the geochemical signature imparted by the fluid phase: mineral solubilities are dramatically higher in H2O–salt solutions, they are capable of shifting the oxidation state of the rock with which they interact, and they can cause large changes in REE geochemistry. Thus, interaction with brines during high-grade processes may play important roles in the overall geochemical evolution of the lower crust, which have not been previously emphasized.

Acknowledgments

Comments by Bob Newton and two anonymous reviewers substantially improved the paper. Anatoly Tomilenko (Institute of


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