



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



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## 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  $H_2O$  activity ( $a_{H_2O}$ ) via migrating fluids. In addition, above 2–3 kbar, brine-saturated solidi for simple granite melting show positive  $dP/dT$  at constant  $H_2O$  mole fraction ( $X_{H_2O}$ ), favoring ascent of fluid-saturated liquids. Finally, a large miscibility gap exists in  $H_2O$ – $CO_2$ –salt ternaries at lower crustal conditions, which may concentrate salts in a separate phase and help explain the common observation of  $CO_2$ -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%  $NaAlSi_3O_8$ , 31 wt%  $SiO_2$ ) at 2 kbar in the presence of aqueous NaCl solutions ranging in concentration from a salt mole fraction ( $X_{NaCl}$ ) 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  $H_2O$ , reaches a maximum, and then declines; however, it salts out at all  $X_{NaCl}$  at higher  $P$ . At granulite-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  $X_{NaCl}$ . In contrast, the solubility of Ca–salt minerals increases exponentially with rising  $X_{NaCl}$ . The solubility patterns reflect variations in complexing and  $H_2O$  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 ( $\pm$ 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 in

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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 H<sub>2</sub>O and dense non-polar gases (mostly liquid CO<sub>2</sub>) in quartz from the lower-crustal migmatites 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 CO<sub>2</sub>-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 chlorine-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  $X_{\text{NaCl}} \sim 0.1$  (where  $X_{\text{NaCl}}$  is the molar NaCl/(NaCl + H<sub>2</sub>O) 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 halide 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, CaCl<sub>2</sub> or NaF) is noted where relevant data exist.

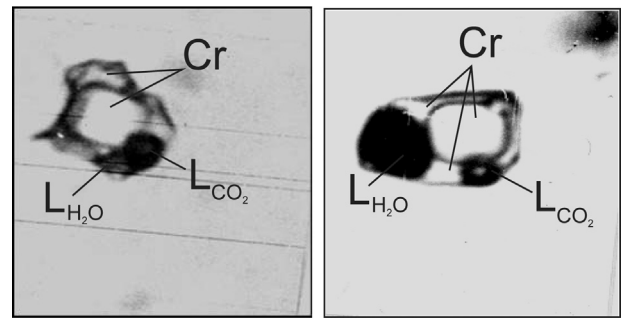


Fig. 1. Polyphase inclusions in quartz from migmatite leucosomes, Aldan shield, Siberia (photomicrographs courtesy of Anatoly Tomilenko). L<sub>H<sub>2</sub>O</sub>, aqueous solution; L<sub>CO<sub>2</sub></sub>, liquid CO<sub>2</sub>; Cr, solid phases (mostly NaCl, KCl, rare carbonates). Note different proportions of L<sub>H<sub>2</sub>O</sub> and L<sub>CO<sub>2</sub></sub> 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 H<sub>2</sub>O 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 Cl 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 CO<sub>2</sub> and S, can be generated in deep fluids.

The especially low solubility of Cl (and CO<sub>2</sub> 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 H<sub>2</sub>O relative to chloride and promote formation of a residual saline fluid. Most conceptual models of fluid-saturated melting focus solely on the role of H<sub>2</sub>O. If the fluid at the solidus is pure H<sub>2</sub>O, it is likely to be completely consumed by the silicate liquid because of high H<sub>2</sub>O solubility and low rock porosity. However, the lower solubility of Cl (as well as CO<sub>2</sub> 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 H<sub>2</sub>O.

Thus, there are likely three main pathways to increasing salinity in fluids associated with high-grade metamorphism. The preferential extraction of H<sub>2</sub>O 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

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